

Interactive comment on “Secondary organic aerosol formation from biomass burning emissions” by Christopher Y. Lim et al.

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Response to referee comments for: Lim et al. “Secondary organic aerosol formation from the laboratory oxidation of biomass burning emissions”

Referee #1

Referee #1: Title: Accurate but not precise, in my opinion. Some reference could be made that this is a lab study and/or utilizes a photooxidation mini-chamber.

Author response: Title changed to “Secondary organic aerosol formation from the laboratory oxidation of biomass burning emissions” to better represent the work presented in the paper.

C1

Referee #1: P4.20 Where/how is the additional O₃ injected? Is there a sufficient jet to induce mixing? Is there any concern about a small area of highly concentrated O₃ chemistry in the chamber? I’m curious about the O₃/OH reactivity in general in your chamber, but more specifically at the injection port.

Author response: Ozone is generated with a pen-ray lamp external to the chamber and air carrying the O₃ is injected through a port separate from the injection port for the biomass burning emissions. The ozone concentration from the pen-ray lamp is about 1 ppm, but is mixed with humid air before injected into the chamber. The resulting O₃ concentration is approximately 200 – 300 ppb at the point of injection with a chamber mixing time of around 20 minutes. It is true that the area near the O₃ injection port will have higher O₃ concentrations relative to the rest of the bag which may lead to enhanced O₃ chemistry. However, from an experiment with no 254 nm UV, we do not observe strong changes in the composition of the aerosol with just O₃. Additionally, 254 UV makes OH in proportion to O₃, so the OH/O₃ ratio should not be sensitive to the O₃ concentration gradient in the chamber.

Referee #1: P5.2 Were seeded blanks (e.g. ammonium sulfate) ever run to establish a background OA production for this chamber and test the efficacy of the cleaning procedure?

Author response: Yes, seeded blanks (with ammonium sulfate particles) were run and showed negligible OA formation indicating that the cleaning procedure was successful. Deuterated butanol was not injected for the blanks (i.e., no OH exposure could be calculated), but O₃ and UV conditions were similar to those used in biomass burning oxidation experiments. The following text was added to the main manuscript (page 5, lines 4-5):

“Seeded blanks (with ammonium sulfate particles) were run and showed negligible OA formation indicating that the cleaning procedure was successful.”

Referee #1: P5.8 Did the black carbon measurements for these two methods agree?

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I wonder because the SP2 can saturate at high number concentrations, and the SP-AMS CE for BC requires some additional considerations (Ahern et al., 2016; Onasch et al., 2012; Willis et al., 2014.)

Author response: SP2 and SP-AMS black carbon mass loadings generally agree within a factor of two, with SP2 mass loadings consistently higher than the measurements from the SP-AMS and a reasonably linear relationship ($r^2 = 0.9$). BC measurements from the SP2 are those reported in the manuscript. The SP2 was operated with time-varying flow rates to account for the large dynamic range in the BC concentrations over the course of an experiment. In this manner, coincidence and under-counting (saturation) issues were avoided. The SP2 was calibrated with size-selected fullerene soot, and mass concentrations were corrected for “missing mass” outside of the SP2 detection window via multi-modal log-normal fitting. However we note that SP-AMS BC measurements were used only to determine which experiments to filter out of the analysis (due to enhanced wall loss), and so any CE-related errors will not affect the results presented. Black carbon measurements and other details about primary emissions will be discussed further in a future publication (Cappa et al., in preparation).

Referee #1: P5.26-30 I find your parameterization of CE very interesting and possibly broadly applicable. But why was it necessary at all? If you can calculate MFR, why not use the SEMS-measured size distribution to correct for CE directly? Given the large amount of variability in your FigS3, it is not obvious that using the correlation is an improvement in accuracy or precision over a size distribution correction. Additionally, I don't agree with the statement that there was no good internal standard available. While I think that your CE parameterization could be very useful, it warrants verification by looking at other measurements more closely. For example, you state that there was an SO₂ monitor, which would allow for a sulfur mass balance. Black carbon, measured by SP-AMS or SP2, was present at useful concentrations for some of the experiments.

Author response: While an SO₂ monitor was present, we observed that the measurements were unreliable due to, most likely, strong interferences from large concentra-

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tions of PAH's and other molecules, despite the internal scrubber in the SO₂ monitor. Further, it is not entirely clear to us how sulfur balance (gas + particle) would provide clear insights into the particle collection efficiency; we did not have an independent particulate sulfate measurement, but a gas-phase sulfur measurement. Given that the SO₂ measurements were compromised by interferences, we have now removed them from the list of measurements that were made. While we can use the SEMS-determined MFR, it is not clear how this would lead to a “direct” correction for the CE. It would provide an alternative approach, but with a complication that the MFR from the SEMS would include contributions from non-refractory material and thus does not directly address the issue of how the organic component of the particles responded to temperature changes. The CE changes observed derive, in part, from changes in the organic MFR that result from oxidation leading to less volatile OA. This would only partially be captured by the SEMS because of the contribution of non-refractory components (e.g. BC). BC cannot be used as an internal standard since the BC and organic mixing state varied dramatically between experiments, with some having the majority of the organic and BC being internally mixed (at low [OA]/[BC] ratios) and some having most of the organic material externally mixed from BC (at high [OA]/[BC] ratios) (McClure et al., in prep.). Given these overall issues, we believe that the organic MFR links more closely to the physical changes that occur. The text in the manuscript was amended (page 5, line 31):

“However, we were unable to find a suitable tracer in these experiments: sulfate changes as a result of oxidation of emitted SO₂, black carbon (when present in high concentrations) exhibited wall losses different from OA (as described below) and appeared not to be homogeneously mixed with the OA (McClure et al., in prep), and POA tracers (such as the C₇H₁₁⁺ ion, recently used by Ahern et al. (2019)) are likely to be lost via heterogeneous oxidation at the high OH exposures examined here. Thus, corrections for CE, dilution, and particle wall loss were carried out individually, as described below.”

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Referee #1: P5.31 Would you please confirm that the experiments used to calculate your CE were devoid of nucleation, particles grown outside the SEMS or AMS transmission/measurement ranges, and weren't unduly influenced by rBC after thermodenuding? Also, out of curiosity, how frequently was the thermodenuder valve switched, and therefore a new CE able to be calculated?

Author response: Yes, only data that did not show significant nucleation and had low rBC loadings were used to calculate the CE parameterizations. In addition, only SEMS and PToF size distributions that could be fit to a lognormal function were used. The thermodenuder valve was switched from thermodenuder to bypass every two minutes. Some additional text clarifying these details is included in the main text (page 6, lines 4-6):

"CE and particle density were calculated by comparing AMS particle time-of-flight (PToF) and SEMS size distributions (Bahreini et al., 2005) for a subset of data points with PToF and SEMS distributions that could be fit to lognormal functions, did not show significant particle nucleation, and had low rBC concentration (see below)."

Referee #1: P6.2-3 Please provide a citation or clarify regarding the relationship between volatility and phase. It might be easier to provide citations that claim that SOA has been observed to be an amorphous solid with low volatility, and therefore is likely to bounce.

Author response: This is an excellent idea; we have included citations for Matthew et al. (2008) describing collection efficiencies as a function of particle phase in the AMS, as well as Virtanen et al. (2010) showing that SOA can be an amorphous solid.

Referee #1: P8.5 What are the possible implications for the chamber OA concentration having decreased by two orders of magnitude from the beginning to the end of the experiment (FigS4)? It stands to reason that fewer of the semi-volatile SOA products will condense at low OA concentrations late in the experiment, but that any that do condense will have a larger impact on OSc.

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Author response: From Fig. S4, the organic concentration decreases by only one order of magnitude (200 $\mu\text{g}/\text{m}^3$ to 20 $\mu\text{g}/\text{m}^3$). Although semi-volatile gases are less likely to condense at low OA concentrations observed at the end of experiments due to significant dilution over the course of each experiment, most reactive gases are likely to have reacted relatively early in the experiment when dilution has less of an impact (see Fig. 6, most SOA growth occurs within ~ 2 days). Indeed, those gases (and potentially secondary products) that do react at longer OH exposures and condense are likely to have a large impact on the calculated average OSC and elemental ratios of the OA. Thus, the calculated OSC and elemental ratios may be more representative of the oxidized long-lived gases (which condense) rather than the BBOA + SOA as a whole. The following additional text was added to the manuscript to clarify this point (page 8, lines 7-8):

"Over longer timescales, when dilution is more significant and OA concentrations are lower, calculated OSC are likely to reflect the oxidation of longer-lived gases."

Referee #1: P10.18 How does this approach compare with the measured PTR-MS NMOG concentrations? It's not obvious to me why you compare [calculated VOC reacted]/[measured SOA formed] instead of [measured VOC reacted]/[measured SOA formed]? Or to go backwards, can you use your [measured NMOG reacted]* this calculated SOA yield to predict SOA formation?

Author response: We are not able to directly measure the amount of NMOG reacted, due to the dilution loss of NMOG (gases removed from the chamber before they can be reacted with OH), formation of secondary gas-phase products, and potential off-gassing of non-SOA forming low molecular weight NMOG from the chamber walls, leading to calculated SOA yields greater than unity. Thus, only initial NMOG measurements are used for the analysis and reacted NMOG are calculated as described in the text. This explanation is now included in the main text (page, lines)

Referee #1: P11.19 Given the importance of dilution and volatility on the results pre-

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sented here, is there information on the volatility of the POA and the SOA from the thermodenuder measurements, that can be compared to past campaigns?

Author response: Hennigan et al. (2011) observe an increase in organic MFR (80 C) for fires that show high OA enhancement as well as fires that show low OA enhancement. We do observe a decrease in volatility with oxidation – POA is relatively volatile, while SOA is less so. However, because we only used one temperature for the thermodenuder (250 C), we cannot obtain a volatility distribution as they do in May et al. (2013) where MFR was measured over a range of temperatures from 20 C to 120 C. Thus, comparing with either data set directly is difficult since our thermodenuder was run only at a single temperature that was much higher than the thermodenuder temperatures of the previously mentioned studies. Page 6, lines 8-9 were edited to mention that increases in MFR with oxidation are consistent with previous studies:

“Generally, POA has low organic MFR (i.e., relatively volatile) and particle MFR increases with oxidation, consistent with previous work (Hennigan et al., 2011).”

Hennigan, C J, Miracolo, M. A., Engelhart, G. J., May, A. A., Presto, A. A., Lee, T., & Sullivan, A. P. (2011). Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber. *Atmospheric Chemistry and Physics*, 7669–7686. <https://doi.org/10.5194/acp-11-7669-2011>

May, Andrew A., Levin, E. J. T., Hennigan, C. J., Riipinen, I., Lee, T., Collett, J. L., et al. (2013). Gas-particle partitioning of primary organic aerosol emissions: 3. Biomass burning. *Journal of Geophysical Research Atmospheres*, 118(19), 11327–11338. <https://doi.org/10.1002/jgrd.50828>

Minor technical corrections:

Referee #1: P3.22 “subalpine fir” rather than “subalpine fire”

Author response: Corrected.

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Referee #1: P7.25 Please include Hennigan et al. 2011

Author response: Citation now included.

Referee #1: P11.20 Missing a period.

Author response: Corrected.

Referee #1: FigS3 No red exponential fit

Author response: Red exponential fit was from an old version of the plot. Text referring to it has been removed.

Referee #1: FigS6 It looks like some plots have multiple y-values for a given time; some boomerangs at 0-5 days where they should be smooth functions. Is it possible that the d-butanol injection is also being plotted? Does this change the OA enhancement ratios?

Author response: D-butanol injection is not being plotted. The left panel of Fig. S6 is actually in units of hours to compare with Hennigan et al. (2011), not days as in the right panel. The multiple y-values for given aging times is due to noise in the OH exposure measurement at very low OH exposures corresponding to the first few minutes of the chamber experiment. The caption on the figure has been edited to describe this effect.

Ahern, A. T., Subramanian, R., Saliba, G., Lipsky, E. M., Donahue, N. M., and Sullivan, R. C.: Effect of secondary organic aerosol coating thickness on the real-time detection and characterization of biomass-burning soot by two particle mass spectrometers, *Atmos. Meas. Tech.*, 9, 6117-6137, <https://doi.org/10.5194/amt-9-6117-2016>, 2016.

T. B. Onasch, A. Trimborn, E. C. Fortner, J. T. Jayne, G. L. Kok, L. R. Williams, P. Davidovits & D. R. Worsnop (2012) Soot Particle Aerosol Mass Spectrometer: Development, Validation, and Initial Application, *Aerosol Science and Technology*, 46:7, 804-817, DOI: 10.1080/02786826.2012.663948 Willis, M. D., Lee, A. K. Y., Onasch, T. B., Fortner, E. C.,

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Williams, L. R., Lambe, A. T., Worsnop, D. R., and Abbatt, J. P. D.: Collection efficiency of the soot-particle aerosol mass spectrometer (SP-AMS) for internally mixed particulate black carbon, *Atmos. Meas. Tech.*, 7, 4507-4516, <https://doi.org/10.5194/amt-7-4507-2014>, 2014.

Referee #2

Scientific

Referee #2: On p. 4 potential losses in the sampling line are discussed, and a figure is provided in the supplement illustrating the difference between gaseous emissions sampled in the stack directly, to those in the community inlet, binned by saturation concentration. The binned comparison does not suggest a systematic loss in the community inlet either across bins or as a function of volatility. However, there is a significant difference in one of the bins (C* 107-108). Is this difference well understood (e.g., likely due to a specific class of compounds)? And, how might this difference affect the results and analysis?

Author response: The compounds in this bin do not correspond to a specific class of compounds but to a variety of compounds, including: acetic acid, furfural, furanone, monoterpenes, and methyl glyoxal/acrylic acid (in order of decreasing average abundance across all experiments). The presence of well-known SOA precursors (e.g., monoterpenes) in this volatility bin suggest that it is possible that some SOA precursors are in lower abundance in the mini-chamber relative to the stack. Another possibility is that acetic acid, the most abundant compound in this volatility bin, is preferentially lost during transport to the chamber due to accumulated water on the surfaces of the community inlet. Although preferential loss of some compounds in this volatility bin may affect SOA yields, the observation that total NMOGs correlates well with SOA suggests that some preferential loss of a small subset of compounds would not greatly affect SOA formation.

Referee #2: On p. 7, line 4 the authors state that the dilution factor prior to oxidation

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influenced observed initial aerosol mass and reference Table 1 in the supplement. It is not clear how the dilution factor is represented in the table. Is it a function of sampling time? This needs a bit more clarification/explanation.

Author response: This text simply refers to the fact that after sampling, experiments are diluted by varying amounts depending on the length of time between sampling and initiation of oxidation (254 nm UV lights). The sentence has been reworded for clarity (page 7, line 8-9):

“The total, initial aerosol mass in the chamber varied widely from experiment to experiment (SI Table 1), averaging $130 \pm 103 \mu\text{g m}^{-3}$ (mean $115 \mu\text{g m}^{-3}$), depending on the amount of fuel burned, fuel type, sampling time, and dilution prior to oxidation.”

Referee #2: The relationship between reported enhancement ratios in this work with previously published ratios is discussed on p. 7, first paragraph. The authors suggest that once aging and collection efficiency are taken into account, the results are broadly consistent with other results, and not overestimates. However, based on Fig. S6 panel b, where OA enhancement ratios are plotted as a function of aging time, the reported enhancements are still a factor of 2+ higher than Ortega et al. Are the Lim et al. enhancement ratios in the right panel actually for CE = 1? They seem significantly higher than what is presented in the left panel (and it is assumed that both are for CE = 1). In addition, the average appears to be ~ 3 , which is the CE corrected-value reported in the main text.

Author response: We thank the reviewer for pointing this out; Fig. S6b was mistakenly showing the CE corrected data instead of CE = 1. The figure has been updated so that both panels show CE = 1; however, even after correcting the figure, OA enhancements measured in the mini-chamber are significantly higher than those seen in Ortega et al. (2013). The text in the manuscript has been changed to reflect this (page 7, lines 18-23):

“The average OA enhancement ratio was 3.5 ± 1.7 . This is considerably higher than

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reported in previous studies (Ahern et al., 2019; Hennigan et al., 2011; Ortega et al., 2016; Tkacik et al., 2017), but once differences in OH exposure (as well as AMS CE) are taken into account, these results are broadly consistent with previous chamber studies and only somewhat higher than previous flow tube experiments (Fig. S6).”

Referee #2: In the discussion of correlation of measured SOA formation with different parameters (pp. 8-9), it is suggested that the reasonable correlations exist between SOA and total NMOG, with some relationship to POA, and when corrected for aging time. On p. 9, line 2, the authors state that the NMOG correlated well with POA (not shown), and thus POA is also well correlated with SOA. The correlation with POA, at least based on r^2 values, actually appears to be better than the correlation with total NMOG. If the goal is a simplified parameterization, why not just use POA?

Author response: While we provide a simple SOA parameterization based on NMOG (i.e., carbon yield from biomass burning emission), the goal of the paper is a more mechanistic understanding of the underlying chemistry and gas-phase precursors. As such, we present the NMOG parameterization in the manuscript, but also provide the relationships between SOA and POA Fig. S9 for purposes where POA measurements may be more readily available. The following text was added to the main text (page 9, lines 12-14):

“As the goal of this work is to provide a more mechanistic understanding of the underlying chemistry, relationships between SOA and NMOGs are shown in the main text; relationships between POA and SOA are given in Fig. S9 for purposes where POA measurements may be more readily available.”

Referee #2: In the discussion of the results presented in Figs. 4 and 5, it is suggested that the relative insensitivity of SOA to NMOG m/z cutoff below m/z 135 is either due to the contribution of higher volatility/lower molecular weight species, or other compounds which are not measured by the PTRMS, but correlated with these smaller NMOG molecules. It seems like there may be sufficient data available to look

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at the ratio of likely SOA precursors to total NMOG to test this hypothesis. Also, while it is not discussed, to the observed carbon yields themselves lend some insight to the likely precursors?

Author response: We appreciate this suggestion. We have looked in more detail at the precursors and their relationships (or lack thereof) with SOA formation. We were not able to determine specific precursors or a specific class of compounds that show significantly stronger correlations with SOA than the total NMOG loading. Monoterpenes, low/high temperature factors, each m/z cutoff, and compounds binned by carbon number or volatility did not show improved correlations with SOA compared to total NMOG loadings. In addition, we also examined the correlation between SOA and the top SOA precursors identified in Bruns et al. (2016), including benzene, phenol, naphthalene, and related compounds and they do not show good correlations SOA formation. These compounds have are now explicitly mentioned in the main text (page 9, line 30).

Editorial

Referee #2: p. 8, line 20: Recommend changing “common SOA precursors” to “monoterpenes”, since that is the only precursors show in S.7.

Author response: Text changed to “monoterpenes.”

Referee #2: p.9, line 23: It would be interesting to see the correlation plots of the two different temperature NMOG factors with SOA. Could these be added to the supplement?

Author response: SOA (carbon mass) correlation plots for low and high temperature combustion factors have been added to the supplement (Fig. S10). High and low temperature factors for each burn are calculated by calculating the fraction high/low factor for the initial NMOG composition (before oxidation) and multiplying by the total NMOG loading (ppb C). Reference to SI added to the main text (page 9, line 34):

“However, correlations between NMOGs and SOA when splitting total NMOGs by fac-

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tor type are weak (Fig. S10), indicating that both factors contain compounds that contribute to SOA formation.”

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-326>, 2019.