# Response to Reviews and Comments

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Characterization of primary and secondary wood combustion products generated under different burner loads

Bruns, E.A., Krapf, M., Orasche, J., Huang, Y., Zimmermann, R., Drinovec, L., Močnik, G., El-Haddad, I., Slowik, J.G., Dommen, J., Baltensperger, U., Prévôt, A.S.H.

We thank the Referees and Commentators for the comments and we have revised the manuscript to incorporate the feedback. We have copied the remarks of each Referee and Commenter in *black italics* and our responses are given in regular black font. Manuscript text with revisions is given in regular blue font.

**Anonymous Referee #1**

Received and published: 20 November 2014

*The manuscript entitled "Characterization of primary and secondary wood combustion products generated under different burner loads" by Bruns et al. investigates the effects of fuel loadings on both primary and secondary wood combustion products in a smog chamber, including the composition of both the gas and the particulate phase. Special interest lies on the contribution of polycyclic aromatic hydrocarbons (PAH's) to organic aerosol mass, determined by an Aerosol Mass Spectrometer (AMS) and by GC-MS analysis from filter samples. Within this study, a novel approach for the quantification of these PAH's from AMS data was therefore developed. Main conclusions from the manuscript include that the contributions of PAH's to total organic aerosol (OA) increase with higher loadings of combusted wood in the burner. The increase of OA concentrations during aging rises with fuel loadings. Furthermore, an increase of functionalized PAH's were observed with aging. The knowledge of the composition of wood burning emissions, especially the contribution of PAH's and their oxidation products is relevant since these compounds are known to have adverse effects on health. Only few publications on the investigations of secondary organic aerosols (SOA) deriving from wood combustions are available. Thus, these results are important for the understanding how gas phase PAH's emissions from this source contribute to the formation of SOA. Overall, the paper is well written and the new data is important to the community. Further, the work is within the scope of work published by ACP. Therefore, I recommend publication once the comments and questions below are addressed.*

*Major comments and questions:*

*1- An important point was made in a previous short comment from Glyn Hughes. The authors explain precisely the preparation of the smog chamber but do not point out how the burner was prepared prior to the loading with wood and burning processes. Such a description for the burner should be added.*

The experiments were not conducted at a combustion test facility, where burning is highly controlled, and instead represent real-world, residential burning. However, care was taken to replicate each burn for each condition as closely as possible (e.g., starting fuel mass, number logs, initial log arrangement in the combustion chamber). Logs were approximately 30 cm in length and 10 cm in width and firestarters were cylindrical bundles of pine wood shavings, paraffin and natural resin and approximately 10 cm in length and 2 cm in width. Prior to starting the burn, logs were arranged in a pyramid shape for the average load, as shown in Figure S1. For the high load, the logs completely filled the combustion chamber and thus, there was no special arrangement, as shown in Figure S1. Firestarters were interspersed among the logs. Burning was started by igniting the firestarters using a hand-held lighter after which the burner door was immediately closed. The damper was left completely open to allow maximum air flow into the combustion chamber until the logs fully caught fire (~10-15 min), at which point the air flow was reduced.

The fuel was burned in a modern log burner: Avant model manufactured by Attika. Photographs of the 0.037 $m^3$ combustion chamber are shown in Figure S1. The combustion chamber surfaces are lined with vermiculite. During burning, ash and residues were not actively removed, but all ash and residues were removed from the combustion chamber prior to beginning each burn. Temperature measurements were not made in the combustion chamber during burning.

Additional details of the burner preparation were added to the caption of Figure S1 and main text (pages 26045-26046).

The main text was revised as follows:

“Six wood combustion experiments using beech wood with a moisture content of 10±2% (mean ± 2 sample standard deviations (2s)) were conducted in a 27-$m^3$ smog chamber (Paulsen et al., 2005) to investigate the effects of wood loading on primary emissions and secondary products. Three of the experiments (1-3, Table 1) were conducted with a starting wood load of 2.21±0.09 kg (3 logs without bark, 4 pieces of kindling and 3 fire-starters comprised of pine wood shavings, paraffin and natural resin) and three experiments (4-6, Table 1) were conducted with a starting wood load of 7.4±0.2 kg (9 logs without bark, 8 pieces of kindling and 4 fire-starters) in the ~0.037 $m^3$ burner combustion chamber of a modern log wood burner (Avant, Attika) (Fig. S1 in the Supplement). Hereafter, these two cases are referred to as “average load” and “high load”, respectively. Prior to each burn, ash and residue from the previous burn were removed. Each burn began by igniting the firestarters using a hand-held lighter and immediately closing the burner door. The damper was left completely open to allow maximum air flow into the combustion chamber until the logs caught fire (~10-15 min), after which the air flow was reduced.

The caption now reads as follows:

“Figure S1. Representative photographs of the loaded wood combustion chamber (lined with vermiculite) before burning for (a) average and (b) high load conditions. Logs were approximately 30 cm in legnth and 10 cm in width and firestarters (~10 cm × 2 cm) were intersperse among the logs.”

*2- Using a chamber presents a limitation on the number of trials possible which creates a scenario like a field campaign. I assume time limitations prevented repeat experiments and experiments with different fuel loadings. Ideally, those experiments would have been completed to allow statistical analysis. Experiment 1 clearly shows different results than experiments 2 and 3 although the fuel loadings are roughly the same. Are there any reasons for these discrepancies, e.g. the very high OA and PAH mass loadings which were seen in experiment 1?*

The Referee is correct that the number of repeat experiments was limited by the practical considerations of operating a large smog chamber (e.g., instrument availability and time and expense required for each experiment). However, three replicates were conducted for each condition. The replicates for each condition all support the main conclusions of the paper, namely that average load conditions result in lower PAH contributions to total OA and lower OA production with aging than high load conditions.

Although the replicates for each condition support the main conclusions of the paper, there is variability among the replicates performed under the same conditions, which is largest for experiment 1, as the Referee points out. There are no obvious reasons why the OA emission factors in experiment 1 were higher than the other high load experiments. Although care was taken to reproduce the same burn conditions during each replicate, the differences in experiment 1 are likely due to the inherent variability associated with residential wood combustion.

The main text has been modified as follows (page 26056) :

"The total PM emission factor was similar for each experiment, except experiment 1, for which it was over 3 times greater than the other burns due to increased organic emissions (Table 1). There were no obvious reasons why the total PM emission factor in experiment 1 was considerably higher than the other experiments. Although the MCEs were similar for all burns (Table 1), this illustrates the real-world variability of wood combustion emissions and the large range of possible emission factors from the same burner and operator."

*3- Why did the authors chose a different experimental strategy for experiment 6 than for the other experiments, precisely the second and third injection of burning emissions?*

A different experimental strategy was adopted for experiment 6 to meet the requirements for a specific filter sample, the analysis of which will be presented in a future publication. Despite the different experimental strategy, the results of experiment 6 are in agreement with the other high load experiments (e.g., higher PAH contribution to total OA).

*4- Currently, the ions C2H4O2+ (m/z=60) and C3H5O2+ (m/z=73), detected with the AMS, are commonly used as tracers for primary biomass burning emissions in ambient measurements, as they are preferably formed from the fragmentation of levoglucosan within the AMS. The HR spectra in figure 1 seem to show large differences in f60 and f73 ratios between the experiments. The authors should also address this issue.*

The temperature in the combustion chamber affects the relative quantities of emitted compounds throughout the burn. A nice summary is given by Fitzpatrick et al. (2007) of the chemical classes emitted as a function of burn temperature. At lower temperatures, products formed from the pyrolysis of lignin and carbohydrates, including levoglucosan, dominate. As the burn temperature increases, the relative contribution of these compounds decreases and products such as polycyclic oxygenates and PAHs dominate.

The fraction of $C_2H_4O_2^+$ relative to the total OA ($fC_2H_4O_2^+$) for the primary emissions was higher in the average load conditions (0.050-0.094) compared to the high load conditions (0.012-0.029), whereas the fraction of PAHs in the total primary OA (*f*PAH) was lower in the average load experiments. The higher $fC_2H_4O_2^+$ and lower *f*PAHs in the average load experiments suggests that the burn temperatures were lower compared to the high load experiments, likely due to different fuel/air ratios. Future experiments with temperature measurements made directly in the combustion chamber would provide further insight into this matter.

A discussion of biomass burning markers was added to the main text: (page 26060, after line 6):

"The ion $C_2H_4O_2^+$ is used as a biomass burning tracer in ambient AMS data. Interestingly, the fraction of $C_2H_4O_2^+$ relative to the total primary OA ($fC_2H_4O_2^+$) was higher in the average load experiments, ranging from 0.050-0.094, compared to the high load experiments which ranged from 0.012-0.029. As summarized by Fitzpatrick et al. (2007), lower burn temperatures favor the formation of products from the pyrolysis of lignin and carbohydrates, including levoglucosan. As the burn temperature increases, the relative contribution of these compounds decreases and products such as polycyclic oxygenates and PAHs dominate. The higher $fC_2H_4O_2^+$ and lower *f*PAHs in the average load experiments suggests that the variability in $fC_2H_4O_2^+$ was due to lower burn temperatures in the average load experiments, likely due to different fuel/air ratios."

Reference:

Fitzpatrick, E.M., Ross, A.B., Bates, J., Andrews, G., Jones, J.M., Phylaktou, H., Pourkashanian, M. and Williams, A.: Emission of oxygenated species from the combustion of pine wood and its relation to soot formation, Process Saf. Environ. 85, 430-440, 2007.

*5- I have some general questions regarding the analysis of the AMS data, especially the novel approach to detect and quantify PAH-peaks: The fits of the high resolution (HR) peaks of the PAH-ions showed in the supplement look quite nice, as the authors already stated in their publication. I assume that the IGOR-based AMS data evaluation software SQUIRREL (for UMR data) and PIKA (for HR data) was used in this study. It would be helpful to give some information in the supplement, which software versions you used and how the parameters for the m/z calibration, the peak width and peak shape were determined, e.g. did the authors include these PAH ions for these determinations? Currently, PAH contributions are considered in the SQUIRREL UMR fragmentation table as an additional aerosol subclass, but are not considered quantitatively by default. Did the authors use these entries in a certain way?*

The Referee is correct that SQUIRREL and PIKA were used in this study. SQUIRREL version 1.53F and PIKA version 1.12F were used. To improve the mass calibration in the higher *m/z* range, PAH ions with sufficiently high signal to noise were used in the determination of the *m/z* calibration and peak width parameters. PAH contributions were considered quantitatively by selecting the option to "define Org and PAH separately" in the fragmentation table and incorporating the modifications described in the main text.

Additional information was added to the main text and supporting information. The following information was added to the AMS data analysis section (page 26051):

“AMS data were analyzed in Igor Pro 6.3 (Wavemetrics) using the SQUIRREL (version 1.53F) and PIKA (version 1.12F) data analysis programs.”

(page 26053):

“To achieve satisfactory fitting in the higher *m/*z range, PAH ions with sufficiently high signal to noise were used in the determination of the *m/z* calibration and peak width parameters.”

*Detailed comments:*

*Page 26046, line 20-21. How did the authors judge if the burning conditions are stable and there were no emissions from the fire starters? Which parameters were used which indicated that the injection into the chamber had to be done at least 15 Minutes after the ignition?*

Injection into the smog chamber began at least 15 min after starting a burn to ensure that the emissions were free from the influence of the firestarters. According to the manufacturer, the firestarters burn for ~10 min after ignition. This was confirmed during experiments with only the firestarters in the combustion chamber where the fire starters were consumed in less than 10 min. Visual inspection during the wood burning experiments also confirms that the firestarters were consumed within the first 15 min of burning.

The description ‘stable burning’ was meant to indicate that the highly variable starting phase and smoldering phase were not included in the emissions, as described on page 26046-26047, lines 28-6. However, online measurements of the direct emissions during the burn were not conducted to chemically separate the different burn phases, as done in a recent study (Elsasser et al., 2014). The sentence referenced by the Referee was modified (page 26046):

“Emission injection into the chamber began at least 15 minutes after ignition to ensure that the emissions were not influenced by firestarters.”

Reference:

Elsasser, M., Busch, C., Orasche, J., Schön, C., Hartmann, H., Schnelle-Kreis, J. and Zimmermann, R.: Dynamic changes of the aerosol composition and concentration during different burning phases of wood combustion, Energ. Fuel 27, 4959-4968, 2013.

*Page 26048, line 12. Was the W-mode of the AMS also used in this study? It would be interesting, how the PAH-peaks at the high m/z look like in this mode. The pictures of the fitted peaks of the V-mode in the supplement show quite high signals, indicating there might be enough signal to get nice peaks also in the W-mode. The use of Wmode data would also enhance the identification and quantification of HR-peaks with sufficient signals and to distinguish not only between PAH and non-PAH related ions at the same nominal mass, but also between several different PAH related ions at the same nominal mass, if these cases exist. As the authors already stated out, the last two issues are difficult, but important to achieve.*

W-mode data was not collected during this study. We agree with the Referee that the W-mode data would enhance the identification of HR peaks, particularly at higher *m/z*s, and will be collected during future experiments.

*Page 26048, line 20. Was the humidity of the sample air after drying with a Nafion dryer measured to assure that the air was really dry? We well know, that at high humidities, the collection efficiency (CE) of the AMS changes, despite the fact that the CE was already set to 1 in this study.*

The humidity of the sample air after the Nafion dryer was not measured during the experiments. Higher relative humidity is expected to increase the collection efficiency towards 1. As a collection efficiency of 1 was applied to all experiments based on the findings of previous biomass burning studies (Hennigan et al., 2011; Heringa et al., 2011; Heringa et al., 2012; Ortega et al., 2013; Eriksson et al., 2014), the AMS data are already lower limits with respect to collection efficiency. Also, the relative humidity in the smog chamber was similar in each experiment (57-63%) and remained constant throughout each experiment which would eliminate potential biases between experiments due to altered collection efficiencies from un-dry particles/underperformance of the Nafion dryer.

References:

Eriksson, A.C., Nordin, E.Z., Nystrom, R., Pettersson, E., Swietlicki, E., Bergvall, C., Westerholm, R., Boman, C. and Pagels, J.H.: Particulate PAH emissions from residential biomass combustion: time-resolved analysis with aerosol mass spectrometry, Environ. Sci. Technol. 48, 7143-7150, 2014.

Hennigan, C.J., Miracolo, M.A., Engelhart, G.J., May, A.A., Presto, A.A., Lee, T., Sullivan, A.P., McMeeking, G.R., Coe, H., Wold, C.E., Hao, W.M., Gilman, J.B., Kuster, W.C., de Gouw, J., Schichtel, B.A., Collett, J.L., Kreidenweis, S.M. and Robinson, A.L.: Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber, Atmos. Chem. Phys. 11, 7669-7686, 2011.

Heringa, M.F., DeCarlo, P.F., Chirico, R., Lauber, A., Doberer, A., Good, J., Nussbaumer, T., Keller, A., Burtscher, H., Richard, A., Miljevic, B., Prévôt, A.S.H. and Baltensperger, U.: Time-resolved characterization of primary emissions from residential wood combustion appliances, Environ. Sci. Technol. 46, 11418-11425, 2012.

Heringa, M.F., DeCarlo, P.F., Chirico, R., Tritscher, T., Dommen, J., Weingartner, E., Richter, R., Wehrle, G., Prévôt, A.S.H. and Baltensperger, U.: Investigations of primary and secondary particulate matter of different wood combustion appliances with a high-resolution time-of-flight aerosol mass spectrometer, Atmos. Chem. Phys. 11, 5945-5957, 2011.

Ortega, A.M., Day, D.A., Cubison, M.J., Brune, W.H., Bon, D., de Gouw, J.A. and Jimenez, J.L.: Secondary organic aerosol formation and primary organic aerosol oxidation from biomass-burning smoke in a flow reactor during FLAME-3, Atmos. Chem. Phys. 13, 11551-11571, 2013.

*Page 26057, line 19-21. It is confusing that the fragmentation table is linked also to the inorganic aerosol species at this point, because on page 26053, line 11, it was stated that these species were determined by using HR spectra, where most of the ions are fitted and not assigned by the fragmentation table. This section should be revised.*

The text was clarified as follows (page 26057, lines 19-21):

"The mass spectral signal is separated into different chemical classes (i.e., organic, PAH, nitrate, sulfate, ammonium and chloride) as described in the data analysis section."

*Minor comments:*

*Page 26057, line 15. Within "as discussed in previously", the word "in" has to be deleted.*

This has been corrected.

*Page 26061, line 3. Between "measured" and "m/z", a space character is missing.*

This has been corrected.

**Anonymous Referee #2**

Received and published: 2 December 2014

*The manuscript of Burns et al. with the title "Characterization of primary and secondary wood combustion products generated under different burner loads" presents a study that describes methods and results of wood combustion experiments. The primary and secondary products under different burner loads were investigated using up-to date online techniques and more conventional filter methods. A special focus was on study of polycyclic aromatic hydrocarbons (PAHs) and their determination using aerosol mass spectrometer (AMS). The aging of emission products was also tested in a chamber.*

*The topic as well as the presented questions and answers of this manuscript fit well in the scope of this journal. The manuscript presents novel ideas and data and it presents substantial and reliable conclusions. The presented methods and assumptions are valid and clearly outlined. The results are sufficient and the interpretations and conclusions are valid. The experiments are adequately described in the manuscript. The results and investigations of this manuscript are well compared to the other scientific publications of the field. The title describes the content of the manuscript reasonably well as well as does the abstract. The presentation and structure of the manuscript and the used language are clear and of high quality.*

*This reviewer strongly recommends publication of this skilfully prepared manuscript after the scanty modifications presented below are made and after the comments and questions raised by Anonymous Referee #1 and by Glyn Hughes are addressed.*

*General comments:*

*Throughout the manuscript, the adjective 'significant' has been used to mean 'considerable, noteworthy, notable, remarkable' but as I understand, not to imply any statistical significance. I recommend using other adjectives than significant when you do not mean to express statistical significance.*

We have taken the recommendation of the Referee and have replaced or removed the word 'significant' throughout the text when not discussing statistical significance.

*Specific comments:*

*This is probably not your fault but in the text all -ff-'s and –ffi-'s are in italics (e.g. in words difference, coefficient, etc.).*

This was not the case in the originally submitted document and it will be checked in the next set of page proofs.

*Don't place space in 'm/z'. Check throughout the manuscript.*

There was no space in '*m/z*' in the originally submitted document and it will be checked in the next set of page proofs.

*Page 26056, lines 19-23. This sentence does not read well. Please, clarify it.*

This sentence has been split into two sentences and now reads as follows:

"Orasche et al. (2013) found total PM emission factors were a factor of about 1.4 higher for high load flaming conditions than for average loads, whereas Elsasser et al. (2013) found four times higher PM emissions generated under high load conditions compared to average load conditions. However, it is noted the Elsasser et al. (2013) result was determined from a single measurement."

*In the text and in the tables, you use numbers 1-6 for the experiments but in the figures, the letters a-f are used. Why not use the same logic throughout the manuscript?*

The labelling on Figures 1-3, S5 and S6 has been modified to include the experiment number.

*Anonymous Referee #1 has already asked you about the m/z ratios of 60 and 73. Also I would like to see more discussion related to these m/z's in this manuscript.*

A discussion on this issue has been added to the text. Please see the response to Referee 1 for more details.

**G. Hughes**

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*Most interesting, but, unless I've missed something, you don't explain precisely how the fuel was burned, in what shape and size of what sort of container, on what surface, how insulated and at what temperatures, nor what shapes and sizes the fuel elements were, or how placed. Was ash and residues left around, or allowed to fall away? We well know that these factors can alter combustion and emissions by more than an order of magnitude.*

Please see response to similar comment made by Referee #1.

**C. Herring**

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*PAH molecular ions have been shown to occur at even molecular masses. In the case of the HR-ToF-AMS, the strongest signals are seen at the [M]+ unless there are an odd number of carbons, in which case the strongest signal is typically at [M-1]+ (Džepina et al. 2007). In Table 2 of the manuscript, the authors provide a list of "PAH parent ions" and include five ions with odd molecular masses (m/z 139, 163, 165, 189, 199). It is not made clear which PAH compounds these ions are expected to be originating from. Bente et al. (2009) had previously attributed some of these ions (m/z 139, 165, 189) to alkylated aromatic fragments of PAH compounds. Could the authors clarify how they determined the classification of these odd-molecular mass ions?*

*References*

*Bente, M., Sklorz, M., Streibel, T. and Zimmermann, R. (2009). Thermal Desorption-Multiphoton Ionization Time-of-Flight Mass Spectrometry of Individual Aerosol Particles: A Simplified Approach for Online Single-Particle Analysis of Polycyclic Aromatic Hydrocarbons and Their Derivatives. Analytical Chemistry 81:2525-2536.*

*Džepina, K., Arey, J., Marr, L. C., Worsnop, D. R., Salcedo, D., Zhang, Q., Onasch, T.B., Molina, L. T., Molina, M. J. and Jimenez, J. L. (2007). Detection of particle-phase polycyclic aromatic hydrocarbons in Mexico City using an aerosol mass spectrometer. International Journal of Mass Spectrometry 263:152-170.*

Table 2 shows the parent ions included for the quantification of PAHs from the AMS data. As described in the AMS data analysis section, "Signal from $[M]^{2+}$, $[M\text{-}H]^{+}$, $[M\text{-}H]^{2+}$, $[M\text{-}2H]^{+}$, $[M+H]^{+}$, $[M+H]^{2+}$ and isotopic contributions from each of the singly charged ions from the presence of a single $^{13}C$, referred to as associated ions hereafter, for each non-oxygenated PAH parent ion were included in the analysis."

Original phrasing referred to [M]+ peaks used in PAH analysis as 'parent ions'. Parent ion implies an unfragmented species, however, as stated in the manuscript, "There are considerable PAH signals as low as *m/z* 128 (Fig. 1), which if interpreted as a parent ion would indicate naphthalene; however, this compound is expected to be fully in the gas phase (Pankow, 1994). Therefore, this suggests that the PAH signals observed in the lower *m/z* region are likely from PAHs that have undergone fragmentation in the AMS vaporization/ionization process." To eliminate the confusion with this terminology, we have changed the wording throughout the text and in Table 2 from PAH 'parent ion' to 'base ion', these base ions are likely fragments of larger (parent) PAHs, especially in the lower *m/z* range and for the ions noted in the comment.

Unfortunately, from the AMS data alone we are not able to determine the PAHs from which the fragments originate, including for the odd molecular mass peaks. As stated in the comment, peaks at *m/z* 139, 165 and 189 have been observed previously in the mass spectral analysis of wood ash sample and attributed to fragments of alkylated aromatics, although with a different ionization method (Bente et al., 2009). Bente et al. (2009) also observed considerable signal at *m/z* 163 in these samples.

The text has been modified to move the additional discussion of PAH fragmentation (page 26060, lines 17-22) from the results and discussion into the AMS data analysis section (page 26053) and to discuss the odd molecular weight ions as follows:

“PAH base ions included in the analysis are shown in Table 2. Signal from $[M]^{2+}$, $[M-H]^{+}$, $[M-H]^{2+}$, $[M-2H]^{+}$, $[M+H]^{+}$, $[M+H]^{2+}$ and isotopic contributions from each of the singly charged ions from the presence of a single $^{13}C$, referred to as associated ions hereafter, for each non-oxygenated PAH base ion were included in the analysis. From the HR analysis, it was observed that the oxygenated PAHs do not have significant signal at the (non-isotopic) associated ions listed above, likely due to fragmentation differences from the presence of oxygen atom. There are considerable PAH signals as low as *m/z* 128 (Fig. 1), which if interpreted as an unfragmented species would indicate naphthalene; however, this compound is expected to be fully in the gas phase (Pankow, 1994). Therefore, this suggests that the PAH signals observed in the lower *m/z* region are likely from PAHs that have undergone fragmentation in the AMS vaporization/ionization process. The PAH ions at odd *m/z*s are also likely fragments, as observed by Bente et al. (2009).”