Response to editor: “Chemical evolution of primary and secondary biomass burning aerosols during daytime and nighttime”

Amir Yazdani[1], Satoshi Takahama[1], John K. Kodros[2], Marco Paglione[2,3], Mauro Masiol[2], Stefania Squizzato[2], Kalliopi Florou[2], Christos Kaltsonoudis[2], Spiro D. Jorga[2], Spyros N. Pandis[2,4], and Athanasios Nenes[1,2]

[1]Laboratory of atmospheric processes and their impacts (LAPI), ENAC/IIE, Ecole polytechnique fédérale de Lausanne (EPFL), Lausanne, Switzerland
[2]Institute for Chemical Engineering Sciences, Foundation for Research and Technology Hellas (ICE-HT/FORTH), Patra, Greece
[3]Italian National Research Council - Institute of Atmospheric Sciences and Climate (CNR-ISAC), Bologna, Italy
[4]Department of Chemical Engineering, University of Patras, Patra, Greece

1. More experimental details are needed in Section 2. Specifically,

   - Sect. 2.1: Please clarify: Have the experiments been done by filling the chamber with smoke from the entire burn event including both the flaming and smoldering phases or not? The current description in the first paragraph in Sect. 2.1 is insufficient. Authors should carefully present the experimental conditions so the data here can be compared to other literature results. In Line 85, model numbers for these Teledyne instruments should be provided. Please note somewhere that the chamber experiments were conducted in a batch mode to help broad readers to understand.

     The burning phase was mainly flaming. The filling of the chamber lasted from 15-30 min, depending on the concentration of bbOA inside the chamber. The MCE (Florou et al., submitted, 2023) also supports these observations. We have noted this in the text.

   - Table 1: For dark experiments, what are the nitrate radical concentrations? Estimations should be provided.

     For similar experiments conducted with NO_3 measurements, the NO_3 range was 0-400 ppt (Kodros et al., 2022) We can expect a similar range in this study as the concentrations used were quite close in terms of NO_2 (40-100 ppb) and O_3 (50-200 ppb). This has been added to the experimental section.

   - Sect. 2.2: AMS data collection and key parameters should be provided. TD measurements should be described more clearly with key parameters. Then, the filter sampling information needs supplement. When were the filters collected during each experiment? It looks like two filters were collected for each experiment. But it is not described clearly. Readers have to guess from Fig. 4 and Fig. S4c. Were the aged filters all collected around 3.5h or differently? For the presented FTIR results throughout the paper, please clarify the filter number and experiment number in the text and in the figure captions.

     We have revised the AMS methods and the filter sampling procedure as as follows:

     “The composition of non-refractory aerosols in the chamber was measured by a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc., Billerica, USA) (Jayne et al., 2000; Drewnick et al., 2005) sampling in V mode every 3 min. The sampling inlet was shared by the AMS and a scanning mobility particle sizer (classifier model 3080, DMA model 3081, CPC model 3787, TSI), which was used to measure the particle number size distribution in the 15–700 nm range. No dryer was placed before the inlet of HR-Tof-AMS and SMPS. Ionization efficiency (IE) calibrations were performed twice a month using size-selected ammonium nitrate particles (300 nm in mobility diameter, Dm). For certain experiments, the AMS also measured the composition of chamber aerosols after being passed through a thermodenuder (TD) to study their volatility in the 25–400 °C temperature range. The TD consisted of an insulated heating section for evaporation of the more volatile compounds and by a cooling section with activated carbon which was used to avoid vapor condensation during the cooling stage (An et al., 2007; Louvaris et al., 2017).“

“Sampling duration was 30 min for each filter at a flow rate of 8 L $\min^{-1}$ for 20 min, using a flow system composed of a silica gel denuder to minimize aerosol water and a sharp-cut-off cyclone. For the fresh bbOA emissions the two filters (one quartz and one FTIR filter) were collected sequentially during this stabilized fresh emission period. The aged filters were collected 3.5 h after the O_3 addition in order to allow sufficient time for the oxidation process to take place, as indicated by the O:C trend reaching is maximum value.”

- Sect. 2.3.1: First of all, V mode data are not good for elemental ratio calculation. Second, Canagaratna 2015 describes various methods in calculating elemental ratios. For laboratory experiments, one should obtain its own ratios for correcting the H2O+, CO+, and CO2+ peaks. If this cannot be done for some reason, the implicit method can be used. Nevertheless, information and uncertainties should be clarified. Comparison to other literature data should be discussed so readers may get a sense about how this BBOA can be compared to others.

  For these measurements only the V-mode was obtained. We acknowledge the fact that higher degrees of certainty can be derived by obtaining our own ratios for correcting the H_2O^+, CO^+, and ${CO_2}^+$ peaks under an argon atmosphere, though this was not possible during this set of experiments. We have added this statement to the manuscript:

  “The uncertainty deriving from the Improved-Ambient method for O:C is 28% while the Aiken-Explicit method could yield better results (20%) when used with specific calibrations (Chen et al., 2011).”

  Chen, Q., Liu, Y. D., Donahue, N. M., Shilling, J. E., and Martin, S. T.: Particle-Phase Chemistry of Secondary Organic Material: Modeled Compared to Measured O : C and H : C Elemental Ratios Provide Constraints., Environ. Sci. Technol., 45, 47634770, 2011.

- Part S4 in SI and Fig S4: These information are important and should be moved to Sect. 2.

  We have moved some of this information to Section 3.1 where we discuss the results of the PCA analysis.

- Are the shown OA concentrations corresponding to filter sampling periods? It is strange that the AMS OA is not corrected for CE. Some of the two filters for one experiment show very different OM:OC but some were not, this should be discussed more clearly in the main text. Again, text and figure captions should be clear about the filter and experiment number. If results from averaging multiple filters were presented (look like not), it should be clear.

  The edited text was clarified:

  [...]However, the absolute values are different. PTFE filters that belong to each experiment (primary and aged in order) are as follows: Exp. 1 (filters F1, F2), Exp. 2 (F9, 10), Exp. 3 (F16, 17), Exp. 4 (F18, 19), Exp. 5 (F20, 21), Exp. 6 (F4, 5), Exp. 7 (F11, 12), Exp. 8 (F6, 7), and Exp. (F13, 14). F3, 8, and 18 were blank filters put in the chamber for a few minutes. Reported AMS OA is averaged over filter sampling period and not corrected for the collection efficiency (CE).

  AMS OA was not corrected for CE as only the agreement of OA concentration trends between AMS and FITR was of importance for the scope of this paper.

- Sect. 2.3.4: Please provide detailed descriptions about the PCA analysis here.

  The edited text was clarified:

  “This allows the better understanding of the evolution of bbOA during the course of aging in the chamber and to compare it to atmospheric aerosols. Before applying PCA, ion fragment data at 6 min intervals were normalized by total OA concentration to exclude the variation of ion fragment signals due to change in total OA mass (e.g., by SOA production or wall loss). PCA calculations were performed on the normalized and uncentered (not subtraction average value at each mass fragment) AMS spectra from the chamber experiments using singular value decomposition (Abdi and Williams, 2010). Different spectra such as positive matrix factorization

(PMF) factors of atmospheric OA from previous studies were projected onto the obtained PC space for comparison."

- The paper used unpublished field data from Florou. Please provide descriptions about that measurements in SI. In figure caption, replace the text "manuscript in preparation" by the citation to SI.

  In the revised version, data from published papers Kostenidou et al. (2015), and Florou et al. (2017) have been used for comparison.

2. The residual spectra that are derived by the method in 2.3.3 cannot represent aged bbOA without careful analysis on vapor wall losses. The problem is that assuming no evaporation, condensation, or heterogeneous reactions is inappropriate. Authors may argue that the increase of OA loading is in a range that would not affect gas-particle partitioning much but we need to see that type of analysis. Certainly, vapor wall losses can be significant and may affect the representativeness of aged bbOA here by the residual spectra, which needs to be discussed. Even if it turns to be a minor influence, the later text in the Result section about the residual spectra still needs to be precisely presented with cautions about this is a derived spectra not exactly aged bbOA spectra.

   We do not assume that there is no evaporation, condensation, or heterogeneous reactions all of these processes are proposed as possibilities for the apparent changes to the POA in our discussion. It is unlikely that these losses would substantially alter our conclusion regarding the changes to the POA, though the magnitude could certainly differ. Given that quantitatively constraining this is far from trivial and actually a controversial topic in the literature with reported values ranging from negligible to significant affecting also the SOA enhancement (Grosjean, 1985; Huang et al., 2018; Bian et al., 2015; Jiang et al., 2021; Ernle et al., 2023; Krechmer et al., 2020; Zhang et al., 2014; Pagonis et al., 2017; Pratap et al., 2020). This increases the uncertainty in the potential formation of SOA from BB and is within our future work frame that will refine the estimate in the overall change.

   We have added a section (3.6) to discuss to this issue:

   "In this work, the changes in apparent mass concentrations reported are not corrected for gas-phase losses of semivolatile organic compounds (SVOCs) to the chamber walls. SVOCs in bbPOA evaporating during the course of the experiment can be adsorbed and absorbed to the walls (Huang et al., 2018), increasing the loss rate of molecules (in addition to degradation due to gas-phase reactions) from the system and driving the partitioning toward the gas-phase compared to the scenario where wall losses are not present (Loza et al., 2010). The reported magnitude of these wall losses and effects on organic aerosol evolution in chamber experiments vary substantially according to study (Grosjean, 1985; Huang et al., 2018; Bian et al., 2015; Jiang et al., 2021; Ernle et al., 2023; Krechmer et al., 2020; Zhang et al., 2014; Pagonis et al., 2017; Pratap et al., 2020). However, unlike for particle wall losses, a generalizable result and correction remains elusive to date.

   Given the above, Florou et al. (in review) carried out 2 experiments (in the same chamber facility used in our study) where BB emissions from a pellet stove were allowed to reside in the chamber for 12 hours (in the dark, no active chemistry). After particle corrections were applied, no significant changes in mass, AMS spectrum and O:C ratio was observed in the BB aerosol, suggesting that vapor wall losses are not a dominating factor. However, in our present study, we also identify hydrocarbon fragments and aliphatic CH bonds that decrease over time, though the responsible compounds remain unidentified. The gas-phase wall loss rates are reported to be greater for those substances where appreciable fraction of mass resides in the vapor phase (Ye et al., 2016), but we do not anticipate the losses to be as significant to change the conclusions of our study. The results of this work establishes the potential importance of bbPOA aging and provides a basis for estimation of rate constants in future studies, while identifying more stable markers that may be suitable for use in field measurements."

3. Please describe clearly the burning material in figure captions.

   This has been clarified in the revised version.

4. The OA mass enhancement after aging seem small in this study. In a previous study (2021 ACP) by some of the authors here, the OA concentration increased by 3 folds. This should be discussed in the main text. More importantly, there should be a specific paragraph to compare the primary and aged bbOA here with literature findings under both day-time aging and nighttime aging conditions.

   Regarding the OA enhancement, in Section 3.1, we have further clarified:

“However, The aCH peaks are more prominent in the FTIR spectra of wood burning aerosols of this work compared to those of Yazdani et al. (2021c). While higher OA loadings can increase partitioning more volatile hydrocarbon compounds into the aerosol phase, the OA concentrations in this work are comparable and the prominent peaks are likely due to the combustion of wood with bark — which was not present in the experiments of Yazdani et al. (2021c).”

The other result presented in this work where the OA enhancement factor may make a difference is in the statement of the apparent aerosol composition (same Section). As the similarity in formation of carboxylic acids from wood burning SOA is corroborated by other studies measured under different conditions, we have not included this specific information as it reduces the scope of the finding.

We have additionally provided comparisons in composition from day-time and nighttime aging conditions close to where discuss our observations. For instance:

“For the residual OA formed using UV lights, however, the trajectories start in the lower section of the triangle and continue upward until they end close to the upper vertex, consistent with previously reported trajectories for wood burning in chamber experiments (Yazdani et al., 2021).”

“[...]the formation of carboxylic acids via the oxidation of major wood burning VOCs and the abundance of carboxylic acids in the bbSOA is consistent with previous reports (Yazdani et al., 2021; George et al., 2015; Chhabra et al., 2011).”

“Contrary to dark and dry conditions, in dark and humid conditions, the trajectories [in the f44-f43 space] resemble more those of UV experiments. The f_{44} and f_{43} increases more significantly, suggesting a stronger oxidation due to aqueous (nitrate radical) reactions. f_{43} is more elevated for aged bbOA in dark and humid conditions compared to those aged using UV (Fig. 1). The latter has also been observed by Kodros et al. (2020) and Kodros et al. (2022).”

5. Figures.

   - Fig. 2: Mexico city is not a good case to compare here with bbOA. Since there are so many published field results from AMS measurements, please choose the cases that better represent aged air masses influenced by biomass burning sources.

     Factors from newer and more relevant studies have been chosen for comparison in the revised version:

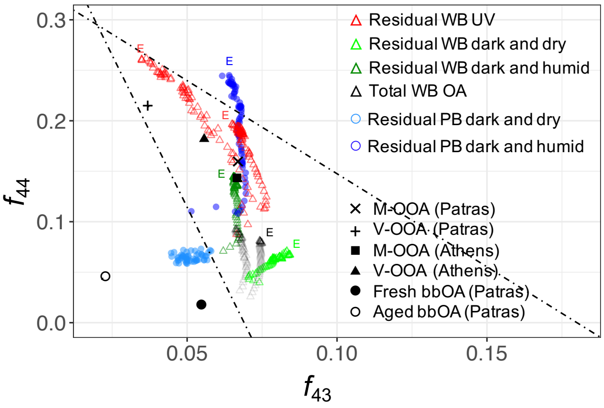

Figure 1: Aging trajectories of wood burning (WB) and pellet burning (PB) aerosols in the chamber with UV lights and dark aging shown in f_{44}-f_{43} ($f_{CO_2^+}$-$f_{C_2H_3O^+}$) plot. Atmospheric OA factors were obtained from Kostenidou et al. (2015) and Florou et al. (2017): V-OOA (very oxygenated OA), M-OOA (Moderately ogygenated OA), fresh and aged bbOA. End of aging trajectories are denonted by letter E.

   - Fig. 2: Instead of using letter E, I suggest the trajectories to be colored by normalized aging time to maximum OA enhancement.

     We kept the original format as coloring by time as suggested made trajectories from different fuel and aging methods hard to distinguish.

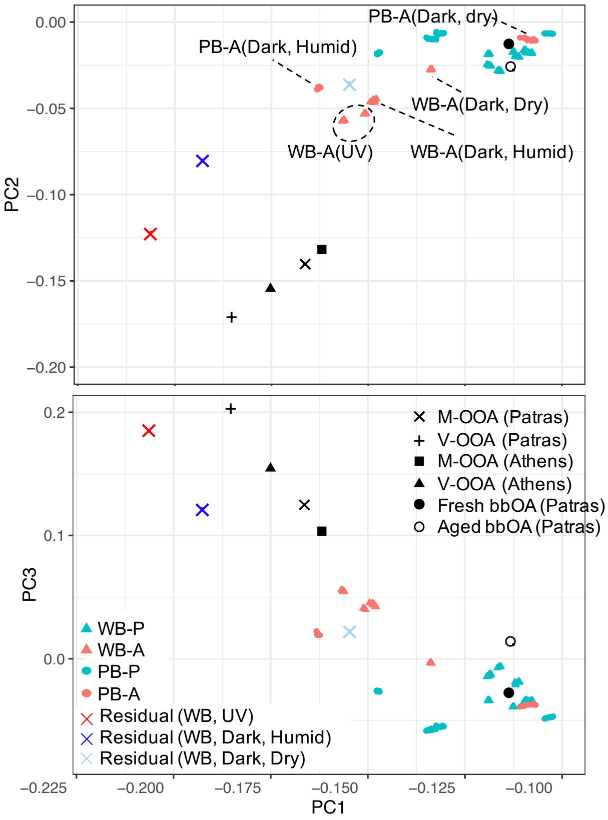

Figure 2: PC1-PC2 and PC1-PC3 biplots for primary, aged, and residual bbOA in the chamber calculated for the period of PTFE filter sampling: WB-P (wood burning, primary), WB-A (wood burning, primary), PB-P (pellet burning, primary), PB-A (pellet burning, aged). Atmospheric OA factors were obtained from Kostenidou et al. (2015) and Florou et al. (2017): V-OOA (very oxygenated OA), M-OOA (Moderately ogygenated OA), fresh and aged bbOA.

- Fig. 3: While PCA for the original AMS spectra is meaningful, doing that for the residual spectra is risky. Are the authors sure that those PC1s have similar physically meanings? Please justify the analysis and descriptions after addressing my comment 2.

  The PCA analysis was performed on the spectra matrix containing the original spectra, and the residual spectra were projected onto this space a posteriori. The physical meaning of PCs stays the same for the residual spectra, though the biplots indicate that residual spectra are being extrapolated in the derived PC space. However, the evaluation against ambient AMS PMF factors indicate that main variations are likely captured to provide a meaningful interpretation.

  It would also be possible to perform PCA on both original and residual spectra. The latter would need more extensive data cleaning as residual spectra tend to be noisy in the beginning of aging where there is insignificant mass enhancement. Additionally, the resulted PCs may not be very suitable for distinguishing differences between different primary aerosols if the overall variance is substantially affected by inclusion of the residual spectra.

- Fig. 4: Please format this figure consistently with others.

  The caption was made consistent.

- Fig. 5: Please label the ion formulae for the top 2 or 3 lines that shows the greatest increase after aging. Also, none of the tracer ions are exclusive tracers for hydrocarbon, levoglucosan, lignin, and acid. Please revise the legend to avoid confusions to readers.

  Ion formulae for the top 2 or 3 lines that shows the greatest increase after aging were labeled in the revised version. The names of species were deleted from legend to avoid implying exclusivity.

- Fig. 6: Figure caption remains quite unclear about how it is averaged. Please revise.

  The new caption reads as follows:

  "Normalized residual AMS spectra of bbOA for different aging experiments. Residual spectra were calculated and averaged for the period of sampling the second PTFE filter for each experiment and then averaged over the experiments of the same aging category including both wood burning and pellet burning. Error bars show the range of variation for each fragment within each category."

6. Polishing of the text is still needed throughout the whole paper. Please highlight the addition of findings (similarity or difference) to literature.

   We have improved the text according to suggestions; including additional references to prior literature as listed in the current bibliography.

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