Interactive comment on "Secondary aerosol formation from photochemical aging of aircraft exhaust in a smog chamber"

Miracolo, M. A. et al.

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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 author responses are in italics.

Response to Reviewer 1

The discussion paper by Miracolo et al. reports results from a smog chamber study on the formation of secondary organic aerosol from the emissions of an aircraft engine. The aircraft engine was operated at the ICAO LTO cycle loads of 4%, 7%, 30% and 85%, using standard JP-8 fuel with a fuel sulfur content of 608 ppm by mass. The aircraft engine exhaust was collected in a Teflon bag and exposed to UV light. Among others, measured aerosol particle properties include particle number concentration, particle number size distribution, black carbon, elemental carbon, organic carbon, and non-refractory particulate mass. Based on this data, the authors report significant SOA production during photo-oxidation which exceeds primary emissions by far. A model based on traditional SOA precursors cannot reproduce the strong formation of SOA. The set-up of the study and the conduction of the experiments are scientifically sound and contribute to an important area of research. The presentation of the material is straightforward. However, few more steps in the data analysis may add further important information on SOA particle number emission and mixing state. It appears worthwhile to invest additional work in order to provide this additional relevant information.

1. During the experiments, mass concentration, chemical composition and particle size distributions were measured for both primary and secondary aerosol. Results are presented in Figure 4 in terms of emitted mass per kg of fuel. It might be worthwhile to summarise the data for 3h ageing in one table because it is difficult to extract explicit

numbers from the figures. Although the characteristics of primary emissions will be published in a companion paper, key properties such as the emission factors for particle number, particle mass, elemental carbon and organic carbon may be added to this proposed table.

The authors agree with the referees comment to include a table of data for primary emissions and secondary aerosol production. The authors will include a table in the paper, which includes primary (OC, EC, PM mass estimated from the SMPS) and secondary (SOA, secondary sulfate, and primary/secondary ratio at hour 3) all expressed as emission factors, as well as whether nucleation occurred in each experiment. Additionally, we will include a table of criteria gas emissions in the Supporting Information for each experiment in the revised manuscript. Both tables are pasted below.

Table 1 – Summary of primary PM emissions and secondary aerosol production. Uncertainty estimates are presented in parenthesis.

	Primary PM emissions			**Secondary PM production @ t = 3 hrs**			**Ratio**
Engine load	**PM mass[1]**	**OC**	**EC**	**SOA**	**Sulfate**	**Nucleation**	$\frac{\textbf{Primary PM}}{\textbf{Secondary PM}}$
4%	27 (12)	22 (9)	3.0 (0.5)	920 (170)	244 (15)	Y	35 (4.1)
7%	4.5 (0)	9.5 (9)	0.4 (0)	42 (15)	50 (5)	Y	17 (2.5)
30%	3.0 (0)	1.5 (0.4)	1.8 (0)	15 (8)	70 (6)	Y	60 (2.2)
85%	37 (12)	13 (4)	24 (4)	15 (9)	74 (3)	Y	2.7 (1.1)

*All units are expressed as mg/kg fuel, unless otherwise noted

[1] PM mass is based on particle volume measured by SMPS measurement and assumed particle density (see text)

Table A2 – Summary of criteria gas emissions for tests conducted with KC-135 Stratotanker [a]Gas-phase data not available [b]Exhaust gas analyzer not operated for this experiment; all measurements taken from chamber data

	Experiment date	Thrust setting	NO (g/kg-fuel^{-1})	NO$_x$ (g/kg-fuel^{-1})	CO (g/kg-fuel^{-1})	SO$_2$ (g/kg-fuel^{-1})	CO$_2$ at engine exit plane (%)
1	07/15/09	7%	[a]	[a]	[a]	[a]	[a]
2	07/16/09	7%	[a]	[a]	[a]	[a]	[a]
3	07/17/09	30%	8.74	8.74	7.52	1.32	3.00
4	07/20/09	4%	0.37	1.57	56.0	1.20	2.75
5	07/21/09	4%	0.35	1.86	66.5	1.14	2.76
6	07/22/09	85%	15.4	15.4	4.28	1.39	4.07
7	07/23/09	7% (center port)	1.27	2.46	60.4	1.17	2.83
8	07/24/09	4%	0.57	1.79	[b]	1.04	[b]

2. From the set of data the authors should be in a position to report also the increase in particle number emissions. Besides SOA mass, information on SOA number is of interest as well.

We have added more information on particle number emissions to the revised manuscript. In the current text, we presented a time-series of particle number for one experiment at 4% engine load in Figure 2. This shows a dramatic increase in particle number due to nucleation caused by photochemistry in the chamber. We have included a new figure (Figure 3) that shows the particle number enhancement ratio and additional text in Section 5.1. Further discussion of particle number emissions from combustion sources will also be highlighted in an upcoming publication from our research group.

"At the onset of photo=oxidation (t=0), nucleation occurred in every chamber experiment at all engine loads, dramatically increasing particle number concentrations in the chamber. Figure 3 plots the particle number enhancement ratio, which is defined as the ratio between the particle number and an exponential fit of the particle number decay prior to photo-oxidation. The exponential fit used to calculate the particle number enhancement ratio is shown in the Supporting Information (Figure A2). Particle nucleation events are strong, initially increasing particle concentrations in the chamber between a factor of 3 (85% load) and 15 (30% load). The particles quickly begin to coagulate, decreasing the particle number enhancement ratio throughout the oxidation period."

Figure 3 – Particle number enhancement ratio for photo-oxidation experiments at all engine loads. Enhancement ratio is defined as ratio between particle number and exponential fit to data during primary characterization period (see Supporting Information).

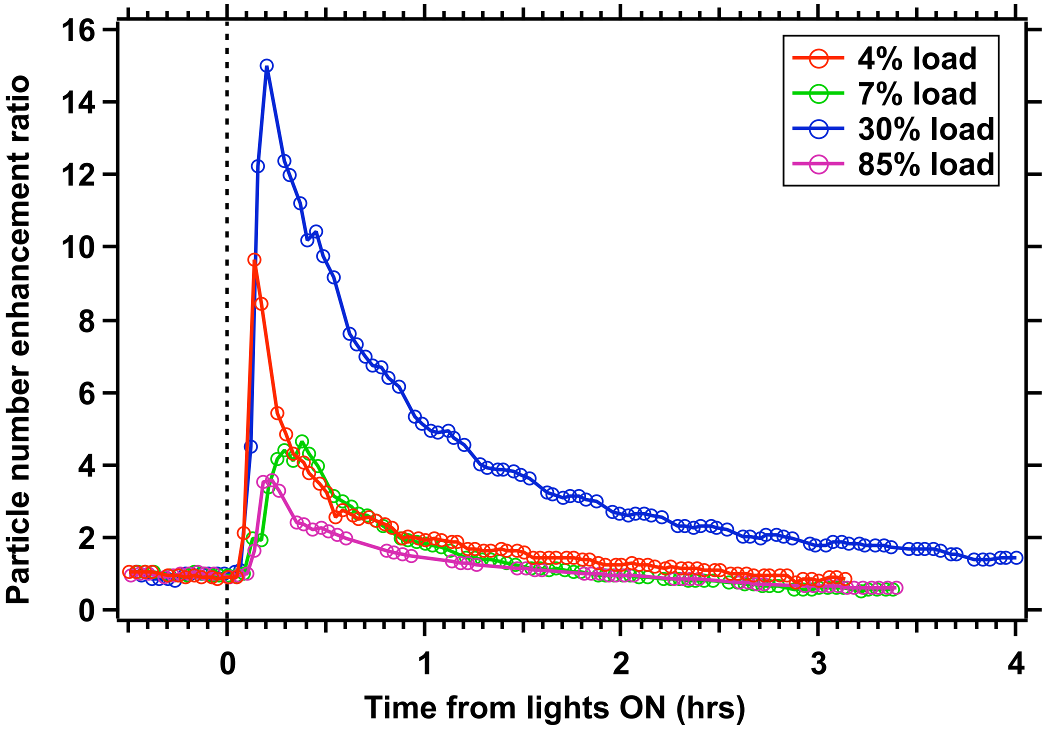
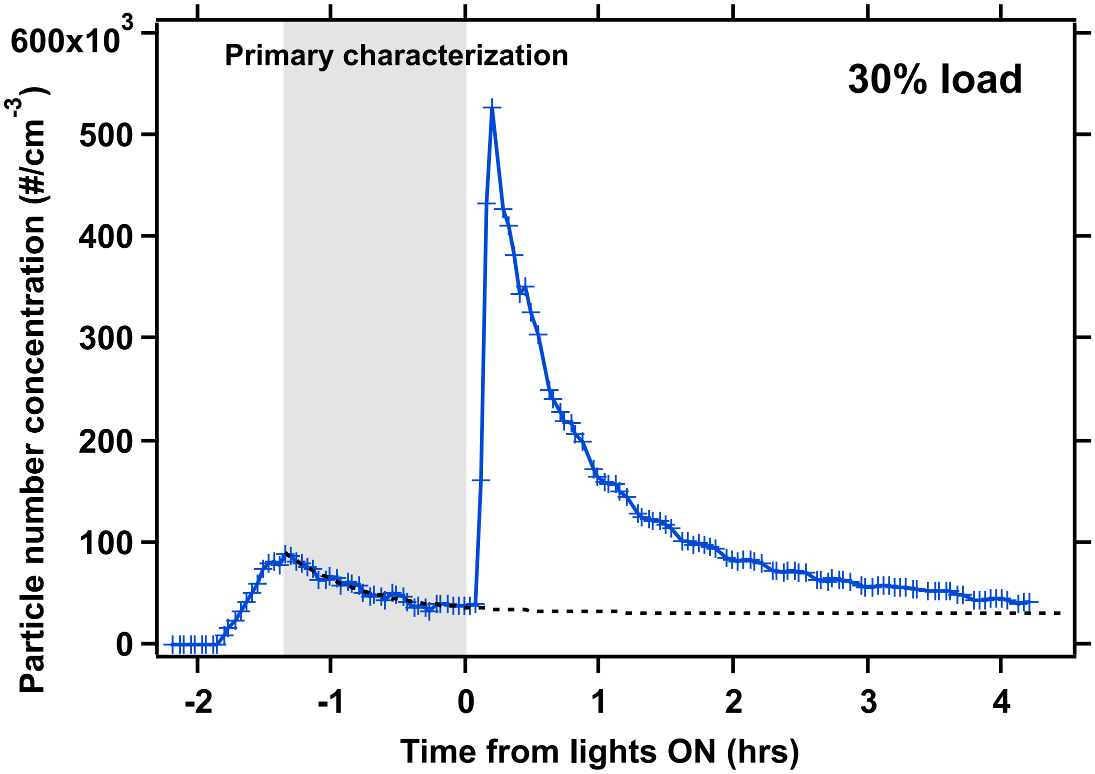


Figure A2 – Particle number concentrations for photo-oxidation at 30% engine load. Dashed line represents exponential fit to particle number data during primary characterization period. Particle number enhancement ratio is defined as ratio between particle number and exponential fit. Similar fits were performed for experiments at other engine loads.



3. The size distributions shown in Figure 3 suggest that the aerosol in the chamber starts as a mono-modal size distribution at t = 0 and develops into a bi-modal size distribution after photochemically induced formation of nucleation mode particles. The modal diameter of the primary particle mode shifts from approx. 50 nm at t =0h to 70-80 nm at t = 0.17h, and finally to > 100 nm after 3h of ageing. The amplitude of the mode also increases from t = 0h to t = 3h which suggests that an externally mixed mode of super-100 nm sized SOA particles has developed. The authors may also discuss the changes in microphysical properties of SOA particles which would add an important piece of information to this work.

There was a discussion of the changes in particle size in the original manuscript (Page 27904, lines 10-21). However, we have added an additional discussion in Section 5.1 highlighting changes in the size distribution and mixing state of the aerosol.

"Immediately after filling, the primary PM emissions in the chamber were concentrated in the nucleation mode, with a number median diameter of approximately 35 nm. During the approximately one hour primary characterization period, the number size

distribution grew from 35 to 65 nm due to coagulation. Figure 3 shows that photo-oxidation created a bimodal size distribution with a clear nucleation mode (20 nm) and a larger primary mode (75 nm). Therefore, nucleation created an externally mixed aerosol, with the larger mode containing a primary core and a secondary nucleation mode comprised of sulfate and organic particles. The AMS p-ToF data indicate the larger size mode is composed of both organic and sulfate particles. Photo-oxidation caused rapid and substantial growth in the median particle diameter of both modes. Both the nucleation and primary mode continued to grow and mix throughout the photo-oxidation period due to both coagulation and condensational growth. By the end of the experiments, the two modes have largely merged."

4. Figure 2 suggests a very good agreement between SMPS volume and SOA mass after lights were switched on. Is this true for all conditions? And what about the agreement of SMPS volume and primary particle mass taken e.g. from the SUNSET data? Combining size information and mass information should enable the authors to investigate the mixing state of the aerosol after 3h of photochemical ageing. This would add another important aspect to the presented work.

Comparisons of SMPS volume and SOA mass measured with the AMS generally showed similar behavior as shown in Figure 2. However, in some experiments, the PM mass estimated by the SMPS was systemically higher than AMS measurements because of contributions from non-refractory PM (EC, especially at higher loads) and freshly nucleated particles being outside the AMS size window. In order to correct for this difference, the SMPS data were converted to particle mass using measurements of aerosol composition from the AMS and the Aethalometer, as described in detail the text (Page 27900, lines 1-9).

A discussion of agreement between the different measurements of primary PM (e.g. SMPS volume and primary particle mass (OC + EC)) is found in a companion paper (Presto et al., 2010). As presented in that publication, the total mass balance for the chamber data (SMPS versus OC+EC) agrees within 10%, with the exception of the 7% load case. The authors agree that it is of interest to also present that data in this manuscript and have included emission factors of primary OC, EC, and SMPS mass in Table 1.

The mixing state of the particle is addressed in a response above.

5. Figure 6 suggests that for 85% load more single-ring aromatics are emitted compared to total SOA. This fact should be included in the discussion of Figure 6 on page 27906, lines 24ff.

The authors agree that this is an important point to highlight and have included this information in the text. The discussion in Section 5.1 quantifies the relationships *between single-ring aromatic emission and SOA formed. We have included additional discussion for the 85% load case (shown below).*

"However, Fig. 6 indicates that emissions of single-ring aromatics alone cannot describe the measured amount of SOA formation. For example, the mass of SOA produced after three hours of photo-oxidation at 4% load is greater than the total emissions of single-ring aromatics. Therefore, to explain the measured production at 4% load, not only would the single-ring aromatics have to be completely oxidized during the aging portion of the experiment, but the SOA yields from these compounds would need to be greater than 100% to explain the amount of SOA formed. Therefore, other precursors must contribute significantly to SOA formation. At 85% load, the emissions of single-ring aromatics are higher than the mass of SOA produced by a factor of ~8. Therefore, aromatics could plausibly explain the SOA. If all the single-ring aromatics were completely oxidized during the experiment, the SOA yields from these compounds would be ~ 12%. However, only a small fraction of the aromatic compounds are oxidized throughout the photo-oxidation period and the SOA yields from these compounds would need to be greater than 100% to explain the amount of SOA formed."

TYPOGRAFIC ERRORS:

Page 27895, line 7: correct citation to Petzold and Schröder, 1998.

The authors corrected this in the text.

Page 27897, line 16: correct to ": : : initial particle mass concentrations : : :"; line 23: correct to ": : : increased on average by 4.C : : : ".

The authors corrected both typos in the text.

Page 27900, line 2: delete "measurements".

The word "measurements" has been deleted from the text.

Page 27903, line 19: correct citation to (Seinfeld et al., 2006).

Citation has been corrected in the text.

Page 27911, line 3: correct to "Aircraft engines emit : : :".

Line has been changed to reflect referee comments.

Reference Grieshop et al. 2009b is missing; correct the numbering of references.

The authors have deleted the Grieshop et al. 2009b reference, which was incorrectly placed in the manuscript and corrected the reference numbering.

Figure 7: Figure caption: correct “: : : Only undenuded (no TD) : : :”.

The authors have corrected the spelling error in the text.

Response to Reviewer 2

The authors present some interesting work on the secondary aerosol formation potential of an aircraft engine operating at 4%, 7%, 30%, and 85% load points. The paper is generated as a companion paper to an AE paper (unpublished) that apparently details the sampling platform and basic emission factors for these engines. This paper focuses on the surprisingly large secondary aerosol formation measured during these tests using a portable Teflon chamber. The authors compare the predicted SOA formation from the monoaromatic compounds to the SOA formation observed, noting that the monoaromatic compounds appear to attributable for significant SOA formation but unable to explain the total SOA formation seen. The remaining SOA is attributed to the IVOC emissions in the chamber. Overall, the paper is written well with sufficient explanation as to the experimental and modeling approach used.

Presumably transport losses of particulate matter through the necessarily long sample lines and at the sample inlet are discussed in the companion paper. However, some indication as to the extent of these losses is necessary since the paper discusses the ratio of secondary aerosol/primary aerosol. These losses have been reported to be quite significant in other aircraft emission sampling papers/reports. How much of a change in the ratio is seen when the loss of particles in the lines is accounted for?

Experiments were performed to measure the penetration efficiency of the sampling system as a function of size at 150 °C (operating temperature of the transfer line) using sodium chloride particles. The transfer line efficiency was largely independent of size in the range of 50-400 nm (within the uncertainty of the measurement). The average measured penetration efficiency of 85% was used to correct the primary EC data, while 100% efficiency was assumed for organics, which assumes the OA is evaporated in the transfer line (Huffman et al., 2009). In our study, the high penetration efficiency is attributed to the large diameter of the sampling line. The transmission efficiency correction does not change the primary to secondary organic aerosol ratios because we assume 100% efficiency for OA. The authors have included additional discussion in Section 2.1 to highlight the treatment of transfer line losses.

"The emissions were transferred from the rake inlet to the chamber through a 21 m heated stainless steel transfer line held at 150 °C to minimize thermophoretic and condensation losses. Particle losses in the transfer line were characterized in separate experiments using dried sodium chloride aerosol. The transfer line efficiency was largely independent of size in the range of 50-400 nm (within the uncertainty of the measurement. The average measured penetration efficiency of 85% was used to correct the primary EC data, while 100% efficiency is assumed for organics, which assumes the OA is evaporated in the transfer line (Huffman et al., 2009). The data were corrected for transfer line losses."

Additionally, at what point are losses accounted for in the chamber? Are the losses corrected back to the point of introduction of aerosol in the chamber? Were the losses similar for these early, very small particles compared to the larger particles later in the experiment? A bit more discussion of these effects will be helpful.

The primary emission factors have been corrected for the measured penetration efficiency of the transfer line, as described above. After the introduction of the primary emissions into the chamber, losses to the chamber walls are accounted for separately using the approach described in the paper. Therefore changes in particle number and mass are not sensitive to losses in the transfer line.

In the smog chamber, we account for vapor and particles losses to the smog chamber walls, which are assumed to be size-independent. We have provided a detailed description of the treatment of wall-losses in Section 3. Other loss processes, such as dilution, are negligible, as indicated by constant chamber CO_2 *levels throughout the oxidation period.*

How repeatable were the experiments conducted at the same load points (is that the error bar in Fig 6a, if so, is that one or two standard deviations)? Perhaps a table summarizing the observed SOA and secondary sulfate formation along with primary emission rate of EC, OC, BC and particle number for each test is warranted.

We have included information on repeatability in the primary and secondary emission factors (Table 1).

Experiments were not repeated at 30 and 85 % loads. However, at 4 and 7% loads the experiments shown good repeatability with measured secondary aerosol production, aerosol composition, and aerosol volatility within experimental uncertainty. For example, the ratio between primary/secondary aerosol mass within ± 5% across the three 4% load experiments.

The error bar in Figure 6a corresponds to the uncertainty associated with the treatment of wall-losses in the chamber, as well as the two estimates of secondary sulfate. The authors have included additional discussion to explain this error bar:

"The error bars in Figure 6a represent the uncertainty associated with the wall-loss rate, the calculation of $\omega=0$ *and* $\omega=1$*, and the two estimates of secondary sulfate production."*

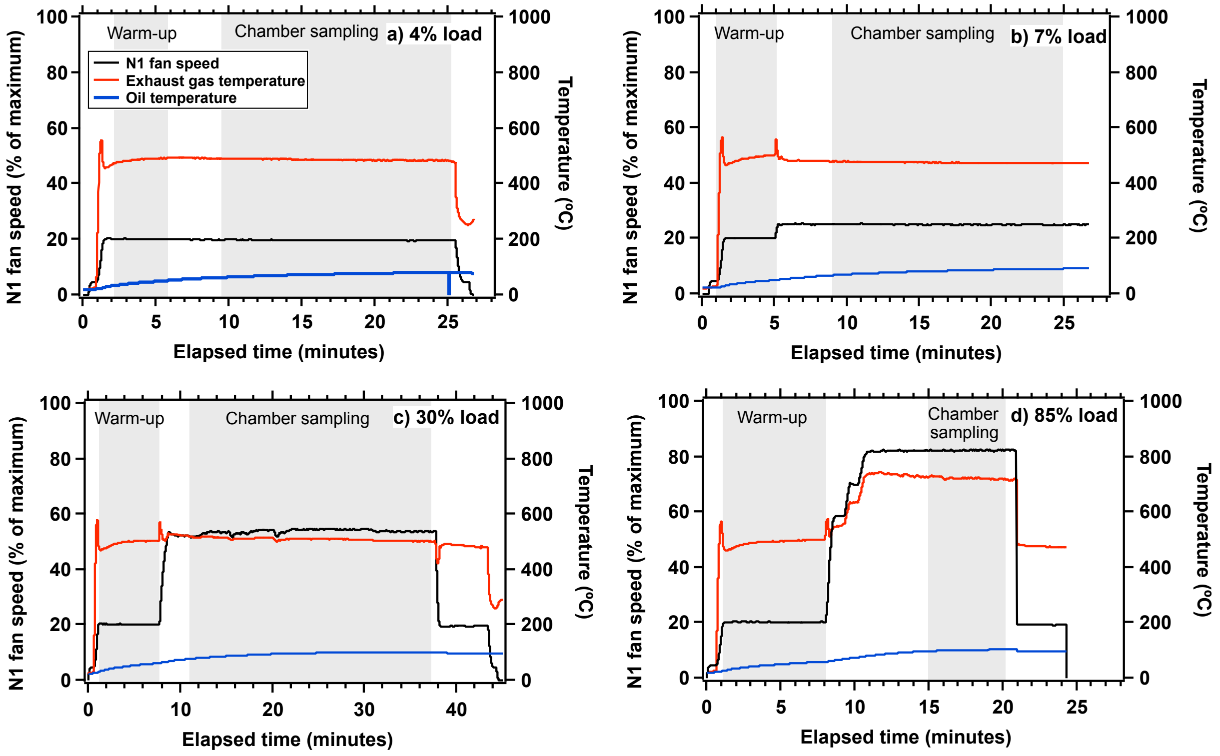
How did you verify that the engines were warmed up? What was the load sequence put on the engine? Some work has indicated that the emissions, especially at the low-loads are influenced by the testing sequence.

After start up, engine operations were stabilized at 4% load for approximately 5 minutes to allow for warm-up. After the warm-up period, the engine was brought to the test point and allowed to stabilize for a few minutes. We started sampling into the smog chamber between 5-10 minutes after the warm-up period was over. For all experiments, the exhaust gas temperature was stable before we began sampling into the smog chamber. The reviewer brings up an interesting point about the effects of loading sequence on emissions. Duplicate load experiments were performed with a similar loading sequence, and thus we did not investigate how changes in the testing sequence might effect emissions.

We have included an additional figure in the Supporting Information to illustrate the loading sequence on the engine. The figure plots a time-series of N1 fan speed (% of maximum speed), exhaust gas temperature, and oil temperature for each of the engine load cases. We have also included additional text in Section 2.1 to explain the warm-up sequence. The text is pasted below:

"After start up, the engine was run for approximately five minutes at low load (4%), allowing time for warm-up, before the test point was set. Sampling into the smog chamber began several minutes after the test point was set. Time-series of fan speed, exhaust gas temperature, and oil temperature during the testing sequence at each engine load is provided Supporting Information (Figure A1). The engine exhaust gas temperature was stable throughout the experiment. In some experiments, the engine oil temperature slowly increased throughout the sampling period"

Figure A1 – Time-series of N1 fan speed (% of maximum), exhaust gas temperature, and oil temperature for experiments conducted (a) 4% load, (b) 7% (c) 30% and (d) 85% engine loads. Warm-up and chamber sampling periods are indicated by vertical grey bars.



SO2 loss was used to estimate the OH levels in the chamber. Why is SO2 decaying before the lights were on? Also, was there any difference in the experiments conducted with the UV lights and the experiments using outdoor light? How similar is the light intensity of the blacklights to outdoor light used in these experiments?

It is not clear why there appears to be some apparent SO_2 *decay before the lights are turned on in the experiment presented in Figure 2. For the other experiments, the* SO_2 *in the chamber did not decay by a significant amount. One possible explanation for this decay is that the* SO_2 *data was recorded manually because of data acquisition failure during the campaign. It is possible that recording the data manually introduced a small error in the recorded* SO_2 *concentrations for the experiment presented in Figure 2.*

Duplicate experiments were performed at 4% with UV lights or ambient sunlight. Comparisons between the experiments do not show significant differences in secondary aerosol formed, aerosol composition and volatility, or OH exposure. Duplicate experiments were not performed at higher loads with different light sources. Previous studies have shown that under high-NO_x *conditions, SOA yields are not sensitive to UV effects on yields (Kroll et al., 2006). We do not expect significant differences in our results for comparisons between experiments with UV lights and ambient sunlight for the higher load cases, which are at high-*NO_x *conditions.*

Also, why do you suspect the AMS sulfate formation and SO2 decay varied as much as they did?

One possible explanation for the differences between AMS sulfate and SO_2 decay is the transmission efficiency of aerosol lens of the AMS. For sub-100 nm particles, transmission efficiency is poor. Therefore, the AMS did not see a significant fraction of the particle mass, especially early in the photo-oxidation period of the experiment. We have added more explanation to the text in Section 5.1 (shown below), as well as additional discussion about the mixing state and size of the aerosol presented in response to Reviewer 1 comments.

"One possible explanation for the differences between the estimates of secondary sulfate from the AMS and the SO_2 monitor is the transmission efficiency of the AMS. The lens on the Q-AMS allows 100% transmission of particles between approximately 200-400 nm, with a steep drop in transmission efficiency for particles smaller than 200 nm (Liu et al., 2007). Therefore, early in photo-oxidation period of the experiment the AMS is sampling only a small fraction of the aerosol mass. As the particles grow into the size window of the AMS throughout the oxidation period, the agreement between the two estimates improves."

The SOA model calculations indicate an underprediction by about 50% the SOA predicted using only from the monoaromatic compounds. They then go on to discuss IVOC emissions and how they trend with the missing emissions. I do not disagree with the observation. However, could it also be possible that the model is off by a factor of two for the monoaromatic compounds given uncertainties remaining in SOA chemistry from monoaromatic species?

Yes, it is always possible that the model is off by a factor of two for the mono-aromatic compounds. However, increasing the yields by a factor of 2 would not explain the measured SOA. In order to address this issue, we have used the highest published yields available for the mono-aromatic compounds to place an upper bound on the extent of SOA formation. For example, we have used the toluene yields of Hildebrandt (Hildebrandt et al., 2009), which are higher than any previously published toluene yields and more than a factor of two times higher than the original yields for toluene used by Odum et al. (Odum et al., 1997). In addition, the "effective yield" (predicted aerosol formed from toluene/reacted toluene) in the model at 4% load is high (~85%). The authors believe it is unlikely that these yield changes could account for the significant levels of SOA formation measured in these experiments. We have added additional discussion to highlight the reviewers interesting comment in Section 5.3.

"*Additionally, the model uses the highest published yield data available for the mono-aromatic compounds. For example, the model uses the toluene yields of Hildebrandt (Hildebrandt et al., 2009), which are higher than any previously published toluene yields. Therefore, the results shown here represent an upper bound on the modeled SOA estimates based on traditional precursors. In order to explain the measured SOA* *formation at 4% load, the mono-aromatic yield would have to be greater than 100%, which are not realistic yield values."*

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