**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber" *by* C. J. Hennigan et al.

Anonymous Referee #1

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Biomass burning emissions are a significant source of particle- and gas phase pollutants in the atmosphere. The authors investigated twelve different fuels commonly burned in wildfires. The paper shows that the mass enhancement ratios after photo-oxidation are highly variable between the different fuels. On the one hand the secondary organic aerosol production can triple primary organic aerosol (POA) concentration while in other cases photo-oxidation leads to loss of organic aerosol. For both types of fuels a pronounced change in chemical composition was observed by aerosol mass spectrometry.

In the case of low organic mass enhancement ratios this indicates a strong chemical transformation of the primary organic aerosol. From this the authors conclude that the traditional concept of an inert POA onto which secondary organic aerosol condenses is not tenable anymore. To quantify the transformation of POA the authors use levoglucosan as a surrogate for POA. Since they measure a strong decrease of levoglucosan with photo-oxidation it is concluded that levoglucosan is semi-volatile and suitable as surrogate species. Based on this assumption it is found that on average about 60% of the POA is chemically transformed. For this transformed fraction of POA the authors introduce the term oxygenated POA (O-POA). In my opinion this term may be somewhat confusing. While POA from diesel exhaust is hardly oxidized, POA from wood combustion is already considerably oxidized. We would then end up with a slightly oxidized POA directly emitted from wood combustion and an oxidized POA (O-POA) after processing. I suggest using the term "aged POA" which describes the process by which it was created.

Generally, the paper is well written. The paper contains interesting results and should be published in ACP. However, there are several issues with the determination of O-POA, which I would like to have clarified.

Levoglucosan is taken as a surrogate for POA. However, the volatility of levoclucosan can only be representative of a certain volatility fraction of POA. If the volatility of levoglucosan belongs to the highest volatility bin of POA then O-POA may be strongly overestimated. In that case the temperature increase of 11 degrees may also affect the partitioning of levoglucosan strongly and explain at least part of its loss. Therefore, the statement in the abstract "unreacted POA only contributed 17% of the campaign-average OA mass after 3.5 h of exposure" may be much too low. Eventually no additional mechanism beside heterogenous reactions is needed.

In Figure 6 the authors assume that about 50% of levoglucosan evaporates due to dilution of the exhaust between the FSL chamber and the smog chamber. However the amount of evaporation strongly depends on the POA concentration. For example

if the POA concentration is 1000 times larger than the levoglucosan saturation vapor concentration a dilution by a factor 15 would not affect levoglucosan : sulfate ratio. Thus, the levoglucosan:potassium ratio given at time =0 is somehow arbitrary as the POA mass concentration varies by a factor of 10 in the experiments.

Only 10-20% of the decay of levoglucosan can be explained by heterogeneous processing as the authors show. Therefore, they propose that semi-volatile levoglucosan evaporates and is oxidized in the gas phase which would lead to the strong loss of levoglucosan in the particle phase during photo-oxidation. This implies that at high OA mass concentration levoglucosan is found preferentially in the particle phase and its reaction in the gas phase will deplete it less in the particle phase than under the condition of low particle mass concentrations. However, from Figure 7 it seems that the high OA mass concentration experiments lead to a higher POA processing (i.e. levoglucosan decay) than low POA concentration experiments. Do the data show such an effect?

Can the authors give an estimate of the saturation vapor pressure of levoglucosan from models (e.g. SIMPOL from Pankow and Asher, Atmos. Chem. Phys., 8, 2773–2796, 2008) and compare with estimates which would fit the observations in this work.

Other comments: Page 12001, line 24: How was HONO added and was it continuously added?

Page 12003, line 3: how do the authors make sure that the signals for benzene, toluene, C-8 aromatics are not disturbed by other compounds. A unit mass PTR-MS does also not detect new oxidized product compounds on these m/z ratios. For the C-8 aromatics it is also difficult to define a reaction rate constant to derive OH concentration.

Page 12003, line 6: how was the PTR-MS calibrated? Was it calibrated for formic acid?

Page 12004, line 2,3: please give the units for all parameters. Is it all in gram-carbon?

Page 12004, line 9: please give the units for all parameters.

Page 12008, line 5,6: You refer Figure 2f not 2e. I do not see a decrease of 30% rather 10%.

Page 12008, line 9: Figure 2f not 2e

Page 12008, line 18: burns 37, 38 and not 38, 39. Experiments 37 and 38 did also not produce very similar OA mass enhancements according to Table 2. Figure 3 shows other values for these experiments.

Page 12008, line 20: you also compare experiments with very different VOC/NOx ratios. This may also influence the variability of OA mass enhancements.

Page 12009, line 5 ff: Since there is a large variation of OA enhancements a correlation with temperature may not be observed. The temperature increase was in some cases even higher than 11 degrees. With a temperature sensitivity of 1-2% per $^\circ$C this might end up with an OA loss of 15-30%. Does this concern the low OA enhancement cases?

Page 12011, line 11f: The decrease of f60 is Figure 5b can be fully explained by the addition of SOA. Assuming SOA does not contain m/z 60 then condensation of SOA would reduce f60.

Table 2: How was the VOC measured? NOx is defined as NO+NOx. Here HONO also seems to be included. This would be more like NOy.

Figure 2 d, h, i, j: After 2 hours of reaction the signals of isoprene, toluene and monoterpenes remain constant despite further oxidation reactions (see formic acids). This shows that the m/z signals of those compounds are interfered by other compounds or fragments of other compounds.