AUTHORS' COMMENTS

The authors would like to thank both reviewers for their helpful comments and suggestions. All comments are addressed below. Reviewer comments are in plain text and our responses are in italics.

Response to Reviewer 1

1. Abstract, pg. 8082, ln. 27-28: ". . .possibly indicating a higher ratio of acid to non-acid oxygenated compounds in wood burning OA compared to other OOA." Given the harsh ionization source employed by the AMS, I don't believe such a conclusion can be drawn about the nature of the oxygenated functional groups. Of course, it is appropriate to discuss O:C and H:C, but not functional group contributions.
Thermal decomposition of acids at the heater of the AMS is known to be an important origin of the CO_2^+ *fragment whereas Ng et al. (2010) hypothesized that the* $C_2H_3O^+$ *fragment is dominated by non-acid oxygenates. Therefore these fragments can give information about functional groups. Because of the harsh ionization method there is always the possibility to have contributions from more than one functional group to a single fragment ion. Therefore the phrasing "possibly indicating a higher ratio of acid to non-acid oxygenated compounds…" was chosen carefully to emphasize the uncertainty.*
The following text will be added to the revised version:
Thermal decomposition of acids at the heater of the AMS is known to be an important origin of the CO_2^+ *fragment whereas Ng et al. (2010) hypothesized that the* $C_2H_3O^+$ *fragment is dominated by non-acid oxygenates.*

2. Pg. 8086, ln. 27: upper size range of the AMS is given as 1.5 μm, however, the particle transmission efficiency in the AMS decreases for particles > ~0.7 μm. If this size range of 35nm to 1.5 μm is stated, it should accompanied by some discussion of the transmission efficiency in the 0.7-1.5 μm range.
The following sentence will be added: "The inlet system shows 100% transmission for particles in the vacuum aerodynamic diameter range 70 - 500 nm and substantial transmission for particles in the range of 30 - 70 nm and 500 nm - 1.5 μm."

3. Figure 2 shows results from experiment 15 – which in Table 1 lists a POA concentration of 31 μg/m3. However, in Figure 2, the POA concentration after mixing appears to be ~8 μg/m3. What is the cause of this difference?
This should have been experiment 5. The text and legend will be updated.

4. Pg. 8089, ln. 23: Since the wall loss correction method is the same as that used by Grieshop et al. (2009), it is appropriate to cite that reference here.
The wall loss correction method used here is similar to the one described in Grieshop et al., 2009. The difference is that here an exponential fit of the BC concentration was used to find the decay rate instead of the measured BC. The citation will be added.

5. In the determination of emission factors and MCE values, CO2 and CO measurements were used. Based on the factor of 220 dilution, it seems as though the CO2 and CO enhancements in the chamber were quite low, as compared to the instrument spans – what is the uncertainty in emission factors due to this issue?

The average increase of CO_2 was 57ppm, and the average increase of CO 990ppb. The relative uncertainty in both numbers is expected to be small compared to the accuracy of the AMS and therefore not to be a large source of error in the estimated emission factors.

6. Also on the topic of emission factors, Table 2 gives emission factors +/- some value, which is presumably a standard deviation from the repeated tests, and not an actual uncertainty. For these emission factors, an uncertainty should also be given due to the uncertainty in estimating the amount of fuel burned and uncertainty in the measurements (see above comment).
The burn-to-burn variation for wood burning is generally large and is for most experimental conditions expected to have the largest contribution to the variations observed. Therefore, the standard deviation of the emission factors between multiple tests is more suitable than the standard deviation from the measurements of a single test.

7. Pg. 8094, ln. 26-28: some of the pure SOA experiments also seem to show a decrease in O/C with aging?
The pure SOA experiments do not show an increase in O/C which is discussed a few lines later in the same section. The sentence "All experiments show…" will be changed to make it clear that only the experiments with the primary emissions including the particles are what is being referred to.

8. Grieshop et al. 2009a and Grieshop et al. 2009b should both be cited
The citation will be added.

9. This current work relates to some other studies that also investigate aging of biomass burning emissions. Perhaps some discussion comparing the present results to these other studies would be interesting: Capes et al. (2008); Cubison et al. (2011); and Hennigan et al. (2011).
The last two papers (Cubison et al., 2011 and Hennigan et al., 2011) appeared five weeks after this manuscript was published in ACPD and therefore could not be used to compare to the results presented here. We will make a reference to these papers in the revised version.

10. One of the unique features of this study is the observed increase in m/z 60 from SOA production. The uniqueness of this result should be highlighted more than it is, and the discussion expanded (i.e., why is it that m/z 60 increases in the log wood burner experiments, but never in the pellet burner experiments?). Also, is there any evidence from ambient measurements that m/z 60 production occurs in the atmosphere? My impression from the extensive body of AMS studies is that m/z 60 is not produced from secondary processes, but is thought to characterize primary BB emissions. Some additional discussion on this topic would be appropriate.
The ion at m/z 60 is used as marker to estimate primary wood burning or biomass burning OA in ambient aerosol. However, m/z 60 was found to contribute ~0.3% to ambient OA during non-fire periods (DeCarlo et al., 2008; Docherty et al., 2008; Aiken et al., 2009). In addition, m/z 60 was also found in OOA spectra retrieved by PMF which are generally assumed to be dominated by SOA. This additional information will be added to the text in the revised version.

11. Is there any correlation (or can one be derived) between the increase in O/C and the amount of SOA formed?
No correlation was found between these two parameters.

12. Could variability in the amount of SOA formed be accounted for by differences in OH levels? It would be interesting to view Figure 3 (and possibly Figures 6 and 7) on an OH exposure axis in addition to time. Since emissions from the appliances used should be highest in winter (corresponding to lowest OH levels), OM enhancement ratios vs. OH are important for the atmospheric implications of this work.
There was no instrument present that was able to determine the OH level inside the smog chamber during the experiments. However, the light intensity and the typical OH concentrations observed in the PSI chamber are ~1E6 - 4E6 cm^{-3} *and comparable to a clear winter day.*

13. Figure 9; pg. 8096 – is it necessary to call the CO2+ ion ‘pCO2+’?
We decided to use pCO2 to stress the fact that it includes only the CO_2^+ *fragment ion from the aerosol without contribution of the gas phase* CO_2*.*

14. Conclusions: “This implies that the gas phase emissions from log wood burners play an import role in the total contribution of OM from residential wood burning appliances to ambient OM and should be considered to be included in future legislations” – Dilution ratios were >200, could this SOA not be from evaporated POA (i.e., according to the mechanism proposed by Robinson et al. (2007))?
The emissions from wood burning (and other combustion sources) consist of a complex mixture of organic compounds that occupy a wide range in volatility. When the observed system is in equilibrium, the concentration and temperature determine which fraction of the semi-volatile compounds are in the gas phase and particle phase. When the sample is injected into the chamber it undergoes a combination of dilution, which supports evaporation, and cooling, which supports condensation. POA was defined as the OM that is in the particle phase at the combination of these conditions where the dilution ratio was chosen to get ambient relevant concentrations. Indeed, higher emission factor are found at low dilution ratios, due to the mechanism proposed by Robinson et al. (2007). One could argue to use the emission factors at low dilution ratios and forget about additional SOA formation, as these two effects will compensate each other to a certain extent. However, we do not recommend this procedure, as this will result in unknown and potentially high errors in the emission factors.

Response to Reviewer 2

My major concern is related to wall losses corrections (WLC) used here. Indeed biases in WLC can greatly affect the conclusions of this study and especially the relative increase of m/z60 during the photo-oxidation phase (see specific comment). WLC are determined using BC concentrations and based on the assumptions that the aerosol is internally mixed (One can regret the absence of VHDTMA measurements). Thus the WL are assumed to be the same for BC and OA and it sounds like a suitable assumption. However in a recent study carried out in a combustion chamber (data not published yet) we observed a systematic higher deposition rate for BC (measured by MAAP5012) than for OA (measured by AMS). These experiments had also been performed with atmospherically relevant concentrations of biomass burning aerosol particles but in dark conditions. Such behavior is still unexplained in our case. If this behavior is also observed here the conclusions regarding m/z 60 could be drastically different. Please can you verify this specific point with your data obtained before the photoxidation phase. Considering fig 15, this verification appears possible in order to validate your WLC procedure.

We agree with the reviewer that WLC is a very important process to consider in the interpretation of the results, and was the subject of many discussions during the analysis of the data. Also note that H-TDMA measurements were performed during all experiments described in this paper and show a single growth factor mode for all the experiments using the two log wood burners, which supports the assumption that the aerosol is internally mixed. These H-TDMA measurements will be the focus of a separate paper, currently in preparation. In addition, when the lights were switched off after 20 hours of aging, a faster decrease in the measured OM concentration was observed compared to the lights on phase which indicates that after 20 hours SOA production was still adding mass to the OA. The slow increase in the WLC corrected OM concentration shown in Fig. 2 therefore seems to be correct and is an indication that the WLC is not overestimating the wall loss rate of the OA.

For the pellet burner the used wall loss rate was confirmed by the stable burning experiment which did not show an increase for organics, nitrate or sulphate. An overestimation of the wall loss rate would result in an increase in these species even in the absence of SOA production.

Also on a related topic, BC time series presented in fig15 is a bit suspicious. I assume that the spacing between each series of points correspond to the filter spot changes. Here I do not comment the global increase of “BC” after the lights were switched on, but the slight increase of BC in almost each series of points. Can you comment this behavior? Does any intercomparison between MAAP and Aetholometer has been performed in this study?

The increase in the consecutive data points of the MAAP after each filter change is most likely the result of imperfect corrections for the filter loadings. An Aethalometer was compared to the MAAP during smog chamber experiments on diesel emissions (Chirico et al., 2010) where the Aethalometer also showed a filter loading dependent behavior.

It would have been valuable for the paper to present and discuss some pToF results. What are the size distributions of the aerosol and their evolution during the photooxidation phase? Is the aerosol mass distribution close to 1µm ? As particle transmission efficiency in the AMS strongly decreases for particles larger than 800-

1000 nm and as BC measurements are associated with TSP, the presence of particles larger than 1 µm can affect the WLC used here.
pTOF data or other sizing data (e.g. SMPS) were not discussed in this paper because it was found to be more suitable to be discussed in the paper that will focus on the hygroscopicity measurements during these experiments. However, the largest mass concentration mode observed in the AMS pTOF mode was 404nm which is well within the transmission window of the AMS. This information will be added to the text.

1. p 8082, line 16. “Average emission factors of BC+POA+SOA, calculated from CO2 emission,. . .” From a conceptual point of view, it is difficult to assess a SOA emissions factor as SOA formation is not a linear process, depending on many external parameters. Especially in urban areas where NOx concentrations should be more higher than those encountered here. In this respect no NOx concentrations are reported in the paper although measurements have been performed (p8088, line 15 and fig 1). Is it possible to dissociate the SOA emission factor from the other two (BC and POA) and had one or two sentences to avoid misunderstanding with this SOA emission factor.
While we agree with the reviewer that SOA formation is dependent on the conditions into which the emissions are injected. We feel that this information is important to provide to give an estimation of what is possible. We will modify the sentence in the manuscript to make clear that the “measured SOA formation potential” is what is being discussed and is included in the numbers stated. BC and NOx concentrations will be added to table S.1.

2. p8084 line 20 : “In addition, results from pure SOA experiments, where only the gas phase emissions are injected and processed, are presented”. According to this sentence I would have expect more information related to these very interesting pure SOA experiments. Results of these experiments are not highlighted in the text. Is there any significant differences between this pure SOA and the classical OOA factor? Do you observe a modification of the mass spectra during aging? Does the absence of POA affect substantially the SOA formation?
A more comprehensive set of pure SOA experiments will be described in a separate paper and therefore only some results were shown as comparison to the POA characteristics.

3. P8086 line 16 : Is there any influence of the use a gas torch ?
The gas torch was used to light the fire without the use of paraffin or any other type of starters that would still be burning during the sampling period. Using the gas torch before sampling is not expected to have any influence on the experiments.

4. P8086 line 27 : AMS results are generally assumed to correspond to the PM1 fraction. This sentence suggests that the results presented here correspond to the PM1.5 fraction. Transmission efficiency for particles larger than ~1µm should be discussed in the text.
The follow sentence will be added: “The inlet system shows 100% transmission for particles in the vacuum aerodynamic diameter range 70 - 500 nm and substantial transmission for particles in the range of 30 - 70 nm and 500 nm - 1.5 µm.”

5. P8087 line 19-22 : As CO2 has been measured during the experiments, does the fragmentation table has been modified in order to consider the real concentration of CO2?
The fragmentation table was modified based on the CO_2 *signal measured by the AMS sampling through a HEPA filter. This was done after the emissions were injected into the chamber to account for the increase in* CO_2*. This is described at P8087 line 16-19.*

6. P8087 line 25 : The inlet of the TEOM was heated at 50?
Correct, the TEOM was running at 50°C.

7. P8093 line 12-13. Do you have an explanation of the increase of the CHN family? Is this increase significant?
The main ions that contribute to the CHN family are CH_4N, C_2H_6N *and* C_3H_8N *where* CH_4N, *and* C_3H_8N *showed the largest increase. The described increase of 1.2% found for the V-mode data is in agreement with the 1.0% found for the W-mode data (not shown). The agreement between the two modes and the relatively high contributions of these two main ions at their nominal mass were the basis to mention this difference as an increase. The increase could come from nitrogen containing organics that are in the gas phase at the start of the experiment and condense as SOA after oxidation lowered their vapor pressure and/or from the reaction with nitrogen containing compounds during the aging process.*

8. P8093 line 25. As almost every organic compound levoglucosan is not inert. The reactivity of levoglucosan is still a hot topic, and need to be discussed in more than a sentence.
The corresponding text will be adapted to read:
Levoglucosan, a product from wood burning and biomass burning, has been used as molecular marker in ambient organic aerosol (Fraser and Lakshmanan, 2000; Simoneit et al., 1999). The ion at m/z 60, a dominant fragment in the mass spectrum of levoglucosan, has been used as a wood burning marker for AMS measurements in order to estimate the wood burning contribution to the ambient organic aerosol (Alfarra et al., 2007; DeCarlo et al., 2008). An ideal molecular marker is inert, however, recent observations show that levoglucosan may be lost during aging (DeCarlo et al., 2010) and laboratory studies showed that levoglucosan is not stable under atmospheric conditions with an atmospheric lifetime of 0.7 - 2.2 days at an OH exposure of $1x10^6$ *molecules* cm^{-3} *(Hennigan et al., 2010; Hoffmann et al., 2010). This reactivity can lead to an underestimation of the wood burning contribution to ambient OM.*

9. P8093-8094. m/z 60 increases during photo-oxidation processes is most probably the point of this paper and needs to be discussed in more details. Such results have not been observed in the study performed by Hennigan et al (2010) (cited line 22). As discussed in the general comments I consider that WLC can play an important role on this unique behavior. In addition to what I propose in the general comments do you observe the same behavior for PAHs or m/z 137 (for example) ? In a more general point of view, regarding fig 6, only one experiment exhibits a high increase of m/z60. If we do not consider this particular experiment, the average relative increase of m/z60, considering all the other experiments, is more or less equal to 1 or 1.2. The

important variation of this relative increase between experiments is also puzzling. Results should therefore be discussed more carefully.

The increase in the intensity of the $C_2H_4O_2^+$ *ion was also observed without the WLC for several experiments. After a long experiment (20 hours), when the lights were switched of, an increase in the wall loss rate was observed for the* $C_2H_4O_2^+$ *ion indicating that the production of the* $C_2H_4O_2^+$ *fragment was still taking place. Also note that this ion is not unique to levoglucosan and is why m/z 60 is found to contribute ~0.3% of the OA mass in the absence of biomass burning (DeCarlo et al., 2008; Docherty et al., 2008; Aiken et al., 2009). In addition, the fact that the increase is not observed for the pellet burner experiments, nor the smoldering phase log wood experiment nor two other log wood experiments strengthens the assumption that the observation is not the results of a general overestimation of the OM wall loss rate but a SOA contribution with a strong dependency on burning conditions. An enhancement ratio of > ~1.5 was observed for 75% of the starting and flaming phase log wood burner experiments.*

The signal at m/z 137, containing multiple ions, is increasing during most experiments and also formed in the pure SOA experiments. The PAH, as defined in the AMS fragmentation table, showed an increase for 25% of the experiments and was stable or showed a decrease for 75% of the experiments after the wall loss correction was applied. The observed differences for biomass burning / wildfires compared to the emissions of the tested domestic wood stoves could be the result of the different combustion characteristics as a result of the combustion chamber and the quality of the fuel (e.g. water content of living trees vs. dried wood logs).

10. P8095 line 10 : “indicating that the condensing OM has a similar O/C ratio during the entire experiment”. Do you suggest that the increase of O/C ratio for the other experiments is due to the aging of POA and not the aging of SOA? Since O/C ratio of SOA is constant all along the experiments, we should observe a decrease of O/C ratio for experiments in which POA exhibit higher O/C ratio than SOA.

Stable O/C ratios were observed for the pure gas phase experiments during the first five hours of aging which is the period where the OM concentration increase is most prominent. Upon nucleation, compounds with the lowest volatility are expected to form the first aerosol particles. Then, the increase in OM drives more volatile compounds into the OM which are expected to have a lower O/C ratio as observed in Duplissy et al., 2008. After 6.5 hours an increase of O/C was observed when the effect due to aging become more important than the one related to the addition of new mass

Another possibility is a higher O/C ratio for the gas phase organics for experiments where the POA exhibits a high O/C ratio. In addition, heterogeneous aging of POA and the evaporation of POA, oxidation in the gas phase and re-condensation can not be excluded. The corresponding text will be adapted to read:

The pure SOA experiments did not show an increase during the first two hours (-0.03 ± 0.03) and no significant increase during the last two hours (0.003 ± 0.005), indicating that the O/C ratio of the OM stayed constant during the first five hours of the experiment, which is the period where the OM concentration increase was most prominent. This increase in OM drives more volatile compounds with a lower O/C ratio into the OM which could compensate the expected increase of the O/C ratio by SOA addition. During a long pure SOA experiment, an increasing O/C ratio was observed after 6.5 hours when the effect due to aging becomes more important than the one related to the addition of new mass. The fact that some experiments showed POA with a higher O/C ratio than the SOA produced during the pure SOA *experiments could be the result of the influence of the burning conditions to the O/C ratio of the VOC's similar to the OM.*

11. P8096, line 9 : aging instead of ageing.
Corrected.

12. P8096 line 14 : "which represent the OA functionalities better than the UMR data" As O/C and H/C ratios have been calculated here, Van Kervelen diagram could be a better representation in order to discuss the functionality of OA and its evolution during aging.
The Van Krevelen diagram was considered but recent publications presented SV-OOA, LV-OOA, ambient data and smog chamber data projected in the 44 vs. 43 space. To make comparisons with these data sets easier, it was decided to use the 44 vs. 43 plot instead of the Van Krevelen diagram. A publication focused on the aging of OA in the Van Krevelen space, including this dataset, is in preparation.

13. Table 1 : Can you add in this table BC and NOx concentrations?
BC and NOx concentrations will be added to table S.1.

14. Figure 3, 6 and 7: These 3 figures are not clear (too many curves). I suggest to split them in two figures : one for log wood burner and one for pellet burner. Also the use of point + fitted curves instead of lines between point could increase the readability. At last a link between each curve and experiments listed in table 1 could be very useful for the reader.
All traces were used in these graphs to visualize the variability between the single experiments and to show that there is no separation between the starting and flaming phase experiments. Showing the log wood burner and pellet burner experiments in two different graphs will not increase the readability since the pellet burner shows only minor overlap compared to the starting and flaming phase experiments with the log wood burner. Since there is no theoretical function to fit, a line between the data points was found to be appropriate to use. Experiment numbers, as used in table 1, will be added to the curves in figure 3, 6 and 7.

15. Figure 9 : Can you reverse the color scale (time after lights on)?
The figure will be updated.