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“Chemical and Physical Transformations of Organic Aerosol from the Photo-oxidation of Open Biomass Burning Emissions in an Environmental Chamber”

Author Response to Reviewers:

We thank the reviewers for their detailed suggestions and helpful comments. We have addressed the reviewer comments below, with reviewer comments italicized and our responses in plain text.

Reviewer 1:

“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.”

We agree with the reviewer’s suggestion, and have changed all text from ‘O-POA’ to “Aged POA”, including the data label in Figure 8.

“Levoglucosan is taken as a surrogate for POA. However, the volatility of levoglucosan 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.”

We agree with the reviewer’s comment that using levoglucosan as a surrogate for POA may overstate the amount of POA that actually reacted in our experiments. We have stated this concern in the revised text. However, this follows the same widely-used assumption of many

source apportionment studies that assume levoglucosan is a conserved tracer for biomass burning marker. Therefore we feel like it is an appropriate comparison. The manuscript contains the following discussion related to this point (pg. 12018, ln. 16-20): “Our definition of aged-POA assumes that all POA reacts at the same rate as levoglucosan. This likely is not true because levoglucosan appears to be semi-volatile and the reaction of vapors likely contributed to its depletion in the particle phase. However, receptor models often use levoglucosan as a tracer for biomass burning POA; therefore, it is a widely applied assumption.”

“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.”

We used the m/z60-to-sulfate ratio in each experiment to estimate the potential evaporation of levoglucosan due to dilution. Thus, although Figure 6 presents campaign-average levoglucosan data, we are accounting for major differences in POA concentrations. We have clarified this point in the text (Pg. 12012, ln. 16-18): “We estimated the amount of levoglucosan that evaporated upon dilution in each experiment using HR-AMS m/z 60-to-sulfate ratios measured inside the FSL combustion chamber and inside the smog chamber.”

“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?”

Yes, as the reviewer notes, in general, we observed the extent of levoglucosan depletion to be greater in experiments with higher POA concentrations. While this may seem counter-intuitive, if only a small amount of a substance is in the vapor phase, its particle phase can be rapidly reduced because the gas-phase reactions are so fast. Thus, only looking at levoglucosan depletion as a function of POA would miss other more-important factors such as OH level and possible aerosol matrix effects.

“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.”

We have performed this calculation and levoglucosan is predicted to be semi-volatile at our experimental conditions ($C^* \sim 7.6 \mu\text{g m}^{-3}$ at 293 K). We have added the following text (Pg. 12012): “Therefore we hypothesize that some of the reduction in the levoglucosan-to- K^+ ratio is due to changes in partitioning caused by dilution; previous studies have also suggested that levoglucosan is semi-volatile (Huffman et al., 2009; Grieshop et al., 2009a; Hennigan et al., 2010). This agrees with an estimated levoglucosan C^* of $\sim 8 \mu\text{g m}^{-3}$ at 293 K calculated using the SIMPOL.1 group contribution method (Pankow and Asher, 2008). It also agrees with an experimentally-derived sub-cooled liquid vapor pressure of levoglucosan of $\sim 12.6 \mu\text{g m}^{-3}$ at 298 K (Booth et al., 2011).”

“Page 12001, line 24: How was HONO added and was it continuously added?”

We have added the following text to clarify (Pg. 12001, ln. 24-25): “In 10 experiments (Table 2), nitrous acid (HONO) was added to the smog chamber following the method of Ng et al. (2007) before adding smoke from the FSL burn chamber.”

“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.”

In their very thorough overview of PTR-MS measurements, de Gouw and Warneke [*Mass Spectrometry Reviews*, 2007] demonstrate the utility of the PTR-MS in measuring benzene and toluene at good sensitivities and with little interference from other compounds. Since the PTR-MS cannot distinguish the xylene isomers and ethyl benzene, the reviewer is correct that it is difficult to define a single reaction rate constant to derive the OH concentration. Here, we assumed equal concentrations of the four C8 aromatics, and used an average rate constant of $1.45 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [Atkinson and Arey, *Chemical Reviews*, 2003]. The error in this assumption is at most, a factor of two, if all of the C8 aromatic was ethyl benzene and no xylenes were present. Emission data indicate that this is not possible, though: for example, if the C8 aromatic emissions in our experiments were proportionally similar to those measured by Schauer et al. [*ES&T*, 2001] (that is, if the ratios of m-, o-, p-xylene, and ethyl benzene to the total C8 aromatics were similar), then our rate constant would be off by less than 5% (1.45×10^{-11} vs. $1.51 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). In addition to the C8 aromatics, we used the benzene and toluene decays to get an average OH concentration, which will lessen any error introduced by assuming a single C8 aromatic rate constant. The justification for including the C8 aromatics in this calculation, rather than using benzene and toluene alone, is that our OH levels were moderate ($\sim 2\text{-}5 \times 10^6 \text{ molecule cm}^{-3}$) and our oxidation time was relatively short (3-4.5 hr), thus, the C8 aromatics exhibited a greater dynamic range, which helps for calculating OH.

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

The PTR-MS was calibrated by directly measuring a custom blend of gases in N_2 (Scott-Marrin, Inc., Riverside, California). The instrument was not calibrated for formic acid (included in Figure 2), but instead, the average calibration response of two other light oxygenated compounds (methanol and acetaldehyde) was used to estimate the formic acid response.

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

Yes, the units are g-C m^{-3} – the text has been updated to include the units.

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

The units are g-C m^{-3} – the text has been updated to include the units.

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

First point (Figure 2e changed to 2f): corrected. Figure 2f has been updated with the correct OA enhancement.

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

Corrected.

“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.”

First point (Burns 37 and 38 rather than 38 and 39): corrected. Figure 3 was an older version, which did have the incorrect value for Burn 38. The updated Figure 3 is now correct.

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

We have added the following to the text to account for this point (pg. 12008, ln. 22-23):

“Differences in VOC:NO_x ratios (Table 2) also likely contributed to different 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 C this might end up with an OA loss of 15-30%. Does this concern the low OA enhancement cases?”

Yes this is a concern. As we described in the manuscript, we do not believe that the change in temperature significantly affected the OA enhancements. For our experiments, TD results showed that the OA sensitivity was less than 1% per °C. For the six experiments with the lowest OA mass enhancements (Experiments 40, 49, 51, 55, 57, and 65), the average temperature increase in the smog chamber over the aging period was 12.4 °C. For these six experiments, the average OA mass enhancement ratio was 1.0, showing that on average, no new OA mass formed due to photo-chemical processes. In contrast, the six experiments with the highest OA mass enhancements (Experiments 38, 42, 43, 47, 63, and 65) had a very similar temperature increase

(Avg. $\Delta T = 11.4$ °C) but had an average OA mass enhancement ratio of 2.52, demonstrating significant OA production. Based on both the lack of correlation between chamber ΔT and OA mass enhancements and the TD data, we expect that the increase in temperature produced minor effects on OA mass enhancements. We have added the following text to clarify this point (Pg. 12009, ln. 14): “TD analysis of the aged OA suggests that a temperature increase of 11.5 °C would cause, on average, only 7% of the OA to evaporate, which is similar to the temperature sensitivity of 1-2% of OA per °C observed by previous studies (Grieshop et al., 2009a; Huffman et al., 2009). Thus, it is possible that the temperature increases in the chamber masked modest enhancements in OA concentration.”

“Page 12011, line 11f: The decrease of f_{60} in 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 f_{60} .”

After 3.5 hours of photo-oxidation, the net decrease in f_{60} in Figure 5b can be explained by the addition of SOA (red trace = data vs. grey shaded region), however, the rate of OA mass addition was much slower than the rate of the f_{60} decrease, indicating chemical processing. See the discussion further in that section (Pg. 12011, ln. 16-21): “This trend was also seen in experiments with substantial SOA formation (Figure 5b). In these experiments, the rate of f_{60} decrease was much more rapid than the SOA production; therefore the data clearly indicate significant chemical processing of POA in experiments with substantial SOA production.”

“Table 2: How was the VOC measured? NO_x is defined as $NO+NO_x$. Here HONO also seems to be included. This would be more like NO_y .”

The VOC was measured in the burn chamber with a Total Hydrocarbon Analyzer (Thermo Environmental Model 51). We have updated the text to include this information (Pg. 12003, ln. 21-22): “Total hydrocarbon concentrations were also measured in the burn chamber using a Total Hydrocarbon Analyzer (Thermo Environmental, Model 51)”. NO_x only includes $NO + NO_2$ – the reason that $VOC:NO_x$ decreased for the HONO experiments is that the method to introduce HONO into the chamber (Ng et al., 2007) also introduces typically a few hundred ppb of NO_x as well. This is commonly used in smog chamber experiments as a high- NO_x OH source.

“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.”

In Figure 2e, the monoterpene concentration flattens out because it approaches 0. In Figure 2j, it does decrease rapidly, and then flattens out – this is why monoterpenes (and isoprene) were not used like the C8 aromatics to estimate OH levels. We have not attempted to do any quantitative analysis with the isoprene or monoterpene PTR-MS data, but we feel it is constructive to show their time series in several representative experiments to demonstrate qualitatively their behaviors. The toluene concentration in Figure 2c continues to decrease throughout the aging period while the toluene concentration in Figure 2h does appear to flatten out, but only over the

final ~30 min of photo-oxidation time. This may be a function of instrument noise, compared to small concentration changes, and it is why multiple aromatic compounds were used to assess the OH levels.

Reviewer 2:

“The paper highlights the wide range in mass enhancement ratios for the different biomass types, but there is very little discussion on the potential factors that may explain these differences. The authors state that another paper will focus on explaining these changes. Since these results are an important part of this work, a short discussion on possible factors that may be responsible for the variable mass enhancement ratios would be very useful. Some possible factors that might be considered include initial POA mass concentrations, particle phase, initial degree of oxidation of POA, NO_x/VOC ratios, predominance of specific SOA precursor types, VOC concentrations, oxidant:VOC ratios, temperature changes (this was considered in the paper) and the modified combustion efficiency. It would be useful to evaluate whether our current understanding of the SOA formation and aerosol aging mechanisms is sufficient to provide an explanation for both the mass enhancements and the changes in aerosol degree of oxidation.”

We completely agree with the reviewer that explaining the variability in OA mass enhancement ratios is of very high interest. Given the wide range of OA mass enhancements that we observed, we have a very rich data set with which to explore this topic. In our follow-up manuscript, we will consider the factors that the referee mentions, and will expand it to include non-traditional SOA precursors as well. This will include a very extensive modeling analysis. Due to the considerable length of the current paper that just describes the dataset, we felt that it is best to address this important issue in a separate manuscript, rather than giving it cursory mention here.

“The photochemical loss of levoglucosan was used to quantify the degree of processing of the initial POA. Could positive matrix factorization analysis be also used to confirm that the photochemical loss rate of the overall POA mass is consistent with the loss of levoglucosan?”

Yes, certainly PMF could be applied to demonstrate the chemical changes in POA. We feel that Figures 4, 5, and 6 demonstrate through different AMS analyses that the POA underwent chemical changes (i.e., even for the low OA enhancement experiments, the POA chemically evolves, as evidenced by the decreasing R^2 in comparison to the POA spectra and the increasing f_{44} and decreasing f_{60}).

“Page 12001, line 11: Did you perform any dark experiments (with and without addition of HONO) over 3-4 hrs to ensure that the chemical aging of the organic aerosols (i.e. AMS mass spectral changes) is solely due to photochemistry? A dark experiment would also allow for the quantification of levoglucosan:K⁺ ratios after dilution in the smog chamber (Figure 6).”

We did not perform any dark experiments over an extended time period in this campaign: at most, our dark period with and without HONO present was 1.7 hr. We did not see substantial changes over this time period. In previous studies (Grieshop et al., 2009a, 2009b) we have performed dark experiments over a much longer time period and observed no changes in gas phase composition (as measured with PTR-MS) and, at most, modest changes in aerosol composition which we attribute to the aerosol slowly reaching equilibrium. This is a good suggestion for future experiments, especially to quantify the effects of dilution on levoglucosan. Given the results in Figures 4 and 5, which show little chemical change before the lights were turned on compared to large changes with photochemistry, we feel confident that the changes were due primarily (if not solely) to photochemistry.

“Page 12002, line 3: What particle transmission efficiency was used here to calculate AMS organic masses? Can it be confirmed that this value is appropriate for OA from all biomass types used here and that the transmission efficiency hasn’t changed during the aging experiment?”

We assumed an AMS collection efficiency of 1 for all experiments, based on comparisons with SMPS volume measurements. We have added the following to the text (Pg. 12002, ln. 5-6): “Based on agreement with SMPS measurements, the collection efficiency in the Q-AMS was taken to be 1, in agreement with other AMS laboratory investigations of biomass burning aerosol (Heringa et al., 2011).”

“Page 12002, line 23: Why is there no mention of HR-AMS measurements? A discussion of O/C and H/C ratios would be very useful here. Will these measurements be presented in a future paper?”

The HR-AMS confirmed the trends that were observed with the Q-AMS. Because the data set from the Q-AMS was more complete, we have chosen to present and discuss this data most extensively. However, we have added the following discussion to the manuscript (Pg. 12011, ln. 21): “Fifteen minutes of every hour the HR-AMS sampled from the smog chamber. These measurements confirmed the trends seen in the Q-AMS data (Figures 4, 5, and 6). The HR-AMS consistently observed an increase in the CO_2^+ -to-organic ratio with photo-chemical aging, and a simultaneous decrease in the $\text{C}_2\text{H}_4\text{O}_2^+$ -to-organic ratio with aging as well, supporting the overall conclusions drawn from the Q-AMS analysis. In addition, the HR-AMS indicates that the dominant ion contributing to the signal at m/z 44 was CO_2^+ , while the major ion contributing to the signal at m/z 60 was $\text{C}_2\text{H}_4\text{O}_2^+$. For example, during Burn 47 (Gallberry, 25 September 2009), CO_2^+ accounted for $89.3\% \pm 4.5\%$ (mean $\pm 1\sigma$) of the m/z 44 signal, and $\text{C}_2\text{H}_4\text{O}_2^+$ accounted for $98.1\% \pm 0.8\%$ (mean $\pm 1\sigma$) of the m/z 60 signal during the HR-AMS sampling periods.”

“Page 12008, line 15: It is somewhat misleading to call these experiments “repeat experiments” as most of the experiments were repeated with the addition of HONO, and therefore not repeated under the same conditions as experiments they are being compared to (i.e. different NO_x/VOC ratios) using the same fuel. It should be emphasized that HONO was added to these experiments, therefore changing the conditions. It appears that the addition of HONO has reduced the mass enhancement ratio for the repeat experiments in all cases, some of which were statistically

significant. Could this be an indication that the addition of NO_x enhances the fragmentation pathway of the VOC oxidation?”

We agree, and have changed the text to read (Pg. 12008, ln. 15-22): “The photo-oxidation of several fuels were investigated under different VOC:NO_x conditions to better understand variability in the experiment. Experiments performed with ponderosa pine (burns 40 and 57) and sage (burns 49 and 53) produced similar OA mass enhancements despite differences in VOC:NO_x ratios. However, experiments with wire grass (burns 42 and 67) and gallberry (burns 47 and 65) fire emissions under different VOC:NO_x conditions produced very different OA mass enhancements (Figure 3, Table 2). This demonstrates the dynamic nature of biomass burning emissions, as some of the variability shown in Figure 3 reflects the inherent variability of poorly controlled biomass combustion while differences in VOC:NO_x ratios (Table 2) may have also contributed to different OA mass enhancements.”

“Page 12011, line 1: Figure 5a shows that f₄₄ does not appear to increase for the first hour of lights on, whereas f₄₄ increases from start of lights on in Figure 5d. Can these differences be explained?”

We do not know the explanation. There was variability in the evolution of the OA in different experiments, as can be seen in the magnitude of the standard deviations in Figures 5a, b, d, and e. The standard deviation in f₄₄ for the four experiments with the highest OA mass enhancements (Figure 5a) was larger than the f₄₄ standard deviation in the four experiments with the lowest OA mass enhancements (Figure 5d). We have added Figure 6 and discussion (Pg. 12011, ln. 22), which shows evolution of f₄₄, f₄₃, and f₆₀ for all experiments, not just those with the highest and lowest OA mass enhancements.

“Page 12014, line 21: It would be more appropriate to call this gamma value an ‘effective gamma’ since the real uptake coefficient value cannot be greater than unity by definition.”
We agree and have changed the text accordingly.

“Figure 3. Define error bars.”

We have added the following text (Figure 3 caption): “Error bars (values given in Table 2) represent instrument uncertainty and differences in OA mass enhancement ratios calculated from BC ratio method and direct wall-loss estimate (Section 2.2).”

“Figure 4. It may be helpful to show the standard deviations of the average R₂ values to show that the trends are statistically significant.”

We have added standard deviations of the average R₂ values for select data, so as not to make the plots too busy, but still showing the variance in data.

“Figure 5. Why is there no expected range of f₆₀ in Fig 5b normalizing changes due to SOA formation and wall losses?”

We have added the expected range of f60 to Figure 5b.

References

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