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

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Reviewer 1

This paper examines the chemical evolution of primary and secondary biomass burning aerosols using typical daytime and nighttime oxidants in the laboratory. The combination of online AMS and offline FTIR provides a unique analysis of the chemical characteristics of the aging of bbPOA and its conversion to bbSOA. The high-quality paper addresses an important area of atmospheric chemistry and is well-suited for publication in ACP. Below are minor comments on clarification issues for the authors’ consideration.

We thank the reviewer for the encouraging assessment.

1. Page 3 Line 74, The authors should give more details of the UV light source in the text here. Also, see the last comment since there might be potential photo-induced reactions worth discussing in conclusions/implications.

   The vertical walls are covered with ultraviolet (UV) fluorescent lamps (Osram, L 36W/73), resulting in a $J_{\mathrm{NO_2}}$ of 0.59 min^{-1} when all lights are turned on. This has been added to the manuscript.

2. Page 5 Line 133, Sres(0), is it a typo? 0 should be t?

   The typo was corrected in the revised version.

3. Page 7 Line 171, What are "the first three principle components"? A clearer discussion of the figure using consistent terms in text and legend/caption would help. Please also note a few typos of "principle" components.

   The typos were corrected. The section was edited to use terms more consistently in the plot legend and text. For example, the term “aged in the dark” is now used in the text instead of “aged with the nitrate radical”.

4. Page 7 Line 179, it is interesting to see the differences between dark and dark/humid conditions. Please explain these differences. Also, what are the directions of these changes in the dark in the f44/f43 plot? I notice the trends for WB and PB under dark and dark/humid are not the same. Please explain the differences.

   The differences are more clearly explained in the revised version, which reads as follows:

   “The residual OA from wood and pellet burning emissions aged in dark and dry conditions occupy the lower part of the triangle plot with a relatively less significant change in f_{44} and f_{43} with aging (Fig. 2), implying only mild oxidation. Contrary to dark and dry conditions, in dark and humid conditions, the trajectories 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. Although the general oxidation trend is observed to be similar between PB and WB OA in dark conditions, the length of oxidation trajectories and their starting point appear to be somewhat different. These differences are believed to be related to different levels of aging in different experiments and slightly different composition of fresh PB and WB OA, respectively."

5. Figure 2, please provide clearer legends. WB dark and PB dark mean dark and dry condition? What is WB total OA? Why did it not show PB total OA? Need clear descriptions.

   We thank the reviewer for the suggestion. The legends were made clearer:

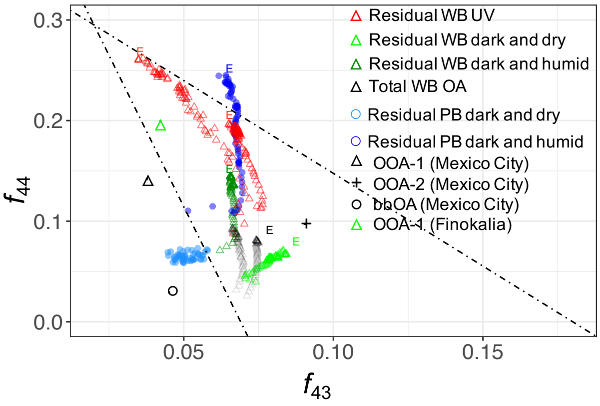


Figure 2: Aging trajectories of wood burning (WB) and pellet burning (PB) aerosols in the chamber with UV lights and dark aging. Finokalia OOA is obtained from Florou (*in review*, 2023).

   In this figure, total PB trajectories are not shown as appear similar to those of total WB. Total WB, represents raw spectra of WB aged with UV before the calculation of residual spectra.

6. Figure 3, please give better figure captions to avoid ambiguity.

   The revised caption reads as follows:

   "PC1-PC2 and PC1-PC3 biplots for primary, aged, and residual bbOA. WB denotes wood burning, PB denotes pellet burning, P denotes primary, A denotes aged. WB-P, WB-A, PB-P, PB-A, and ambient aerosols from Mexico City and Finokalia are raw bbOA spectra (no estimation of residual spectra). Finokalia OOA-1 is obtained from Florou (*in review*, 2023) and Mexico City OOA-1, 2, and bbOA from Aiken et al. (2009)."

7. Why does Fig. 5 use experiments 1, 4, 6, and 8, while Fig. 7 uses experiments 1, 4, 7, and 8? Typo?

   Exp. 6 FTIR spectra were discarded due to very low mass collected on the filter. Exp. 7 was used instead to represent the dark and dry conditions FTIR spectra. This has been reflected in Table 2 footnote.

8. Page 10 line 273 275, please consider rewriting so that the changes in the gas phase and particle phase can be distinguished.

   We have now clarified which phase discussed in different occasions. The revised paragraph reads as follows:

   "Gas-particle partitioning, heterogeneous oxidant reactions, and photolysis can play a role in the diminution of the mentioned species in the particle phase. Bertrand et al. (2018) proposed the prominent role of gas-particle partitioning and the subsequent vapor loss to the chamber walls for the depletion of levoglucosan in the particle phase. Comparing the trends of AMS levoglucosan-related fragments (particle phase) between reference and UV experiments of this work, the reaction of levoglucosan with the hydroxyl radical appears to be the dominant factor for its depletion in the particle phase. For semi-volatile compounds like levoglucosan, particle-phase depletion might be the result of gas-phase depletion and the subsequent gas-particle partitioning. However, the fast diminution of AMS fragments that are produced by less volatile species (e.g., heavy lignin-like compounds) highlights the role of photolysis and heterogeneous reactions. In addition, a similar fast depletion of $C_xH_y{}^+$ fragments in the particle phase merely due to heterogeneous reactions with the hydroxyl radical was also reported by George et al. (2008)."

9. Table 2, why is the kOA under UV larger than under dark conditions?

In this set of experiments, loss rates between SMPS and AMS were observed to be consistent (higher or lower rates were confirmed by both devices), real variations. Different loss rate constants are partly due to different conditions of the chamber (e.g., static charge on the chamber walls). In addition, loss rates of certain fragments (e.g., those related to levoglucosan) have been observed to increase with increased humidity. The reason for the latter is not yet clear to the authors.

10. The reference experiments are helpful, but why was there no 50% RH data? Also, why were different RH used in the wood and pellet experiments for the dark and humid conditions?

    The reference experiment 3 (Exp. 3) has an RH of 50%. The main reason why experiments with different RH values have been reported for WB and PB in this manuscript is that FTIR data was only available for the limited experiments. Authors, however, believe that the data can show highlight qualitative differences among different humidity regimes.

11. Page 12, Line 345, heterogeneous reactions and photolysis of bbPOA are indeed complex. Recent work on bb particles and model bb chemical compounds has suggested photosensitization can be an important process in SOA and sulfate formation (Matabo et al., 2022, Liang et al., 2022). Furthermore, I would be interested in knowing if the particles contain nitrate. Furthermore, nitrate photolysis can be an effective pathway to form sulfate (from SO2) and possibly SOA due to the formation of in particle OH, NO2 and nitrite (Zhang et al., 2022). Some discussions on these possibilities and their potential influence on the experimental results would be helpful.

    Florou et al. (*in review*, 2023) discuss this point in depth, as it is important for inferring BB aerosol pH. That study demonstrates a significant skill in predicting inorganic nitrate partitioning, which means that for the purposes of our and their study — inorganic nitrate levels is captured well. The amount of sulfate present in the experiments here is rather low, but we now mention in the revised text that photosensitization may be a possible pathway for oxidative aging of pBBOA.

References:

Liang et al., Sulfate Formation in Incense Burning Particles: A Single-Particle Mass Spectrometric Study. Environmental Science Technology Letters. 2022, 9, 9, 718725.

Mabato et al., Aqueous secondary organic aerosol formation from the direct photosensitized oxidation of vanillin in the absence and presence of ammonium nitrate. Atmospheric Chemistry and Physics 2022, 22, (1), 273-293.

Wang et al., Atmospheric Photosensitization: A New Pathway for Sulfate Formation, Environ. Sci. Technol. 2020, 54, 6, 31143120

Zhang et al., Photochemical Reactions of Glyoxal during Particulate Ammonium Nitrate Photolysis: Brown Carbon Formation, Enhanced Glyoxal Decay, and Organic Phase Formation. Environ. Sci. Technol. 2022, 56, (3), 1605-1614.

Reviewer 2

The data presented within Yazdani et al. is interesting because it shows a potentially overlooked process (heterogeneous processes or photolysis) that is changing the composition of the POA. The text, figures, and tables needs to be seriously checked and cleaned up. There are a multitude of errors or unclear aspects of the text, figures, or tables that resulted in assumptions about what the authors intended. I would argue that this text can be seriously streamlined to tell the main message.

The initial discussion was centered on differences in the FTIR measured between different burning conditions, but the discussion requires more discussion on the variability of the burning conditions and day-to-day variability to say anything of substance. The authors then talk about the different oxidation processes and their impact on the bulk chemical properties measured by the AMS and FTIR. There are minor points where the authors do not provide enough information to make an informed assessment about the presented information (see thermal denuder discussion, NH4 subtraction in the FTIR data). The interesting point of the manuscript comes from the

My biggest uncertainty regarding this manuscript comes from the assessment of levoglucosan with the FTIR. There appears to be a sizeable disconnect between the values reported in Table 2 and those shown in Figure 7 for levoglucosan. I cannot reconcile these differences. These apparent discrepancies and the errors / unclear aspects of the text do not provide confidence that they are simple to explain. I do not recommend publishing at this time and a major revision is necessary.

We thank the reviewer for the thorough comments, which has improved the precision of our manuscript. Regarding the levoglucosan analysis by FTIR, we have provided additional description of the analysis and citations to support our claims.

Major Comments:

1. Table 1: I believe that SO2 is supposed to be O3. The OH concentration noted in Table 1 does not correspond to the initial conditions and was determined from the PTR-MS with the d9-butanol injection. What was the error of these values in Table 1? In the text the average is 3-5 x 106 molecule cm-3, but this is purely both of the values reported in Table 1.

   In experiments 4 and 5 SO_2 was indeed injected into the chamber.

   As correctly stated the OH concentration noted in Table 1 does not correspond to the initial conditions and was determined from the PTR-MS with the d9-butanol injection. The error in OH estimation by d9-butanol tracing is reported to be on the order of 6% (Allani et al. 2021).

   Allani, A., Bedjanian, Y., Papanastasiou, D. K., and Romanias, M. N.: Reaction Rate Coefficient of OH Radicals with d9-Butanol as a Function of Temperature, ACS Omega, 6, 1812318134, https://doi.org/10.1021/acsomega.1c01942, 2021.

2. Why does the experiment with higher ozone have lower OH exposure?

   As stated in response to comment #1, there is ozone injection the experiment 5 has higher SO_2 injection.

3. What was the modified combustion efficiency of the burns? Were there no CO/CO2 measurements? Does this describe any of the differences / variability between the fuel types?

   Carbon monoxide and carbon dioxide was measured with Teledyne gas monitors (300E and T360). The modified combustion efficiencies (MCEs) were 0.93–0.97 for the pellet burning experiments (Florou, *in review*, 2023) and 0.86–0.95 for the wood burning experiments. Bertrand et al. (2017) investigated the relationship between MCE and AMS mass fragments and found certain mass fragments to be strongly correlated with MCE. The same is observed in our experiments (over the range 0.8 to 0.91). The composition difference in fresh aerosols are believed to be partly due to fuel differences and partly due to variability in combustion conditions (resulting in different MCEs). However, as the changes in chemical composition in our study are most strongly correlated with aging conditions rather than fuel type or experiment number, our conclusions are robust with respect to the differences in initial composition that may be affected by the MCE.

4. Without knowing the modified combustion efficiency how can these measurements be effectively translated between measurements performed here and those performed at other facilities?

   It is true that combustion efficiency is an important parameter when comparing the composition of different bbOAs. However, the main purpose of this study is investigating the effect of different types of aging on primary and secondary bbOA. Combustion efficiency is not believed to affect the conclusions of this study considerably.

5. Page 4 line 109-end of page: I do not believe this section is clearly worded. At first reading, without detailed understanding of the data analysis of the FT-IR it is not clear how the information about the absorption coefficient is needed. A discussion about the absorption coefficient is needed here. Also, can more information be provided about this scaling because it is not clear in Reggente et al. (2019), and about the uncertainty that this introduces to the data presented here.

   The description of the absorption coefficient was made clearer. The revised version reads as follows:

   "Baseline correction was performed on the FTIR spectra to eliminate the contribution of light scattering from the spectra (Russo et al., 2014; Parks et al., 2019) using smoothing splines. After baseline correction, blank subtraction was performed to recover some of the overlapping features with PTFE peaks (e.g., levoglucosan fingerprint bands 860–1050 cm^{-1}). A multiple peak-fitting algorithm was applied on the FTIR spectra to estimate the contribution of absorption related to alcohol (referred to as aCOH), carboxylic acid (COOH), alkane (aCH), and non-acid carbonyl (naCO) groups (Takahama et al., 2013). The area under each peak was related to the abundance of the corresponding functional group using the measured absorption coefficient by Reggente et al. (2019).

The ratio of fingerprint absorbances related to levoglucosan (multiple peaks in the 860–1050 cm^{-1} range; Yazdani et al., 2021) in the FTIR spectra were compared between primary and aged aerosols to estimate the change of this biomass burning marker with aging. Absolute levoglucosan concentrations were estimated using the mentioned fingerprint absorbances, with absorption coefficient estimated from measurements of Ruthenburg et al. (2014).

The single sharp peak at 1515 cm^{-1} related to lignin-like compounds was used to estimate and compare the concentration of this group of compounds in primary and aged aerosols. Due to the lack absorption coefficient for the 1515 cm^{-1} peak, the following approach was taken to estimate the concentration of lignin-like compounds: Fine et al. (2002) found syringaldehyde to be one of the most abundant lignin-like compounds in bbPOA. The total concentration of lignin-like compounds was estimated using the absorption coefficient of the 1515 cm^{-1} peak for syringaldehyde. As this coefficient was not availble in the literature, it was calculated by scaling the measured coefficient of carbonyl Reggente et al. (2019) by the ratio of absorbances at 1515 and 1680 cm^{-1} from a spectrum of the compound prepared in potassium bromide wafer taken from a reference database (SpectraBase, John Wiley & Sons, Inc., 2022)."

6. Section 2.3.2: As the wall-losses can be size-dependent, which can be important for large size-distributions such as those found with combustion emissions, is a mass based wall-loss correction the more appropriate correction? Could the SMPS also be used to provide a size-dependent wall loss correction, as well as a correction that occurs during aging? The argument of well-mixed POA is not necessarily valid when considering these aging pathways.

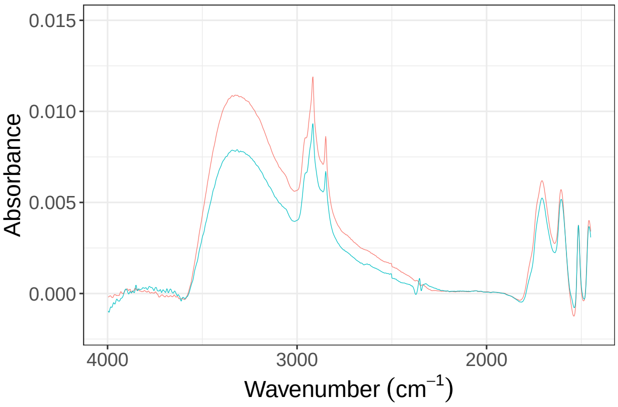
   Although SMPS can be used to provide size-dependent wall loss correction, it does not provide size-dependent chemical information. Using PToF data for individual fragments is one possibility to address size-dependent loss rates. However, the latter suffers from noisy data specially for larger fragments with generally weak signals. Authors accept that the assumption of organic aerosols having size-independent composition might not be entirely correct but there is evidence that this assumption not far from reality based on previous studies (Grieshop et al., 2009) and also fairly similar fragment loss rates in the reference experiments. Additionally, the majority of organic aerosol mass is in the 100–300 nm range as can be seen from Fig S1b.

7. Section 3.1 paragraph 1: I understand the authors are trying to make the point that there are different components coming from different types of burning species. How confidant are the authors that these are unique features and not driven from burning variability? How do the authors verify that the burning conditions from experiment to experiment are reproducible? Where do you show or discuss the variability? Otherwise, I dont see how this part of the discussion is useful, and raises significant questions about the rest of the manuscript. If there are no metrics to say that each burn is starting roughly near the same point, how can the authors be confidant that their results are meaningful? Thankfully, in the later part of the manuscript there are no conclusions about the differences between pellet vs. wood burning.

   As the reviewer correctly states, there is variability among experiments of the same category (fuel and oxidant). Yazdani et al. (2021) show for similar experiments that the variability among categories are statistically greater that that within each category. Our manuscript does not focus on this aspect. However, our data also suggest a similar trend. For example, in Fig. 3a, fresh aerosols of PB are distinguishable form those of WB, which are fairly clustered. FTIR spectra are even more distinguishable between different categories. While the exact extent of pBBOA transformation can vary according to combustion and environmental conditions, the findings reported here can be considered representative for the range of conditions investigated.

8. Figure 1: Are these averages across all experiments? Are these representative spectra from specific experiments? Can these be specified. WB and PB are not defined. What is the variability between experiments? If they are from specific experiments, can you specify which experiments.

   The spectra are taken from fresh wood burning and pellet burning aerosols of experiments 6 and 7. The FT-IR spectra of fresh aerosols from different experiments related to the same fuel are observed to be quite similar and are different mainly in the overall intensity (aerosol mass collected on the filter). As an example, FT-IR spectra of fresh wood burning aerosols of experiment 1 and 6 are shown in the figure below:



FTIR spectra of fresh aerosols in experiments 1 (red) and 6 (green).

Table 1 specifies that we had replicate (2–3) experiments for each type of condition. Table 2 shows the results of each experiment from which a measure of variability can be obtained. The results indicate that the variations emphasized in our conclusions are greater across experimental conditions than within repetitions.

WB and PB are also further clarified in the revision.

9. Figure 2: I guess the legend should change dark to dark and dry to be consistent with the dark and humid Maybe it would be helpful to demonstrate where the initial data point is for each experiment? As an atmospheric scientist that uses an aerosol mass spectrometer, I understand what the beginning of the experiment is when looking at this plot, but it can be clarified better so non-experts can understand this as well. Also, why dont the authors put the same points used in Figure 3 on Figure 2? This would provide consistency in the discussion.

   We thank the reviewer for this suggestion. We have modified Figures 2 and 3 (also shown in response to comment #13 and Reviewer #1 comment #5).

10. Page 7 line 172: where are atmospheric bbOA factors shown in Figure 2?

    Figure 2 has been revised to include atmospheric bbOA factors as Figure 3.

11. Page 7 line 178 182: Many of the authors on this paper are also authors on Kodros et al (2020), and they observed clear enhancements in OA due to the exposure to NO3 radicals under both dry and humid conditions. In the experiments presented here, what is the OA enhancement under dry and humid conditions? Are they the same as Kodros et al (2020)? I would guess not, because the results presented in Kodros et al (2020) show that even under dry and dark conditions there is an increase in f44. Why are there differences between these results (dark and dry / dark and humid) to the results in Kodros et al (2020) see Figure 3A?

    As shown in Figure 5c, there is increase in f44 under dry and dark conditions in these experiments also. While Kodros et al. 2020 focused on overall OA enhancement, we focus on the pBBOA in this work; we note in the revised manuscript that the OA enhancement is similar to that reported by Kodros et al. 2020.

12. Because of the differences in the results presented here vs. Kodros et al (2020) it begs more questions about what drives the observations? Are single experiments good enough to derive meaningful conclusions? For example, these authors in Kodros et al. (2020) had 4 repeats of dry experiments, and 2 repeats of humid experiments.

    As listed in Table 1, we had replicate (2–3) experiments for each type of condition. Table 2 shows the results of each experiment from which a measure of variability can be obtained. The results indicate that the variations emphasized in our conclusions are greater across experimental conditions than within repetitions.

13. Figure 3: What does the legend mean? WB-P, WB-A, PB-A, PB-A?? I guess these are supposed to be P = primary and A = aged. I also suppose that there is a typo in the legend and one of the PB-A should be PB-P. I have no idea what experiments WP nor PB correspond to Are they dark

NO3 experiments? Are the UV experiments? Are they dry? Are they humid? I am going to ignore the points corresponding to WB and PB, because I dont know what they correspond to. I will assume that the markers for each aging point matter the most.

These interpretations are correct but have now been explicitly included in the caption.

14. Page 7 lines 183 200: Wouldnt it be most accurate to talk about this in terms of oxidation rather than aged? The metric that you are using to assess the mass spectra is effectively how oxygenated the molecules are, the aging length is known based on the time scale and the extent of the oxidation that the particles are undergoing. In these terms, you can talk about something concrete, because in these experiments you know what is happening to the particles is not some ambiguous process.

    The apparent increase in oxygenation of aerosols can be due to multiphase reactions (including oxidation but also fragmentation) and gas/particle partitioning; we therefore refer to these processes collectively as aging.

15. Figure 6: The difference between the average value (black) vs. the error bars (red) are difficult to observe the differences. What the error bars correspond to? The variation during the experiment? Standard deviation of the signal over the whole experiment? The standard deviation over a specific window? What time frame of the experiment was chosen for these figures? Why are the B, C, D figures not showing the aerosol constituents that are decreasing? This is an important point in those experiments. I recommend showing the full version of the figures. Also, what experiments do these correspond to? Because in Figure 7 the experimental data does not correspond to the same exact experiments as Figure 5.

    The figure shows normalized, residual mass spectra (aged minus scaled primary). The bars show the range in values across experiments, and show the variability. Examples of negative residuals were shown in Figure 5, and including negative residuals in this Figure made it difficult to visualize the positive residuals discussed in the text and therefore were not included in these plots.

16. Page 9 line 244: I would argue that the negative aspects of the mass spectra are at least as interesting as those increasing and would advocate to add those to the Figure 6.

    We agree that they are interesting and important, but the illustrations of negative residuals are shown in Figure 5. Figure 6 becomes more difficult to read with negative residuals for panels B, C, and D so only positive residuals are included and serve to aid the discussion presented in the text.

17. Section S5: How is this subtraction actually performed? In the text the carboxylic acid portion of the is the focus of how the NH4+ obscures the data in the FT-IR. When looking at Figure S6 the CH bands are also effectively subtracted. Does this mean that the aCH are also obscured here?

    The scaling factor is defined as the minimum ratio of each sample spectrum and reference ammonium spectrum. CH peaks also appear to have been subtracted because there are CH peaks in the ammonium spectrum used for subtraction. This has now been added to the text.

18. Section S6: do you want to compare that to your data? It seems like that would be a reasonable thing to do.

    We perform a very brief comparison here. This has been clarified in the revised version. A more detailed comparison of chamber and ambient aerosols is done by Yazdani et al. (2021).

    “Compared to primary WB aerosols in chamber, weak levoglucosan and lignin peaks in this sample are observed in the ambient spectrum. On the other hand, the broad peak from 2400–3400 cm^{-1} suggests the high abundance of carboxylic acids, which are also observed in the WB residual spectra of S6a. This observation suggest the dominant contribution of wood burning (secondary aerosols) in this atmospheric sample although primary marker are quite weak.”

19. Page 9 line 265: I am very curious about how Table 2 is formed for levoglucosan. When I look at Figure 7b I do not see an appreciable loss of levoglucosan.

    The diminution of the three levoglucosan peaks were not clear in the original figure as they are considerably weaker than other peaks in the spectra. In the zoomed-in version this diminution is more clearly seen.

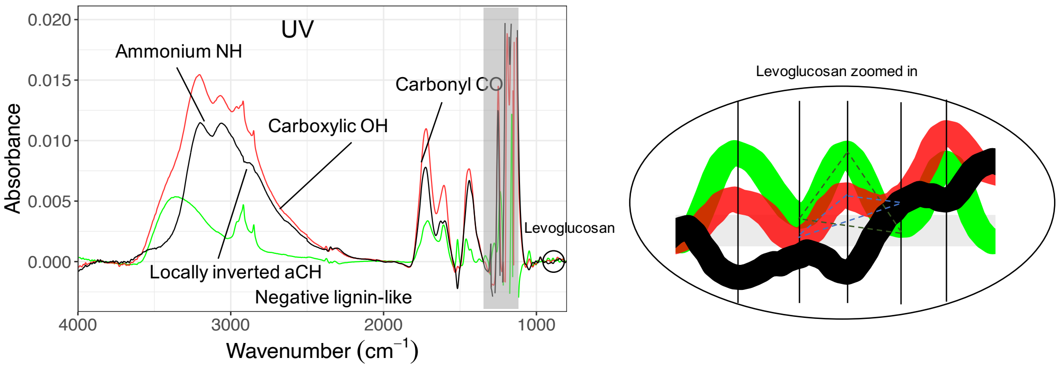


Figure 7b in the main text with the levoglucosan region zoomed in.

The quantification is performed via local baseline correction after blank PTFE spectrum subtraction (as described in Section 2.3.1 and Yazdani et al., 2021). Due to filter variability, regions of the spectra can become negative after this subtraction, but levoglucosan peaks appear as well-defined features superposed on the residual spectrum. Each of the three peaks are locally baseline-corrected (peak minus the average of left and right valleys) and averaged for quantification.

The peak features and spectra preprocessing methods are further described by Yazdani et al. (2021, doi:10.5194/acp-21-10273-2021) and Yazdani (2022, PhD thesis doi:10.5075/epfl-thesis-9382) 2022, and a linear relationship (R2=0.76) with levoglucosan estimated by AMS has been demonstrated by Yazdani et al. (2021, doi:10.5194/acp-21-10273-2021). These peaks are above detection limit of FTIR, which is investigated in further detail by Yazdani (PhD thesis, 2022).

The text in Section 2.3.1 has been edited to add this information:

"Absolute levoglucosan concentrations were estimated by averaging the heights of each of the three peaks in the fingerprint region and applying absorption coefficient estimated from measurements of Ruthenburg et al. (2014). The peak heights were defined relative to a local baseline defined by a linear interpolation among peak valleys (Yazdani, PhD thesis, 2022)."

20. Lets start with Figure 1, there is a clear signal that is associated with levoglucosan just below 1000 cm-1. Now when I look at Figure 7b is there even levoglucosan there? Figure 1 also shows that there is negligible levoglucosan present. So are the values in Table 2 for levoglucosan reasonable and above the limits of detection?

    In general, the absolute intensity of a peak in the infrared spectrum depends on the absorptivity of the specific bond, so cannot necessarily be contrasted against other peaks as a measure of bond abundance (though the intensity of the same peak should scale with abundance). The variations in levoglucosan are not obvious when viewing the entire spectrum, but are better visualized in the revised Figure 2 and quantified as described in response to comment #19.

21. I am at a loss to understand values reported in Table 2 for levoglucosan for the dark experiments for the FT-IR measurements. Note all values are less than 1 meaning that the values should be decreasing with the dark experimental aging times.

    This is correct. Levoglucosan-like compounds do decay over time. Its faster decrease relative to the lignin-like compounds also provide the basis for developing a "chemical clock".

22. Now in Figure 7A, the levoglucosan peak is negative in the POA sample, and is maybe still negative (but less so) in the Aged sample. This results in a net positive residual. Based on this analysis how can the FT-IR data reported in Table 2 be even close to the reported value for experiment 1? I have similar questions about the data in Figure 7C where it looks like the levoglucosan region is increasing with aging

    The variations the reviewer is referring to results from the imperfect blank subtraction, but the quantification of levoglucosan is based on well-defined absorption features that are defined relative to these variations, as described in response to comment #19.

23. Page 10 lines 283-290: without solid evidence for their thermal denuder modelling, I believe the only points the authors can use is that the TD shows levoglucosan is more volatile than their lignin

marker. Wouldnt the most appropriate comparison be investigating the volatility prior to initiating the experiment?

We agree and have removed mention of C^* values in the main text, and modified the text in Supplement Section S2 accordingly (modified portion copied below). As we are measuring markers for lignin-like compounds in the combustion aerosol, we cannot perform this comparative study a priori (outside of the context of chamber sampling).

"In order to qualitatively rank the volatility of different species responsible for marker fragments, we interpreted thermodenuder measurements with a simplified model for a separate reference experiment (Florou et al., *in review*, 2023). This reference experiment is different from those those discussed in the main text. The thermodenuder design and operation is described by Gkatzelis et al. (2016) and Florou et al. (*in review*, 2023). The heating section is 50 cm in length with outer and inner diameters of 10 and 3.64 cm, respectively (the annulus is filled with sand to distribute the heat). The flow rate is 1 Lpm and the temperature profile is described by Wehner et al. (2002) and Lee et al. (2010) for similar systems. The centerline residence time was 16s at 298K (overall 32 s) in the heating section, with a residence time of 30s in the cooling section (cooled by convection).

Detailed (dynamic) modeling of the thermodenuder is described by Florou et al. (*in review*, 2023), but in this work we use a simplified approximation neglecting thermophoresis and assuming thermodynamic equilibrium at all temperatures,..."

24. Section S2: What experiment is shown in Figure S2?

    This is a separate reference experiment performed with the thermodenuder and is different from those discussed in the main text, which is now clarified in the revision.

25. Why is equilibrium partitioning a valid assumption with the thermal denuder? The residence time of the thermal denuder plays a massive role on the extent of evaporation, and if the TD has actually achieved equilibrium.

    We acknowledge that this is a simplified approach that provides an estimate of relative changes in volatility. Application of a more detailed model, as done in Florou et al. (*in review*, 2023), would provide better quantitative estimates, but would not significantly change the conclusions of our study. We have revised the text as descrbied in response to point #23.

26. There are no details about the length, flow rate, temperature homogeneity of the TD, nor residence times. These parameters are required to determine any thermodynamic properties.(Saha and Grieshop, 2016; Bilde et al., 2015; Salo et al., 2010; Saleh et al., 2010) The lack of details presents a major flaw, and a concrete story about the volatility of the bbOA cannot be made without these details provided and discussed.

    We apologize for this oversight. We have revised the text as shown in response to comment #23.

27. Losses due to thermophoreisis are not included, yet this can result in losses of ∼10-15% in other thermaldenuders at elevated temperatures. Typically these losses are more important at high temperatures and longer residence times, where equilibrium can be assumed.

    This is a good point. We expect this to change the absolute value of C^*, but not its relative change. For this reason we did not consider its effects.

28. Why was 40 kJ mol-1 used to model the thermal denuder data? Compilations of data comparing saturation vapor concentrations and the enthalpy of vaporization suggests the enthalpy of vaporization should be in the ball park of 90-120 kJ mol-1 for molecules with a Log C* 1 . See (Epstein et al., 2010) and (Macleod et al., 2007)

    We thank the reviewer for pointing this out. Florou et al. (*in review*, 2023) estimated a value of 77 kJ mol^{-1} in related experiments. We reran our thermodenuder model with a value of 77 kJ mol^{-1} for the enthalpy of vaporization and obtained values for C^*(298K) of 1.09, 0.3, 0.22, 0.51, and 0.1 $\mu g\, m^{-3}$ for $C_2H_4O_2{}^+$, $C_9H_{11}O_3{}^+$, $C_{10}H_{13}O_3{}^+$, $CO_2{}^+$, and $C_4H_9{}^+$, respectively. We have now included these values in the revised manuscript, but the conclusions remain the same as the ranking of C^*s do not change.

29. Page 10 line 291-294: Looking at Figure S7 it appears that the C10H13O3+ increases initially upon irradiation. This means there is also a source for this fragment in the AMS, this would make it a

tenuous marker. (I also disagree with this point in the conclusions)

As noted in the text, the fragment may also originate from other sources, so its use as a marker still remains to be explored. However, part of the increase may also be explained from a continuation of the increasing trend prior to $t = 0$. As the temporal adjustment is based on total OA mass, some species that decrease more rapidly than the total OA (e.g., due to volatilization) will have a decreasing trend and those which are more stable will have a positive trend before $t = 0$. It is possible that at least a portion of the increase in C10H13O3+ can be a continuation of the increasing trend prior to turning on UV lights, before its delayed apparent decay.

30. Page 10 line 301 to end of paragraph: my concerns about the quantification in Table 2, makes me doubt the authenticity of the values reported here.

    The features used to quantify levoglucosan are different from the spectral variations interpreted by the reviewer, and are clarified in more detail in response to comment #19. As also evaluated by Yazdani et al. (2021) and Yazdani et al. (2022, PhD thesis), the method for levoglucosan analysis by FTIR provides a reliable estimate of its abundance .

31. Page 11 lines 310-312 (also page 12 line 345): Cant the net carbon loss and increased oxidation also be a result of evaporation of semi volatile species + OH oxidation in the gas phase with subsequent re-condensation? Based on this experiment, this is not a tell-tale sign of heterogeneous processes.

    It is possible, but we would expect larger fluctuations in the OC mass concentration if the evaporation and recondensation led to a net zero change the OC budget. Instead, the OC levels remain virtually unchanged across the short time intervals of our measurement so we believe this is the more likely hypothesis.

Minor Comments:

1. Section 2.1 How was the NO2 and O3 concentrations assessed? Were they measured?

   Yes, NO_2 and O_3 were directly measured by Teledyne gas monitors.

2. What type of PTR-MS was used? (I guess this should be reported)

   The proton-transfer-reaction mass spectrometer (PTR-MS, Ionicon Analytik) in this study a drift tube operated at 600 V and at a constant pressure of 2.2–2.3 mbar. The sampling flow rate was adjusted to 0.5 $\mathrm{L\,min^{-1}}$ (Florou et al., *in review*, 2023). This has been added to the text.

3. Section 2.2: What was the typical size distributions measured during these experiments? (Were they reproducible?)

   Mass distribution of organic aerosols versus vacuum aerodynamic diameter measure was measured using particle time of flight (PToF) module of AMS in these experiments. The distribution was relatively consistent among the majority of experiments with the peak in the 200-300 nm range.

4. Page 2 line 93: what is the resolution? Is it 1 cm-1 or something else?

   The sentence was corrected:

   The spectra were obtained at a resolution of 4 $\mathrm{cm^{-1}}$ and were averaged over 128 scans.

5. Page 4 line 111: I believe the full citation should be in parentheses.

   The citation has been corrected.

6. Page 4 line 113: The reference database needs to be cited.

   The reference has been added.

7. Page 6 line 164: CE is not defined, but I presume this is collection efficiency. Also, where is this shown in the previous section? I read this to mean in the previous section (section 2.3.4?) that the OA concentrations were correlated with the OM:OC, I dont understand what is meant here.

   The sentence has been clarified:

   OA concentrations of AMS (without CE correction) and FTIR were correlated $R^2 = 0.75$. The OM:OC estimated using these two also showed similar trends upon aging (Supplement S3).

8. Page 7 line 171: What are the first three principle components? <- also I think principle is misspelled.

The spelling has been corrected. The loadings of these principal components are shown in Supplement S4.

9. Page 7 line 184: Does the residual spectra refer to the chamber mass spectrum at the end of the experiment? (Or is this residual from the PCA analysis?)

   The residual spectra are defined in Eq. 4.

10. Page 7 line 186: The authors should note that the mass spectrum from each PC is found in the supplement Figure S5.

    This has been clarified.

11. Page 7 line 187: What is meant by loadings? Is it equivalent to intensity?

    In PCA, loadings refer to the coefficients which scale the linear combination of original variables that make PCs.

12. Page 7 line: 197-198: Additionally, the PCA analysis indicates the functional group content of aerosols discussed in this and following sections. What does the PCA analysis indicate?

    We have changed the main text to “The PCA analysis characterizes the functional group content of aerosols discussed in this and following sections using fewer variables”. For example, pellet burning aerosols have higher PC2 scores compared to wood burning, which is consistent with the higher alcohol content observed in their FTIR spectra.

13. Page 7 line 199 end of page: Does Figure 3 show this?

    The legend of Fig. 3 has been corrected. In the new figure it can be seen that PB_P has higher PC2 score than WB_P.

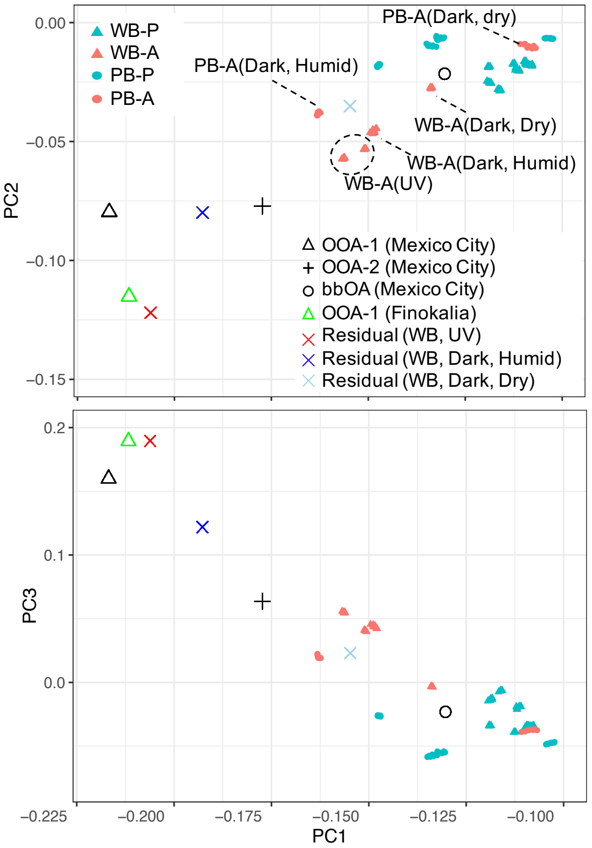


Figure 3: PC1-PC2 and PC1-PC3 biplots for primary, aged, and residual bbOA. WB-P (wood burning, primary), WB-A (wood burning, primary), PB-P (pellet burning, primary), PB-A (pellet burning, aged), and ambient aerosols from Mexico City and Finokalia are raw bbOA spectra (no estimation of residual spectra). Finokalia OOA-1 is obtained from Florou (*manuscript in review*, 2023) and Mexico City OOA-1, 2, and bbOA from Aiken et al. (2009).

14. Page 8 line 210: Doesnt the agreement between the FTIR and AMS just mean that they agree? it doesnt say anything independent about if the wall loss correction was performed correctly.

    Authors meant to highlight that both instruments capture very similarly the diminution of total organic mass and therefore loss rates calculated from AMS are in agreement with diminution captured by FTIR.

15. Page 9 line 243: formation of new oxidized species I would add as expected based on the mass formation observed. But in order to say this you would need to include what the OA mass increase is.

    This has been added to the text:

    "In a UV experiment (experiment 4; Fig. 5b), as soon as the UV lights are turned on, several oxygenated fragment ions increase in concentration, as expected based on around 20% mass formation observed; among those, CO_2^+ has the most prominent growth."

16. Page 9 line 258: It looks to me in Figure 6b there is one other species that decreases more than levoglucosan (but less than C9H11O3+), what is that?

    The fragment is $CH_9O_2^+$ and is believed to be related to lignin-like compounds as well (Bertrand et al., 2017).

17. Page 9/10 lines 269 277: This conversation is muddled. I think the authors want to convey that different processes could be happening, but cant single out a specific pathway that is definitively occurring.

    This paragraph is meant to describe the pathways simultaneously affecting different types of compounds in the particles. We have modified the text accordingly:

    "Gas-particle partitioning, heterogeneous oxidation reactions, and photolysis can simultaneously play a role in the diminution of the mentioned species in the particle phase. For semivolatile compounds like levoglucosan, particle-phase depletion can result from gas-phase losses and subsequent mass transfer from particles to gas. Bertrand et al. (2018) proposed the prominent role of vapor deposition to chamber walls for gas-phase losses. Comparing the trends of AMS levoglucosan-related fragments (particle phase) between reference and UV experiments of this work, however, the reaction of levoglucosan with the hydroxyl radical appears to be the dominant loss pathway. In contrast, the fast diminution of AMS fragments from less volatile species (e.g., heavy lignin-like compounds) highlights the role of particle-phase photolysis and heterogeneous reactions. In addition, a similar fast depletion of CxHy+ fragments in the particle phase merely due to heterogeneous reactions with the hydroxyl radical was also reported by George et al. (2008)."

18. Page 9 line 269: oxidation reactions

    Corrected.

19. Page 9 line 270: Bertrand et al. also includes OH reactions in their assessment of levoglucosan losses. I dont see what is added in the discussion about the results presented here, maybe the authors could say this is consistent with these results.

    Bertrand et al. (2018) discuss that levoglucosan concentrations are more sensitive to partitioning and wall losses and to a lesser degree to OH reaction rates. Our results suggest that levoglucosan concentrations are very sensitive to OH reaction otherwise the differences between reference and aging experiments would be minimal. This has been revised also in response to comment #17.

20. Page 10 line 275: Maybe it would be clearer to say fragments from less volatile having diminution and produced in the same sentence is a bit confusing.

    The sentence was changed according to the suggestion.

Supplemental:

Experiment S1: Why is the SMPS data not used at all in this paper? The size distribution shown in Figure S1 shows a peak at 200nm, but what is the cut-off of the lens used for the measurements?

The standard 1 μm lens was used. SMPS data of the experiments have been analyzed in other papers, and we have focused this paper on chemical measurements that describe the changes to the primary fraction of BBOA.

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