Interactive comment on "Evolution of the chemical fingerprint of biomass burning organic aerosol during aging" by Amelie Bertrand et al.

We thank the Referee for the careful revision and comments which helped to improve the overall quality of the manuscript. A point-by-point answer (in regular typeset) to the referee's remarks (in the *italic typeset*) follows, while changes to the manuscript are indicated in blue font. In the following document, lines references refer to the manuscript version reviewed by the anonymous referee.

Anonymous Referee #1 Received and published: 2 February 2018

General Comments This study investigated the chemical composition of biomass burning organic aerosol using online analysis techniques, principally Thermal Desorption Aerosol Gas Chromatography coupled to an Aerosol Mass Spectrometer (TAG-AMS). Solid wood fuels were burned in stoves and emissions were characterized. The smoke was exposed to hydroxyl radicals (OH), which increased organic aerosol (OA) mass and also reacted with components of the primary smoke aerosol. A variety of compounds were characterized and quantified, and the manuscript documents the quantities thoroughly, if not in such a dense manner as to make the paper challenging to read. Two main scientific comments arose during this review:

(1) The unidentified fraction of OA should be treated more carefully in the presentation of results. It is critical for the community to understand what was, and what was not, measured. In some cases, the treatment of unidentified fraction of OA in the text obscures the meaning of the results, which has been outlined in at least one comment below.

We thank anonymous reviews #1 for his comments. We modified the text page 4 line 10 – 15 to define the following: total OA (OA quantified by HR-ToF-AMS) and identified OA fraction (fraction of total OA identified and quantified by TAG-AMS). In addition, the manuscript was revised in order to explicitly state any time it was needed whether we talked about the contribution of a marker to the total POA mass concentration, to the total OA mass concentration, or to the identified OA fraction.

(2) The authors should be careful in their treatment of Stoves A and B versus Stove C. The authors describe their resolution of different burning conditions, however different fuels were used. At another point in the manuscript, a difference between Stove A/B and Stove C is attributed to the difference in fuel. Since both burning conditions and fuel type were different between the 'smoldering' and 'flaming' experiments, the authors should be vigilant and conservative in their interpretation. With these concerns described and detailed below, it is the judgement of this reviewer that the manuscript is publishable in Atmospheric Chemistry and Physics with relatively minor revisions.

We agree with reviewer #1 that our discussion can be more conservative all throughout this section of the results regarding the influence of the fuels. As the influence of fuels is already extensively described in the literature, we decided to put more emphasis on the impact of burning conditions on both emission factors (EF) and relative composition of OA. From our set of experiments, the burning conditions appear as the main parameter driving both EF and relative contributions for most of the organic markers quantified here. Furthermore, as the stoves represent different technology (logwood stoves for hardwood, and pellet burner for softwood), a specific and relevant discussion on the influence of the fuel burnt is complex if not impossible.

Overall, as evidenced by Figure 4, EFs increase as the MCE decreases whatever the nature of the fuel burnt with the notable exception of methoxyphenols for which the nature of the fuel is

sensitive. But while EF increase, we observe that lower MCE favors lower relative contribution of the compounds quantified here which implies the emissions of compounds not identified nor quantified in our experiments (most probably higher MW compounds). This result is, from our point of view, of prime importance for source apportionment studies.

Therefore we revised the manuscript in the following manner:

Line 27, page 7:

There exists a strong variability between the experiments regarding the contribution of the markers to the total POA mass concentration as well as their EF. The influence of fuels on the EF of organic markers has already been extensively reported in the literature (Simoneit et al., 1993; Fine et al., 2001, 2002)Therefore, in the next sections, we focus on the influence of the combustion efficiency (MCE). While the influence of the fuel (hardwood for stove A and B, softwood for stove C) cannot be neglected, we highlight, from our set of experiments, the overriding importance of the MCE on both the EF of organic markers and their relative contribution to OA. Previous studies have already revealed a relationship between the modified combustion efficiency (MCE) and characteristics of the mass spectral signature of the OA emissions (Jolleys et al., 2014; Bertrand et al., 2017) but the influence of the MCE on individual organic markers emissions is still virtually unknown. The MCE values for the logwood stoves (Stove A and B) range between 0.80 - 0.91 (Table 1), indicating that the combustion in these stoves is typically smoldering (MCE < 0.9), but also highly variable. However, the pellet stove (Stove C) shows little variability and produces a flaming type of combustion. The MCE values for the experiments conducted with this stove are 0.97.

Line 20, p8

Although no clear evidence can be drawn from previous studies (Fine et al, 2001, 2002, 2004a-b, Schmidl et al, 2008, Schauer et al, 2001), it is generally admitted that the contribution of levoglucosan to OA is higher for hardwood than for softwood combustions. As shown in Figure 4e, such behavior is not observed here which implies that the nature of the fuel is not the most important driver of the chemical composition of the emitted particles.

Line 21, p8

Reference to Figure 4b added.

…the chemical composition of the resulting organic aerosol is thus more complex and the identified fraction of the OA is lower (Figure 4b).

Line 21, page 8:

The methoxyphenols :

They include substituted guaiacol compounds such as vanillin, acetovanillone, vanillic acid, 3-guaiacylpropanol, conyferyl aldehyde as well as syringol and substituted syringols such as iso-eugenol, syringaldehyde, acetosyringone, syringyl acetone, propionyl syringol, syringic acid, methyl syringol, and synapyl aldehyde. The total EF of the methoxyphenols is between 7 and 174

mg kg^{-1}. Syringyl acetone and vanillin are the most abundant compounds in their respective category with EFs ranging from 0.4 to 80 mg kg^{-1} and from 2 to 7 mg kg^{-1}, respectively. As for levoglucosan, a strong correlation is observed between the total EF of methoxyphenols and the MCE (R^2 = 0.65, n = 11, Figure 4d) which indicates that smoldering condition favors also the emission of these class of compounds.

Methoxyphenols account for an important fraction of the POA, contributing between 8 % and 27 % of the total POA mass concentration. Unlike levoglucosan, the correlation between their relative contribution to POA and the MCE is more complex (Figure 4f). We observe a similar upward trend when considering the experiments conducted with stove A and B only (Hardwood, R^2 = 0.41, n = 8). Experiments conducted with stove C (softwood pellets) do not follow this trend however. For methoxyphenols, the influence of the fuel is very well established with larger emissions of substituted guaiacols from softwood combustions while hardwood combustion emissions contain a larger proportion of substituted syringols (Fine et al. (2001; 2002; Fine et al., 2004a-b). Here, as the quantification has been performed on the same set of compounds for all the experiments, we cannot exclude an under-representativeness of the substituted guaiacols towards the substituted syringols family.

Furthermore, in an effort to be more conservative regarding this matter, we have also replaced from the original manuscript the comparisons of average contribution between the different type of stove (Figure 3, in the original manuscript) by a more comprehensive figure including the full data set (Figure 3 of this document). We have also added in the supplementary information plots showing the contributions of PAHs, n-alkanes (C_{18} – C_{27}) and fatty acids (palmitic acid, stearic acid, palmitoleic acid, and oleic acid) as a function of the MCE (Figure 1, in this document).

Line 6, page 9:

Overall, the sum of PAHs, alkanes, and fatty acids accounts for less than < 8 (1. 6 – 7.6) % of the total POA mass concentration. The EF of the individual PAHs vary between 3 µg kg^{-1} and 4 mg kg^{-1}, with combined amounts between 2 and 14 mg kg^{-1}. The relative contributions of the PAHs to the POA mass concentration vary between 1.4 and 6.4 %. Phenanthrene and fluoranthrene are the most dominant as they represent over a third of the total PAH contributions. The total EFs of the alkanes vary between 0.5 and 2 mg kg^{-1}. They represent between 0.04 and 0.73 % of the total POA mass concentration. Four series of fatty acids including the saturated acids (palmitic acid and stearic acid), and the unsaturated acids (palmitoleic acid and oleic acid), were identified. Their total EFs are similar to the n-alkanes, and they contribute between 0.03 and 1.3 % of the total POA mass concentration. Like for levoglucosan, we observe an increase of their contribution with the MCE (see Figure S2 in the SI).

Other compounds reported in this manuscript account for a negligible fraction of the primary OA emission, with the exception of experiment 8 (stove B) where they (mainly the nitrocatechols, see Section 3.2) contribute < 3% of the total POA mass concentration.

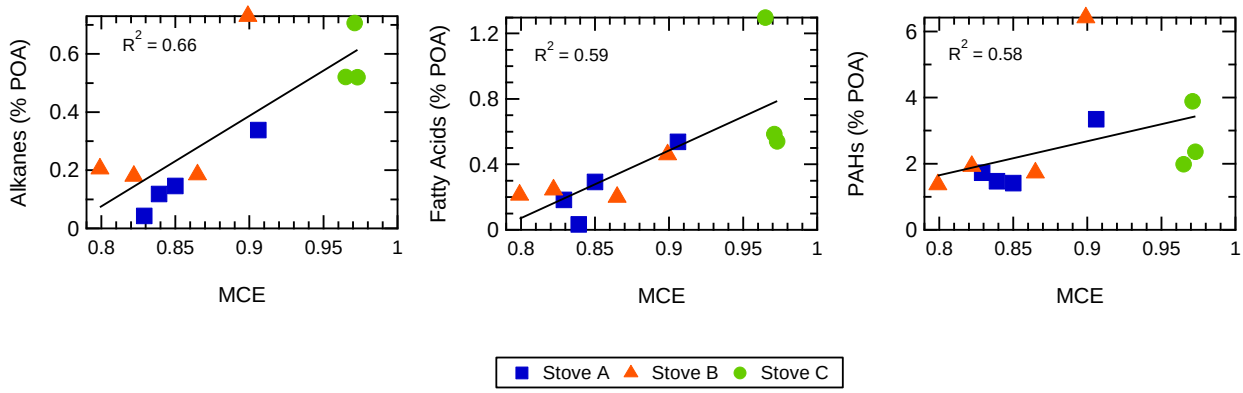

Figure 1: Contribution to the total POA mass concentration of PAHs, fatty acids, and n-alkanes ($C_{18} – C_{27}$).

Specific Comments

Page 3, Lines 18-30: This introductory discussion would be improved by re-organizing the topics. It is suggested that after introducing levoglucosan, the possibility that it can be oxidatively degraded in particles should be discussed, followed by a discussion of the secondary OA mass production from biomass burning emissions. The study investigates the topics of (1) emission factors for POA, (2) oxidative degradation of tracers, and (3) changes in OA composition due to secondary oxidation. The introduction should also follow this logical progression.

The introduction was revised entirely in the following manner:

Organic matter represents a major fraction (20 – 90 %) of particulate matter (PM) (Kanakidou et al., 2005). Organic PM is a complex mixture made up of tens of thousands of compounds (Goldstein and Galbally, 2007), with some of them established to be carcinogenic (Yu, 2002; Yang et al., 2010). Identifying and quantifying their contribution to the organic PM mass is key in order to resolve its origins and impacts on human health and climate.

Extensive characterization of the molecular composition of primary organic aerosol (POA) emissions has already been conducted. For example, biomass burning emissions from both softwood and hardwood combustions (Simoneit et al., 1993; Fine et al., 2001; Fine et al., 2002; 2004 ; Nolte et al., 2001; Schauer et al., 2001; Schmidl et al., 2008), vehicular emissions (Rogge et al. 1993; Rogge et al., 1993b; Fraser et al., 1999; Schauer et al., 2002; El Haddad et al., 2009), and cooking emissions ((Hildemann et al., 1991; Nolte et al., 1999; Schauer et al., 1999) have been broadly characterized. The full characterization of these emissions and their contribution to the concentration of total organic aerosol (OA) is of particular interest for source apportionment of ambient PM using molecular markers. In biomass burning emissions, compounds derived from the pyrolysis of cellulose and lignin are often reported. These include levoglucosan, a sugar anhydride compound and by-product of the thermal degradation of cellulose, and a commonly used tracer of the biomass burning organic aerosol (BBOA) in source apportionment (Waked et

al., 2014; Bonvalot et al., 2016; Maenhaut et al., 2016), as well as methoxyphenols, by-products of the thermal-degradation of lignin. In fresh emissions, the emission factors (EF) of these compounds can vary with the type of fuel (hardwood, softwood, or herbaceous types) (Schmidl et al., 2008b; Schauer et al., 2001, Fine et al., 2002; 2004)), the type of fire (open fire, fire places, wood stove) (Fine et al., 2002; 2004), or even the sampling set-up (in an experimental stack, in a dilution tunnel, or ambient) (Nussbaumer et al., 2010). Anhydrosugars and methoxyphenols are ubiquitous in the atmosphere impacted by biomass combustions and have been used to demonstrate the significant contribution of biomass burning to the total organic aerosol source globally (Robinson et al., 2006; Gelencsér et al., 2007; Puxbaum et al., 20 2007; Stone et al., 2010; Crippa et al., 2013).

Meanwhile data on the evolution of these well-known primary compounds during atmospheric aging of the emissions remain scarce. Authors have typically focused on the gas-phase oxidation of methoxyphenols (Net et al., 2011; Lauraguais et al., 2012; Yee et al., 2013; Lauraguais et al., 2014), only few have specifically addressed the aging of levoglucosan in the particle phase (Hennigan et al., 2010; Kessler et al., 2010; Lai et al., 2014), and only Fortenberry et al. (2017) have attempted to characterize the aged chemical fingerprint of biomass burning emissions at the molecular level, by means of a Thermal Desorption Aerosol Gas Chromatograph (TAG) connected to a Potential Aerosol Mass (PAM) flow reactor. Such data are of prime importance. Considering that the OA mass concentration from biomass burning can increase up to 7 times during photochemical aging in the atmosphere (Grieshop et al., 2009; Heringa et al., 2011; Ortega et al., 2013; Bruns et al., 2015; Tiitta et al., 2016), the knowledge of the sole primary chemical fingerprint is not sufficient to understand and to assess the global impact of biomass burning on the atmospheric aerosol burden.

In a previous publication, we investigated the POA emissions and SOA production potential generated by three woodstove appliances (two logwood stoves and one pellet stove) used for residential heating (Bertrand et al., 2017) using a HR-ToF-AMS. Here, we provide a comprehensive study, including the evolution of the molecular level composition of the emissions during a period equivalent to 5 hours of atmospheric aging. The experiments were conducted using the atmospheric chamber of the Paul Scherrer Institute (PSI, Villigen, Switzerland). The data were obtained by means of a TAG-AMS (Aerodyne Research Inc.). We determine the EF and emission profiles of biomass burning tracers. In a first part, we derive the effect of combustion conditions on the EFs and the contribution of the tracers to the POA mass concentration, and in a second approach we determine the effect of the atmospheric aging on the contribution of tracers to the total OA mass.

Page 3, Line 21-23: Is this statement meant specifically for biomass burning emissions? Please clarify.

Anonymous reviewer #1 is correct, this statement has been corrected.

Figure 2: It appears that TAG-AMS sampling is represented by both light green and light blue. If this is the case, please edit the le gend to clarify.

Figure 2 in the manuscript was edited to clarify the TAG-AMS sampling period (Figure 1)

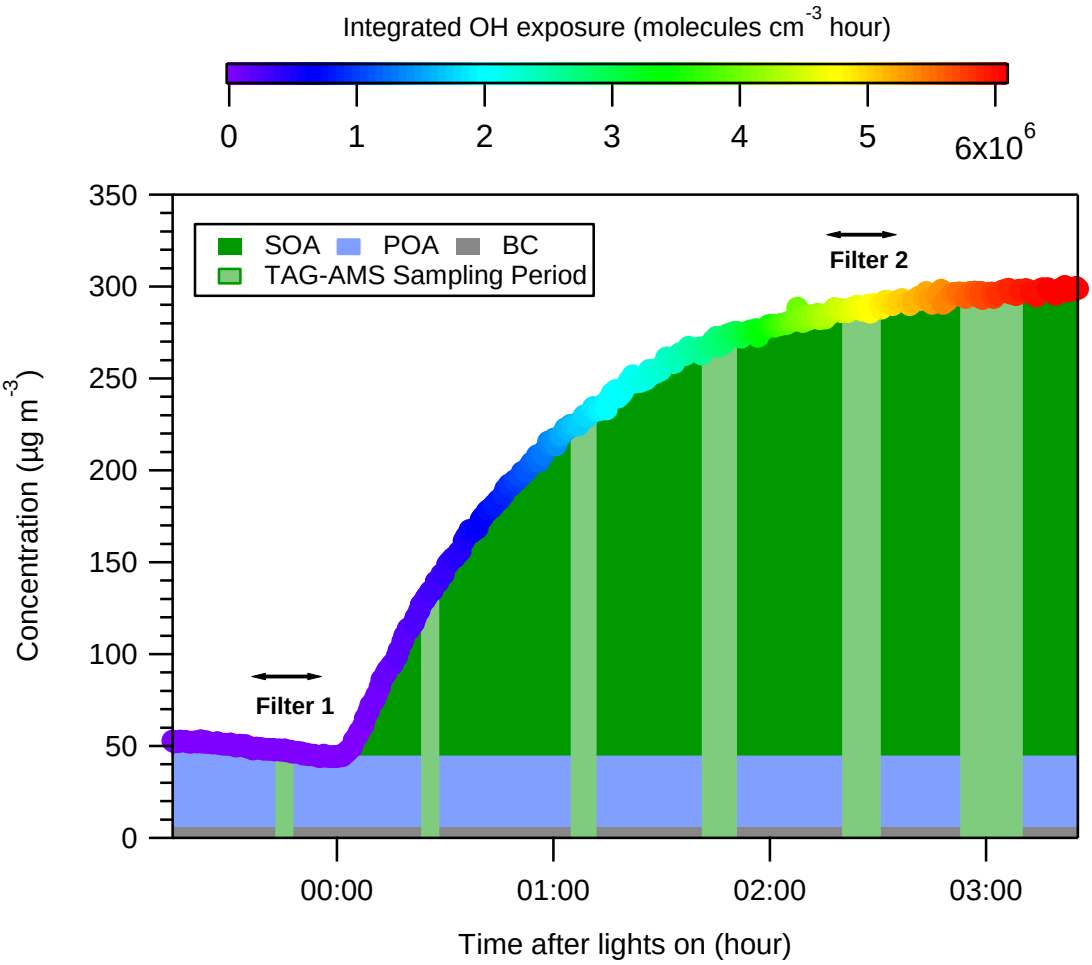

Figure 2: Example of the TAG-AMS and offline (quartz fiber filters) measurements sampling schedule during an aging experiment conducted at the PSI atmospheric chamber with emissions generated from woodstove appliances (Exp. 7, stove B).

Page 4, Section 2.1: How was the total OA quantified? If by HR-ToF-AMS, then this should be clearly specified and qualified by any sampling biases.

OA was indeed quantified using the HR-ToF-AMS. Line 15, page 4 was modified to include this information:

A HR-ToF-AMS (Aerodyne Research Inc.) [was used] for the bulk-condensed chemical composition and quantification of the non-refractory fraction of the aerosol (OA, sulfate, nitrate, ammonium).

Page 6, Lines 17-21: This can be removed from the methods section as it is actually a statement of the results (and will, indeed, be discussed at great length in the results section).

Following the suggestion by anonymous reviewer #1, this section was now moved in introduction of the results section.

Equation 1 (and supporting text): What value of k_wall/p was used?

The particle half time was comprised between 2.1 and 3.5 h or a kwall/p of (0.003 – 0.006 min^{-1}). We included this information line 4 page 7:

t is the time since lights on (in min) and $kwall/p$ is the eBC wall loss rate constant (0.003 – 0.006 in min^{-1})

Page 7, Lines 28-29: Please clarify what is meant by "we identify between 26-85% of the POA mass concentration". Ensure that the manuscript clearly identifies how total OA was quantified. It is assumed that the 'identified OA' is the mass concentration quantified by TAG-AMS.

The total OA mass concentration was quantified with the HR-ToF-AMS (9 – 177 ug m-3 for primary emissions), out of which the TAG-AMS is capable of identifying between 26 – 85 % (for primary emissions). Identified OA corresponds to the mass concentration quantified by TAG-AMS.

This statement was moved line 2, page 5 of the revised manuscript. For clarification purposes, and in addition to our changes already made in line 15, page 4 (as mentioned above), we modified the statement as follow.

These compounds contribute together between 26 - 85 % of the total POA mass concentration measured by HR-ToF-AMS (Figure 3).

Figure 3: Showing this figure with an 'unidentified' section of the bar would be more appropriate, since different amounts of OA were identifiable in each experiment.

Following in the comments by both reviewer #1 and 2 we revised the figure (Figure 3) and show now the contribution of the compounds to the total POA mass concentration measured by HR-ToF-AMS for all the experiments.

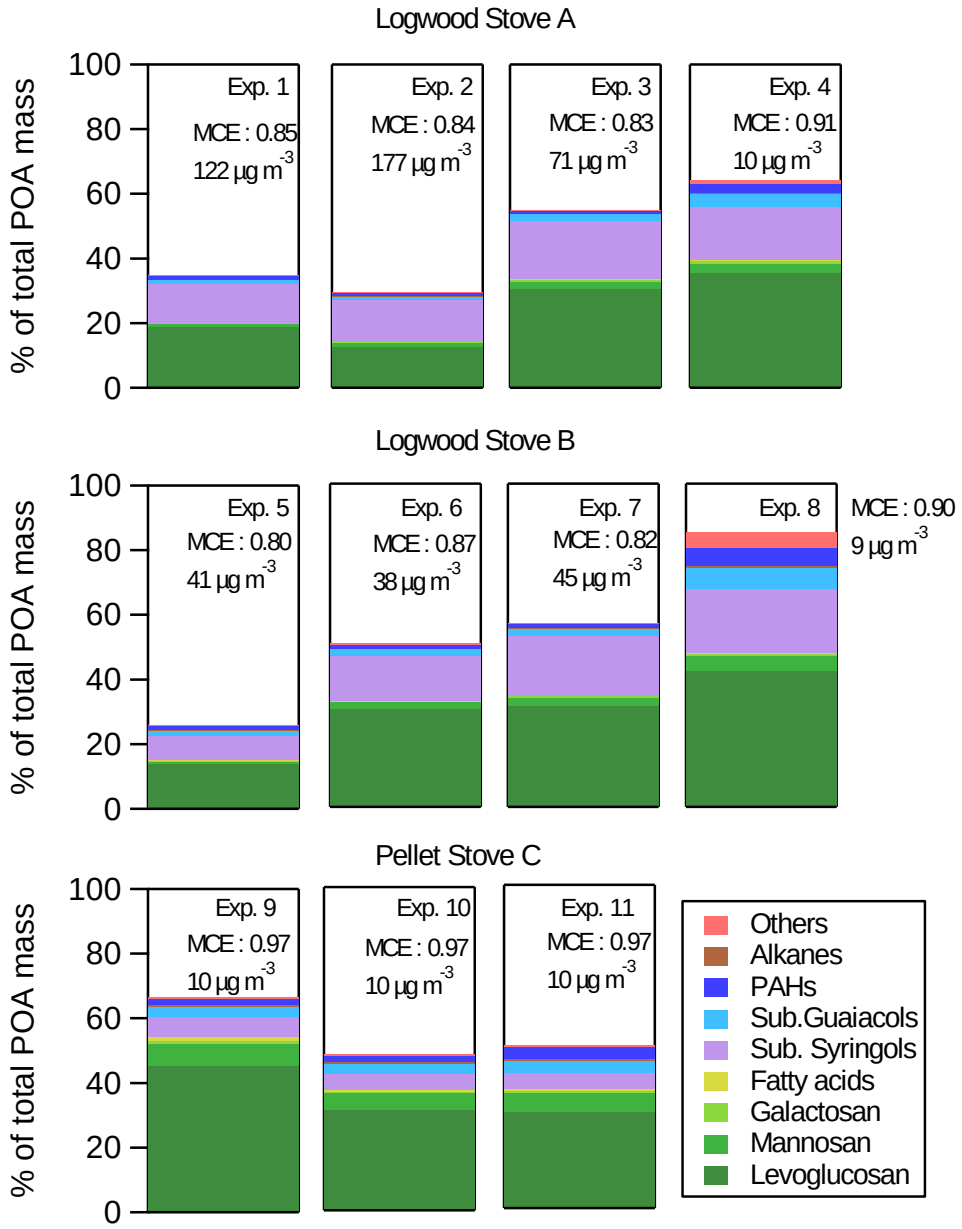

Figure 3: Contribution of the organic markers measured by TAG-AMS to the total POA mass concentration (indicated on graph) measured by HR-ToF-AMS, for all experiments.

Page 8, Lines 2-3: The text states "The MCE values for the experiments conducted with this stove [the pellet stove?] are 0.97," but Table 1 shows "MCE > 0.99" for pellet stove experiments. Which of these values is correct?

The MCE as indicated in the text and on the plot (Figure 4) are the correct values. We apologize for this mistake. Please find the correct version of the Table below:

Table 1: Summary of the experiments and conditions in the chamber before lights-on. MCE stands for modified combustion efficiency and THC is total hydrocarbon.

Stove	Exp #	MCE	Nb of TAG-AMS samples	*[eBC] ($\mu g.m^{-3}$)	*[POA] ($\mu g.m^{-3}$)	**[OA] ($\mu g.m^{-3}$)	*[NO_x] (ppb)	[THC]/[NO_x] (ppb/ppb)	[Cresol]/[NO_x] (ppb/ppb)
Stove A (Beech as logs)	Exp 1	0.85	6	17	122	495	98	31.5	1.1×10^{-1}
	Exp 2	0.84	7	12	177	785	252	26.9	1.1×10^{-1}
	Exp 3	0.83	7	6	71	388	90	38.5	1.2×10^{-1}
	Exp 4	0.91	8	5	10	72	128	7.7	2.7×10^{-2}
Stove B (Beech as logs)	Exp 5	0.80	7	5	41	143	50	47.2	1.2×10^{-1}
	Exp 6	0.87	7	13	38	202	119	18.1	5.0×10^{-2}
	Exp 7	0.82	6	6	45	289	114	24.3	7.2×10^{-2}
	Exp 8	0.90	7	4	9	53	80	19.6	4.5×10^{-2}
Stove C (Softwood pellets)	Exp 9	0.97	5	107	10	19	161	5.2	1.2×10^{-3}
	Exp 10	0.97	6	130	10	19	205	5.8	4.7×10^{-4}
	Exp 11	0.97	5	144	10	22	228	5.9	3.5×10^{-4}

*values retrieved just before lights on

**values retrieved at integrated OH exposure = 5×10^6 molecules cm^{-3} hour

Page 8, Lines 14-17: Please clarify (with evidence and explanation) that the nature of the artifacts that should have been associated with the prior studies based on methodology are actually consistent with the differences between the prior studies and the present study, as is vaguely suggested in the submitted manuscript.

In this section, we highlight the differences observed with other studies regarding the contribution of anhydrosugars to the total POA mass concentration. We argue that the differences stem from the type of set-up used: collection on quartz fiber filter of the emissions in a dilution tunnel vs online collection and analysis by TAG-AMS in a smog chamber.

Different artefacts in each of the method can cause the observed discrepancy. Sampling artefacts with filters are relatively well known although complex. The duration of the sampling period, the temperature, the concentration of OA, the dilution ratio can influence the measured concentration. (Eatough et al., 1990) and (Turpin et al., 1994) have estimated 80 % of the mass collected on filters can be lost due to volatilization (negative artefacts) and up to 50 % of the mass can be added to due partitioning of the semi-volatile compounds (SVOCs) onto the surface of the filters (positive artefact). TAG-AMS is free from these sampling artefacts. Uncertainties remain however regarding the potential degradation of the analytes during thermo-desorption.

An especially relevant point here is the dilution ratio. Between the ejector diluter and injection into a smog chamber, we estimate at 200 the total dilution factor. This is nearly 10 times what (Fine et al., 2001) estimate for their own set-up. In accordance to the partitioning theory of Odum et al., (1996) it is expected at lower dilution that more SVOCs will partition to the particulate phase (Robinson et al., 2007) and onto the filters, thus increasing the overall OA mass and decreasing the observed contribution of primary compounds such as levoglucosan.

Nevertheless, we modified the text as follow:

The conditions and methods with which they sampled the emissions were however different (on quartz fibers filters) with a dilution factor at least 10 times less than what is used in this study. This could result in a higher fraction of SVOCs partitioning to the particulate phase, therefore increasing the overall OA mass, and thus decreasing the individual contribution of the markers.

Page 8, Line 27: Methoxyphenols are not the 'predominant' class of species in the primary BBOA – Figure 3 clearly shows that anhydrosugars comprise the predominant fraction of the identifiable OA.

We modified the text line 27, page 8 to:

The methoxyphenols account for an important fraction of the POA.

Page 9, Lines 5-8: This sentence embodies an important criticism of the data interpretation within this study. The authors describe differences between the softwood and hardwood samples. At the same time, hardwoods and softwood fuels were burned under different conditions. The authors seem to interpret differences between the log wood stoves and the pellet stove as differences in fuel at this point, while at other points, the differences are attributed to burning conditions. If the interpretation given here is thought to be accurate, then an explanation for why burning conditions don't influence the observed difference must be described.

We agree with reviewer #1 that our interpretation of the data was not conservative all throughout of the manuscript. Note, this comment was part of the general comment of the paper by anonymous reviewer 1. Therefore we refer the reader to this section of the review for our response.

Section 3.2.1: The authors state that the primary compounds initially represent 48% of the POA, but after oxidation (4-6 hours) they represent < 8%... of what? Of POA? Of total OA? Can this just be described by the addition of SOA mass to the particles?

After oxidation, the primary compounds represent < 8 % of the total OA mass concentration measured with HR-ToF-AMS. The decrease in their contribution is a combination of at least two main effects:

- Actual depletion (oxidation and/or vapor wall loss)
- Additional SOA mass

We modified line 29/30 page 10 as follow:

The identified primary compounds initially represent 48 % of the total POA mass concentration but < 8 % of the total OA mass concentration after 4 - 6 hours of atmospheric aging (bin 4).

Figure 6 shows that the relative contribution of levoglucosan is somewhat stable around 40 % of identified OA throughout the experiment. Please clarify what is being quantified and to what fraction of the aerosol the percentage is referring.

On Figure 6 we show that levoglucosan represent at any time during the experiment 30 – 40 % of the identified (with TAG) OA mass fraction. The contribution of levoglucosan to the total OA mass concentration measured by TAG-AMS however decreases over time as demonstrated in Figure 8.

We revised Figure 6 (labels and legend) in the manuscript in order to clarify this (Figure 4 here).

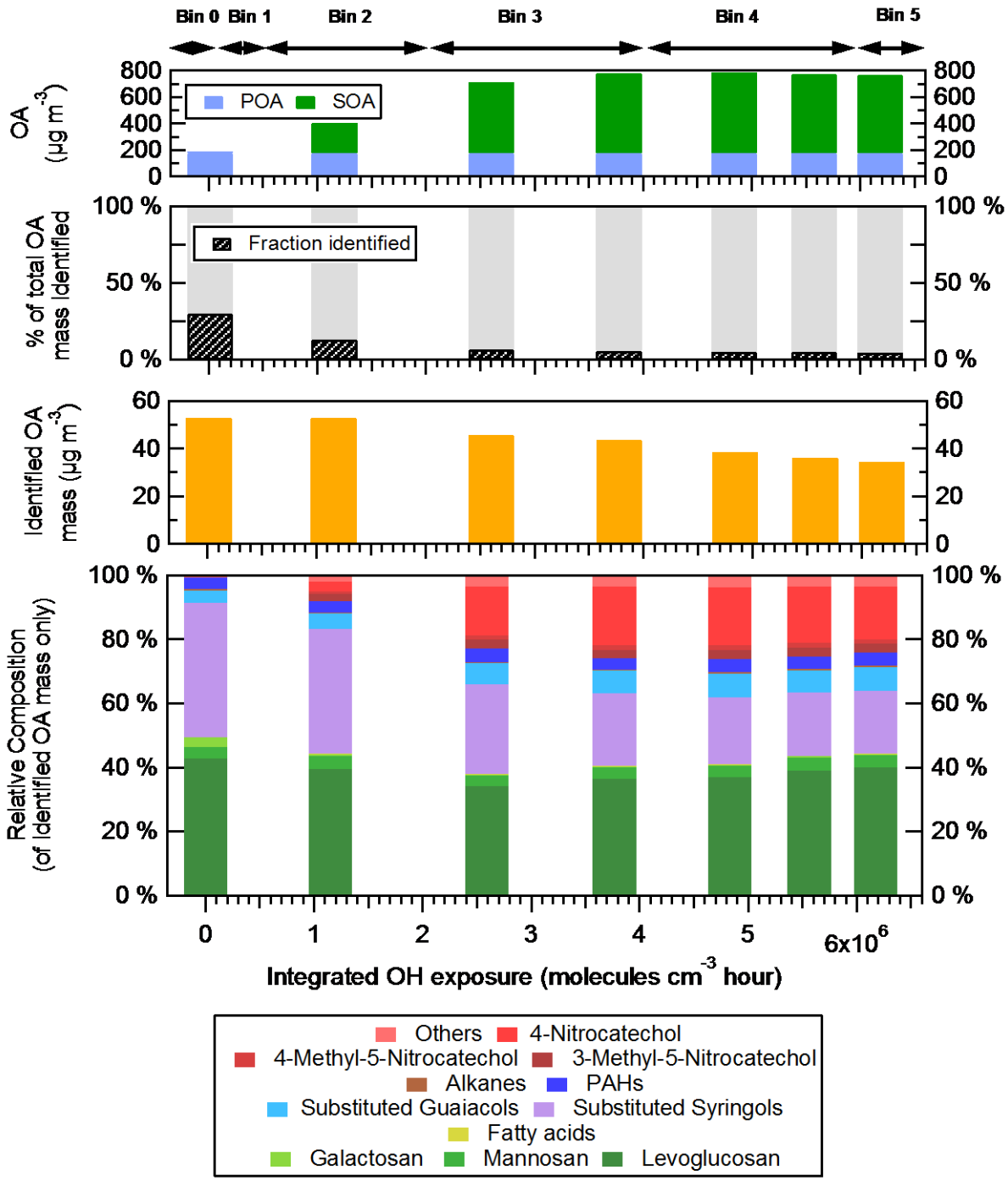

Figure 4: Typical evolution of the chemical fingerprint of the organic aerosol emitted by biomass burning during atmospheric aging (Exp. 2, stove A). "Identified OA mass" refers to the OA mass concentration whose molecular composition is resolved by TAG-AMS.

It seems from this text that the mass concentration of levoglucosan, for example, decreased substantially during exposure to OH, but Figure 6 suggests that it is relatively stable against aging based on how the data are shown. Then again, Figure 7 shows the ER = 0.6, so the actual concentration is decreasing during aging. Figure 8 shows that levoglucosan is decreasing as a fraction of total OA. Basically, Figure 6 seems inconsistent with Figs 7 and 8. Is the change in the identifiable fraction playing a role? It is very likely that the data are somehow telling a consistent story, but it is not presented clearly. [Note that this comment explicitly references levoglucosan, but the comment also applies to other Primary Compounds.]

As noted by anonymous reviewer #1, the figures show different but consistent evolutions regarding levoglucosan (and other markers). As the OA mass increases during aging and as the compounds are depleted, one has to carefully look at the referential to which the concentration of the marker is normalized to. Through figure 6 to 8 we choose 3 different referential. Each one aims at illustrating one specific aspect of the modification of the chemical fingerprint during aging.

In Figure 6 of the manuscript, we show a typical and comprehensive evolution (through one example) of the different parameters measured within this study (top panel : evolution of the OA mass concentration measured by the HR-ToF-AMS, 2nd panel : the fraction of total OA quantified/identifed by TAG, 3rd panel : total absolute concentration of the compounds quantified by TAG - which remains sratherconstant all throughout the aging - and bottom panel : relative contributions of all the compounds quantified by TAG to the identified OA fraction). We agree that showing the relative concentration of the organic markers to the total OA mass concentration would be more pertinent, but the very fast drop of the total identified OA prevents such representation. For better visibility, we choose to represent the contribution of organic markers to the total identified OA. As the total absolute concentration of the identified fraction (3rd panel) is rather constant all throughout the experiment, this plot provides a good comparison of the concentration of the secondary markers with that of the primary markers, during the aging process.

One would have to refer to Figure 8 (top panel) to see the evolution of the contribution of levoglucosan to the total OA mass concentration measured by HR-ToF-AMS. There, the contribution of levoglucosan is shown to decrease as SOA is formed and levoglucosan depletes (due to oxidation and/or vapor wall loss). This information is especially important in the context of source apportionment studies (eg. Chemical Mass Balance model assumes the contribution of the markers to total OA is constant over time).

Finally, in Figure 7, we look at the enhancement ratio. A compound with an ER > 1 would indicate the compound is formed during aging. An ER < 1 relates to the decay of a compound (i.e. if ER = 0.2, 80 % of the mass of the compound is lost during aging). The study of the ER of each of the marker allows us to differentiate between primary and secondary type of compounds.

Page12,Line33–Page13,Line2: What is the relevance of the ratios of nitrocatechols to levoglucosan, since it is known that the latter is consumed during OH exposure?

Page 13, Line 3: Higher levels of 4-NC are discussed with reference to prior observations, however far larger discrepancies between the prior observations and the present study exist for MNC/LG. The 4-NC/LG ratio range at least overlaps the prior studies, but the MNC/LG ratios are shifted by about a factor of 10, yet are not discussed.

The ratios of nitrocatechols to levoglucosan in the smog chamber vs ambient put into perspective the concentration of the secondary markers formed during our experiments.

The ratios NC/LG and MNC/LG for these experiments indicated in the text have been switched. We apologize for this mistake. The 4-NC/LG ratio observed in this study are 0.25 – 0.5 while the MNC/LG ratios vary from 0.06 to 0.15. As such, the ratio of MNC/LG largely overlaps with what is observed in the ambient while the NC/LG is much higher as mentioned later in the text.

As explained, we hypothesize the high level of 4-NC could be related to the high level of NOx also present in the chamber.

We thank anonymous reviewer #1 for his comment and have corrected the text line 3, page 13 as follow.

Here, the 4-NC/LG and MNC/LG ratios vary from 0.25 to 0.5 and 0.06 to 0.15, respectively.

Page 13, Line 7: Does "the mass spectra (EI, 70 eV)" refer to those obtained from a database? Please clarify. If from a database, please cite the reference.

The.4-nitrocatechols mass spectrum was obtained from the NIST database. We have included this reference in the text. The methyl-nitrocatechols mass spectrum was obtained from in-lab analysis of 3-Methyl-5-Nitrocatechol by GC/MS (Thermo Trace GC 2000-Polaris Q) (without derivatization).

Page 13, Line 23-24: The impact of burning conditions is less clear since the fuel was different for Stove C. Please clarify this issue in all instances within the manuscript, including Page 9, Lines 5-8 as discussed in a comment above.

We revised this section of our conclusions in the following manner:

The emissions factors of the individual organic markers are mostly driven by the MCE. Smoldering combustion increases the EF of the reported compounds. Within the experiments conducted with the same fuel, the contribution of the markers to the total POA mass concentration also vary according to the MCE (i.e. lower contribution at smoldering conditions). This indicates that smoldering combustion induces the emission of OA with a more complex composition. The contribution of levoglucosan for instance varies from 40 % – 50 % at the highest MCE, down to 15 % at the lowest MCE.

Page 14, Lines 1-3: How might measurements be improved to detect and quantify a greater fraction of the POA and SOA mass? Can this be inferred from the limitations of TAG-AMS? [A discussion of this topic may not be entirely appropriate for the conclusion section, but may be a worthwhile topic to include elsewhere in the manuscript.]

TAG-AMS, like most GC/MS is limited in its capacity at eluting highly oxygenated and high molecular weight species. While it is understood that the detectable OA fraction by the TAG-AMS could potentially reach 100 % in the case of an aerosol purely composed of hydrocarbons (Williams et al., 2015) the instrument typically only detects around 20 % of the total OA (Williams et al., 2006) in an ambient set-up.

A first approach to circumvent this limitation is to focus on the thermal decomposition window i.e. the signal output by TAG during thermal desorption of the analytes (300 °C – 310 °C). Fortenberry et al., (2017) and Williams et al. (2015) have observed a signal increase for specific ions which they relate to the decomposition of high molecular weight molecules and thermally labile oxygenated OA. While this method does not provide information at the molecular level, it gives insights into the overall oxidation level of the bulk OA sample and can provide time series of fragments which could be used as tracer for fresh and aged BBOA.

However, the version of the TAG-AMS described here could not be operated in this way.

Technical corrections – Page 3, Line 4: correct the in-line citation Page 9, Line 3: correct the in-line citation Page 9, Line 21: consider beginning a new paragraph for fatty acids Page 13, Line 8: "Figure 10" should be "Figure 9"

Corrected as suggested.

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