Dear Prof. Grothe,

Two referees, referred to below as Referee #2 and Referee #3 based on the manuscript submission records, reviewed this manuscript (Referee #1 did not submit a review). Dr. Douglas Day and several researchers from the research group of Prof. Jose Jimenez kindly contributed additional comments. Our final response contains responses to seven comments from Reviewer 2, six comments from Reviewer 3, and fifteen comments from Dr. Day. Thank you for considering our manuscript for publication in Atmospheric Chemistry and Physics. We also express our gratitude to the referees and to members of Prof. Jimenez' research group; in our opinion, their collective input has led to a significantly improved manuscript.

Best regards,
Andrew Lambe

# Referee #2 comments

1) Since the authors do not really discuss oxidation mechanisms in detail, it is not necessary for this manuscript to show the various SOA precursors in Figure 1. I recommend removing Figure 1 and adjusting section 2.2 accordingly, just mentioning the precursors in the text.

   **Response**. Per the referee's suggestion we removed Figure 1 from the manuscript. We revised the text in Section 2.2 as follows (changes in bold and strikethrough):

   **P30582, L1-5**: "~~Figure 1 shows~~ **T**he gas-phase SOA precursors used in these studies **include** two biogenic gases (isoprene, *α*-pinene), three aromatic compounds (toluene, *m*-xylene, naphthalene), and three alkanes (*n*-$C_{10}$, cyclodecane, tricyclo[5.2.1.$0^{2,6}$]decane, also known as JP10)."

2) In section 3.1, the SOA mass spectra generated from alpha-pinene and naphthalene in an environmental chamber and a flow reactor are compared. It is stated that the chamber and flow reactor mass spectra are similar. What is the measure of similarity used for this statement? Did the authors use a quantitative measure for comparing mass spectra, e.g. a cluster analysis approach? What exactly are the SOA signal data shown in the insets of Figure 2c and d? Are these the sum signal of the AMS data? Please extend the comparison of the mass spectra and the explanation of the derived SOA signal!

   **Response.** In the discussions manuscript, we used the linear regression parameters to conclude that the spectra are similar (slope = 0.91-0.92, $r^2$ = 0.93-0.94). These parameters are shown in the insets of Figure 2c and d. We assume the referee views these as insufficient measures of similarity between the mass spectra, and that the referee is additionally suggesting using a cluster analysis as a quantitative measure of similarity. To address this comment we applied a methodology similar to that of Murphy et al. (2003) and Marcolli et al. (2006). These studies calculated the dot product of two normalized mass spectra as a measure of similarity; a dot product of zero indicates the mass spectra are orthogonal and a dot product of one indicates the mass spectra are identical. Using this approach we calculated dot products between SOA mass spectra generated from α-pinene and naphthalene respectively in the Caltech environmental chamber and the PAM flow reactor.

The SOA signal data shown in the Figure 2c inset is a scatter plot of the α-pinene SOA mass spectra shown in Figures 2a and c. Likewise, the Figure 2d inset is a scatter plot of the naphthalene SOA mass spectra shown in Figure 2b and d. We apologize that this was unclear. In an attempt address the referee's request for an extended comparison of the mass spectra, we added two tables to Figure 2 showing dot products and correlation coefficients between six pairs of mass spectra: Figures 2a and b, 2a and c, 2a and d, 2b and c, 2b and d, and 2c and d. With these revisions, the scatter plots that were originally shown as figure insets are no longer necessary and have removed them from the figure. Revisions to the Section 3.1 discussion and Figure 2 are shown below (changes bolded).

**P30584, L3-L22: "**Figure 2 shows representative ToF-AMS spectra of SOA generated in the PAM reactor and the Caltech chamber (Chhabra et al., 2010, 2011) from the OH oxidation of *α*-pinene and naphthalene […] In this range the OH exposure for the PAM reactor and chamber are approximately the same, allowing for direct comparison.

**To quantify the similarity between mass spectra, we calculated the dot product between SOA mass spectra generated in the PAM flow reactor and the Caltech chamber (Murphy et al., 2003, Marcolli et al., 2006). Using this approach, each mass spectral signal is normalized to the square root of the sum of the squares of all signals in the mass spectrum. Each spectrum is represented as a normalized vector A or B, with dot product $\boldsymbol{A \cdot B} = \sum_{i=1}^{n} \boldsymbol{a_i b_i}$, where $a_i$ and $b_i$ are the normalized signals at each *m/z* in the spectrum; $\boldsymbol{A \cdot B} = 0$ indicates the spectra are orthogonal and $\boldsymbol{A \cdot B} = 1$ indicates the spectra are identical.**

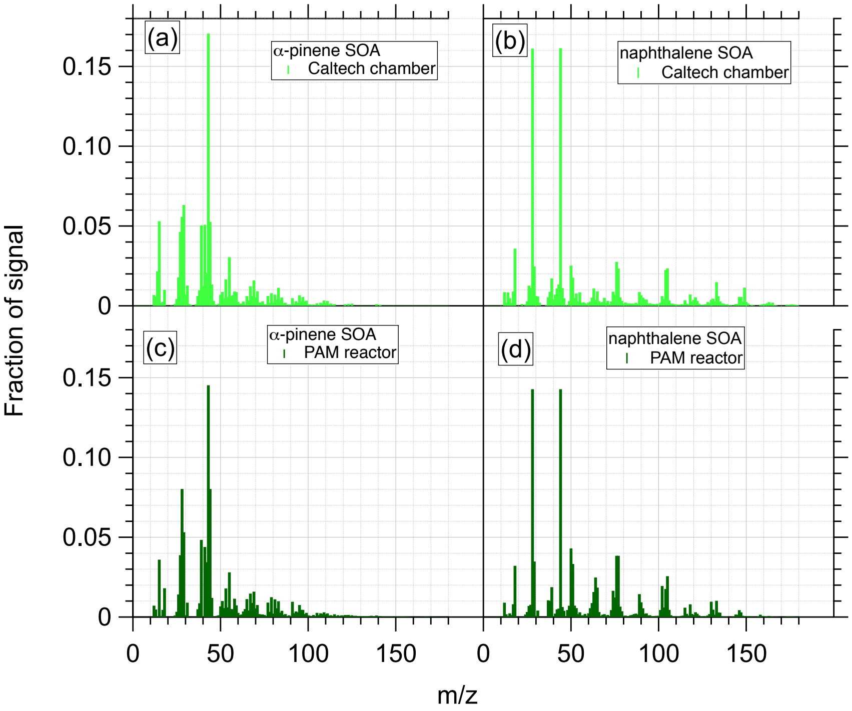
**The top table inset in Figure 2 shows the calculated dot products between each pair of mass spectra. The PAM flow reactor and the chamber produce particles with similar mass spectra, as indicated by dot products of 0.97 between spectra shown in Figs. 2a and c (α-pinene SOA) and Figs. 2b and d (naphthalene SOA), suggesting similar compositions.** Features unique to *α*-pinene and naphthalene SOA are observed in both flow reactor- and chamber-obtained spectra, with linear correlation coefficients of $r^2$ = 0.93 (*α*-pinene SOA) and $r^2$ = 0.94 (naphthalene SOA) as noted **in the bottom table inset** in Fig. 2. […] As is evident from Fig. 2, *α*-pinene and naphthalene SOA mass spectra display pronounced differences, **with dot products ranging from 0.42 to 0.63 and $r^2$ ranging from** 0.**18 to 0.37** between spectra shown in Figs. 2a and b, 2a and d, 2b and c, and 2c and d.

We added the following citations for Murphy et al. (2003) and Marcolli et al. (2006) to the listed References:

D. M. Murphy, A. M. Middlebrook & M. Warshawsky. Cluster Analysis of Data from the Particle Analysis by Laser Mass Spectrometry (PALMS) Instrument, Aerosol Science and Technology, 37:4, 382-391, DOI: 10.1080/02786820300971, 2003.

C. Marcolli, M. R. Canagaratna, D. R. Worsnop, R. Bahreini, J. A. de Gouw, C. Warneke, P. D. Goldan, W. C. Kuster, E. J. Williams, B. M. Lerner, J. M. Roberts, J. F. Meagher, F. C. Fehsenfeld, M. Marchewka, S. B. Bertman, and A. M. Middlebrook. Cluster Analysis of the Organic Peaks in Bulk Mass Spectra Obtained During the 2002 New England Air Quality Study with an Aerodyne Aerosol Mass Spectrometer. Atmos. Chem. Phys., 6, 5649–5666, 2006.

We revised Figure 2 (Figure 1 in revised manuscript) as shown below:



Dot Product Between Mass Spectra

|   | a | b | c | d |
|---|---|---|---|---|
| a | 1 | 0.46 | **0.97** | 0.42 |
| b | - | 1 | 0.63 | **0.97** |
| c | - | - | 1 | 0.59 |
| d | - | - | - | 1 |

Linear Correlation Coefficient ($r^2$) Between Mass Spectra

|   | a | b | c | d |
|---|---|---|---|---|
| a | 1 | 0.18 | **0.93** | 0.15 |
| b | - | 1 | 0.37 | **0.94** |
| c | - | - | 1 | 0.32 |
| d | - | - | - | 1 |

3) I do not agree with the interpretation of Figure 4 in section 3.3! The authors state that their results show that the chambers and the flow reactor provide similar average carbon oxidation states for a specific SOA type over the range of measured SOA composition for comparable OH exposures. They justify this statement by noting that the observed deviations between the flow reactor and the chambers are no larger than deviations between two chambers. From this, the only conclusion I can draw is that for various types of SOA there is no preference for a flow reactor or a chamber experiment. However, the average carbon oxidation states obtained from experiments with different setups may vary substantially. They are not always similar! Please clarify your statement.

**Response.** We assume the referee is referring to the following subset of SOA types where the absolute differences in OSc between flow reactor and chamber are larger than in most other cases:

toluene SOA: OSc = -0.05 (Caltech), 0.55 (PAM)
cyclodecane SOA: OSc = -0.74 (CMU), -0.38 (PAM), 0.03 (MIT)
α-Pinene SOA: OSc = -0.53 (PAM), 0.04 (PSI)

In this context, we assume the referee does not agree with the following statement on P30586, L15-16: "Figure 4 shows that the chambers and flow reactor provide similar OSc for a specific SOA type over the range of measured SOA composition for comparable OH exposures." In an attempt to address the referee's concern we revised this sentence as shown below:

P30586, L15-16: "**For a specific SOA type,** Figure 4 shows that the chambers and flow reactor provide ~~similar~~ OSc ~~for a specific SOA type~~ **with absolute differences ranging from 0.0040 to**

**0.60 (average deviation = 0.10 ± 0.34)** over the range of measured SOA composition for comparable OH exposures."

4) In section 3.4 (page 30587, lines 3/4) it is stated again that mass spectra and elemental ratios of SOA from flow reactor and chamber experiments are similar. What is the used measure of similarity for mass spectra?

   **Response.** Please see our response to Comment #2 above, where we note that we used linear regression fit parameters (and, in the revised manuscript, dot products) between SOA mass spectra generated in the PAM flow reactor and Caltech environmental chamber as measures of similarity. In attempt to clarify this point, we revised the text as follows to refer the reader back to Section 3.1:

   **P30587, L3-4**: "Because mass spectra and elemental ratios of SOA are similar whether it is generated in an environmental chamber or in a flow reactor **(Section 3.1)**…"

5) **P30587, lines 21/22**: It is not evident to me from Figure 5 that SOA yields at comparable OH exposures are a factor of 2 to 10 lower in the flow reactor than in chambers. Given the strong dependence of alpha-pinene SOA yields on OH exposure shown in Fig. 5b, I cannot compare any data points in Fig. 5a. In Fig. 5b, there are no large differences between flow reactor and chamber data points. Fig. 5c may suggest a lower SOA yield by a factor of about 5 in the flow reactor, but given the large uncertainties of the yield estimates, I think a quantitative interpretation of Figure 5 is not adequate. Please clarify this passage.

   **Response**. This is a fair point (see also related Comment # 5 by Douglas Day). We assume that the referee agrees that yields are systematically lower in the flow reactor than in the chambers. We have revised the text as follows (changes in strikethrough:

6) **P30587, L21-22**: "1. SOA yields at comparable OH exposures are ~~a factor of 2 to 10~~ lower in the flow reactor than in chambers, whereas the mass spectra, O/C and H/C of SOA generated in the chambers and flow reactor are similar (Figs. 2–4)."

7) **Technical comments page 30583, line 20**: remove "degree" in "-0.02 per degree K" page 30589, line 27: replace "concentrations" by "concentration"

   **Response.** Thank you for pointing these out. We made the suggested changes.

## Referee #3 comments

1) Title: The title is extensively long and appears to be more a short abstract then a title. I recommend shortening of the title in a focusing form.

   **Response.** Per the referee's suggestion we will change the title from "Comparison of secondary organic aerosol formed with an aerosol flow reactor and environmental reaction chambers: effect of oxidant concentration, exposure time and seed particles on chemical composition and yield" to "Effect of oxidant concentration, exposure time and seed particles on secondary organic aerosol chemical composition and yield"

2) Introduction: The introduction well introduces the reader to the scientific content of the present work. However, present intercomparison studies are not discussed. The discussion of the comparability of these two experimental setups is of highest interest for the community and should therefore be introduced as well. For example: Jang et al. (Environ. Sci. Technol. 2003, 37, 3828-3837, doi: 10.1021/es021005u) studied the aerosol growth by heterogeneous nucleation on seed particles in a flow reactor and an aerosol chamber. Ofner et al. (Z. Phys. Chem., 2010, 224, 1171-1183, doi: 10.1524.zpch.2010.6146) studied and compared the evolution of infrared active func- tional groups using a flow reactor and a smog chamber. The evolution of carbonyls in this study can be linked to the averaged carbon oxidation state. Bernhard et al. (J. Aerosol Sci., 2012, 43, 14-30, doi: 10.1016/j.jaerosci.2011.08.005) compared the ozonisation of mono-terpenes in a flow-reactor with aerosol chamber studies. Further, the cited studies on flow reactor measurements should be discussed in more detail.

**Response.** Thank you for bringing these studies to our attention. We have revised text in the Introduction as follows:

**P30579-P30580, L29-6**: "A growing set of studies […] (Bahreini et al., 2012; Lambe et al., 2012, 2011b; Kang et al., 2011; Massoli et al., 2010; Ortega et al., 2013; Slowik et al., 2012; Wang et al., 2012; Wong et al., 2011). **Other studies have used a combination of aerosol flow reactors and environmental chambers to characterize heterogeneous uptake of organics on seed particles (Jang et al., 2003), SOA formation potential (Kang et al., 2007; Bernard et al., 2012), and evolution of functional groups in SOA with aging (Ofner et al., 2010); in general, similar results are obtained in reactors and chambers.** However, these comparisons need to be extended over a wider range of reactants and experimental conditions than are currently available."

We added the following citations to References:

Jang, M., B. Carroll, B. Chandramouli, and R. M. Kamens, Particle Growth By Acid-Catalyzed Heterogeneous Reactions of Organic Carbonyls on Preexisting Aersols, *Environ. Sci. Technol.*, 37, 3828-3837, 2003**.**

Ofner, J., H.-U. Krüger, and C. Zetzsch, Time Resolved Infrared Spectroscopy of Formation and Processing of Secondary Organic Aerosol, *Z. Phys. Chem.*, 224, 1171–1183, 2010, DOI:10.1524.zpch.2010.6146.

Bernard, F., I. Fedioun, F. Peyroux, A. Quilgars, V. Daële, A. Mellouki, Thresholds of secondary organic aerosol formation by ozonolysis of monoterpenes measured in a laminar flow aerosol reactor, *Journal of Aerosol Science*, 43, 14—30, 2012.

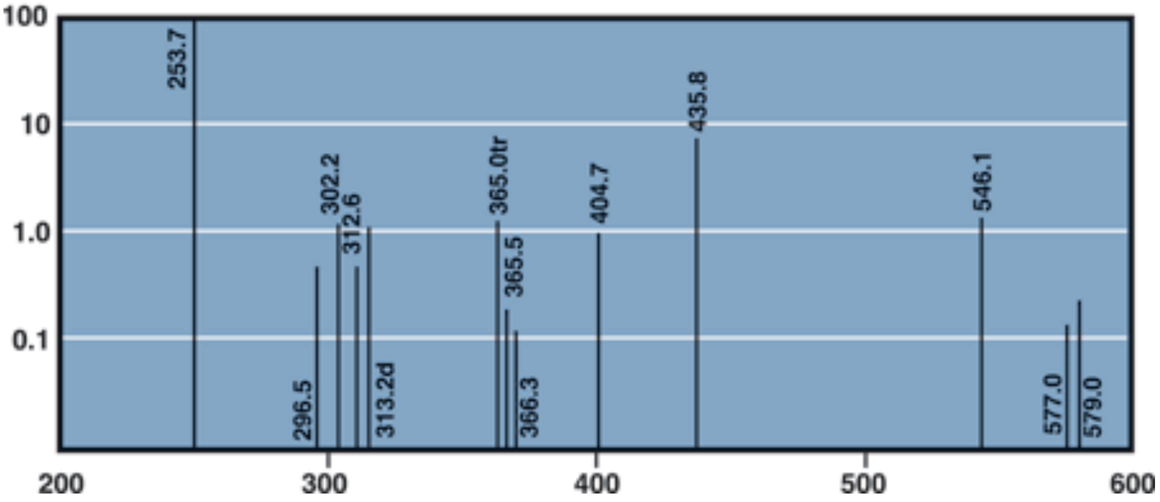
3) Experimental: The experimental setup of the PAM reactor should be reported in more detail. While the involved aerosol chambers are well defined in the literature, only rudimentary information on the PAM reactor is provided. Especially, UV/VIS spectra of the applied mercury lamps, which cause photolysis inside the flow reactor, and photon flux measurements would be interesting. The knowledge of the photon flux inside the reactor would assist the calculation of photolysis rates of several gaseous species.

**Response.** We have added text (changes bolded) to the Experimental section to describe UV/Vis spectra of the mercury lamps and photolysis flux calculations inside the reactor.

**P30581, L4-L13**: "In the flow reactor, OH radicals were produced in the absence of NO$_x$ via the reaction $O(^1D) + H_2O \rightarrow 2OH$, with $O(^1D)$ radicals produced from the reaction $O_3 + h\nu \rightarrow O_2 + O(^1D)$. $O_3$ was generated by $O_2$ irradiation with a mercury lamp ($\lambda$ = 185 nm) outside the flow reactor. The $O(^1D)$ atoms were produced by UV photolysis of $O_3$ inside the flow reactor using four mercury lamps **which emit primarily at $\lambda$ = 254 nm. Additional photons are emitted at the following wavelengths with relative intensities of 1% or more of the UV intensity at 254 nm: 185 nm (~1%; Li et al., 2015); 302 nm (1%); 313 nm (1%) 366 nm (1%); 405 nm (1%); 436 nm (10%); 546 nm (1%) (BHK Inc. Analamp product technical specifications)** […]. The corresponding OH exposures ranged from $2.0 \times 10^{10}$ to $2.2 \times 10^{12}$ molec cm$^{-3}$ s or approximately 0.2 to 17 days of equivalent atmospheric exposure.

**At the highest UV intensity that was used in the reactor, we calculate upper-bound $J_{UV}$ = $2\times10^{13}$ and $2\times10^{15}$ cm$^{-2}$ s$^{-1}$ at $\lambda$ = 185 and 254 nm from ozone and OH exposure measurements. Corresponding lower limit timescales for UV photolysis of several phenols, carboxylic acids, aldehydes and ketones range from 12 to 50,000 sec for absorption cross sections ranging from approximately $4\times10^{-17}$ to $1\times10^{-20}$ cm$^3$ molec$^{-1}$ s$^{-1}$ (https://sites.google.com/site/pamwiki/; and references therein).**"

Below is the UV-Vis emission spectrum of the lamps provided on the manufacturer website:



The following citation has been added to References:

R. Li, W.H. Brune, B.B. Palm, A.M. Ortega, J. Hlywiak, W. Hu, Z. Peng, D.A. Day, C. Knote, J. de Gouw, and J. L. Jimenez. Modeling the radical chemistry in an Oxidation Flow Reactor: radical formation and recycling, sensitivities, and OH exposure calibration equation. *Journal of Physical Chemistry A*, 2015, submitted.

4) Particle monitoring and analysis – p. 30582, line 24ff "While AMS measurements . . . additional supporting measurements . . .": Please specify these supporting measurements. Several other techniques, especially optical spectroscopy in the UV/VIS and IR is able to assist AMS

measurements. Also offline techniques like FT/MS could assist the interpretation of chemical reactions related to aerosol formation in aerosol chamber and aerosol flow reactor beyond O/C ratios and the averaged carbon oxidation state.

**Response.** We have revised the text as follows (changes bolded):

**P30582, L24**: "While AMS measurements provide basic information about SOA composition, additional supporting measurements **such as Fourier transform infrared spectroscopy, nuclear magnetic resonance, gas chromatography – mass spectrometry, and chemical ionization mass spectrometry** are required to investigate SOA chemistry at the molecular level."

5) **p. 30585, l. 17**: "The observation suggests . . ." This sentence is of utmost importance due to the discussion of comparability of these two methods and should therefore be discussed in detail and added to the abstract and the results.

**Response.** We revised the abstract as follows (changes marked in bold and strike-through).

**P30577**: "The OH concentration in the chamber experiments is close to that found in the atmosphere, but the integrated OH exposure in the flow reactor can simulate atmospheric exposure times of multiple days compared to chamber exposure times of only a day or so. **In most cases, for a specific SOA type the most-oxidized chamber SOA and the least-oxidized flow reactor SOA have similar mass spectra, oxygen-to-carbon and hydrogen-to-carbon ratios, and carbon oxidation states at integrated OH exposures between approximately 1 × $10^{11}$ and 2 × $10^{11}$ molec cm$^{-3}$ s, or about 1–2 days of equivalent atmospheric oxidation. This observation suggests that in the range of available OH exposure overlap for the flow reactor and chambers, SOA elemental composition as measured by an aerosol mass spectrometer is similar whether the precursor is exposed to low OH concentrations over long exposure times or high OH concentrations over short exposures times.** ~~A linear correlation analysis of the mass spectra (m = 0.91–0.92, $r^2$ = 0.93–0.94) and carbon oxidation state (m = 1.1, $r^2$ = 0.58) of SOA produced in the flow reactor and environmental chambers for OH exposures of approximately $10^{11}$ molec cm$^{-3}$ s suggests that the composition of SOA produced in the flow reactor and chambers is the same within experimental accuracy as measured with an aerosol mass spectrometer.~~ This similarity in turn suggests that both in the flow reactor and in chambers, SOA chemical composition at low OH exposure is governed primarily by gas-phase OH oxidation of the precursors, rather than heterogeneous oxidation of the condensed particles. In general, SOA yields measured in the flow reactor are lower than measured in chambers for the range of equivalent OH exposures that can be measured in both the flow reactor and chambers. The influence of sulfate seed particles on isoprene SOA yield measurements was examined in the flow reactor. The studies show that seed particles increase the yield of SOA produced in flow reactors by a factor of 3 to 5 and may also account in part for higher SOA yields obtained in the chambers, where seed particles are routinely used."

In addition to the above text located on P30585, L17, similar statements are mentioned and discussed in the following locations of the discussions manuscript:

**P30584, L11-L12** (Section 3.1): "The PAM flow reactor and the chamber produce particles with similar mass spectra, suggesting similar compositions."

**P30586, L14-L16** (Section 3.3): “Figure 4 shows that the chambers and flow reactor provide similar OSc for a specific SOA type over the range of measured SOA composition for comparable OH exposures.”

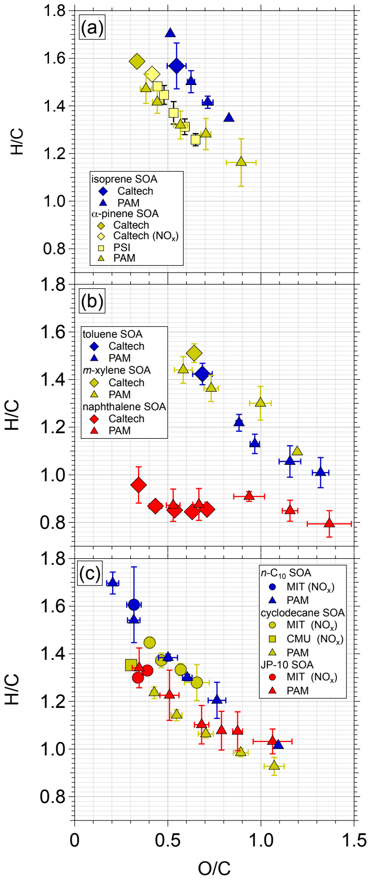
**P30590, L20-L22**: (Section 4): “Within the range of approximate OH exposure overlap of (1–4) $\times 10^{11}$ molec cm$^{-3}$ s, the SOA mass spectra and oxidation state were similar in both systems.”

In our opinion, after revising the abstract in accordance with the referee’s suggestion, this topic is now sufficiently expressed in the revised manuscript.

6) Figure 7 (and some others as well): If the 1 sigma uncertainty is in the size range of the symbol, please remove the error bars to prevent misinterpretation of the kind of symbol.

**Response**. We assume the referee is referring primarily to Figure 3 in addition to Figure 7. Figures 3 and 7 have been revised as shown below (left = figure in discussions manuscript; right = figure in revised manuscript):

**FIGURE 3**



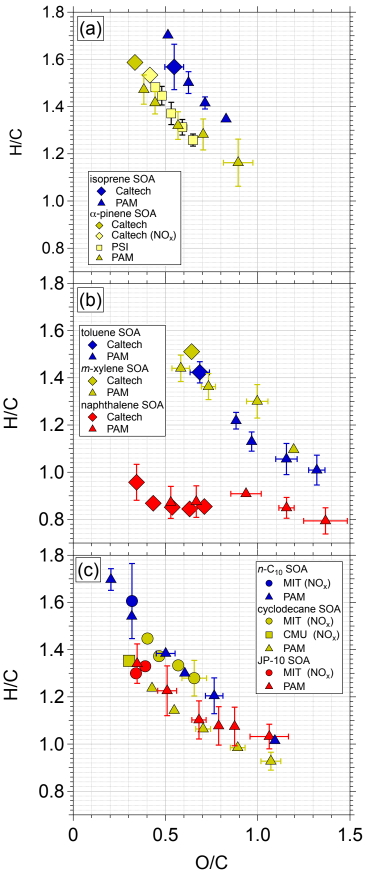
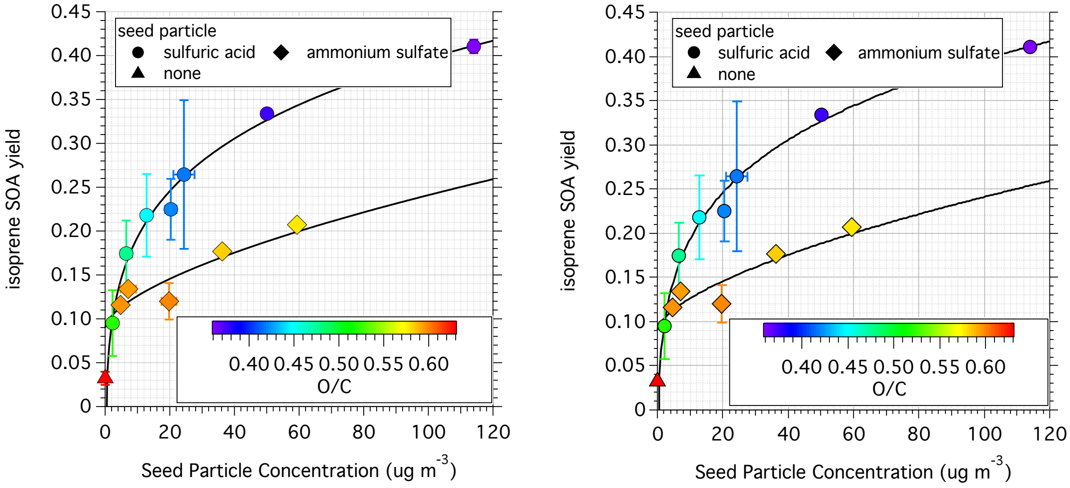


**FIGURE 7**



## Douglas Day comments

1) One critical aspect, in particular, is the lack of information on how the OH exposure ($OH_{exp}$) is calculated. The only reference to $OH_{exp}$ calculations appears in Sect. 2.1 (p 30581, lines 8-13) as "OH concentrations were varied by changing the UV light intensity, and were quantified by measuring the decay of $SO_2$ and applying the known OH+ $SO_2$ rate constant (Davis et al., 1979)." Depending on the details of how such experiments were done, there could be substantial errors in the estimated $OH_{exp}$. However there is not sufficient detail in the manuscript to ascertain whether this is the case or not. It would be very useful to the community and the future users of the results of this paper if more details were provided, so readers and other researchers don't have to speculate whether disagreements may be due to errors or uncertainties in $OH_{exp}$.

2) As discussed in Ortega et al. (2013) and Li et al. (2015), high VOC concentrations (or high concentrations of other compounds that react with OH) can "suppress" OH by shifting OH to $HO_2$ in the reactor, resulting in much lower OH exposures than measured for the same conditions in the absence of added "external OH reactivity" ($OHR_{ext}$). Measurements and modeling carried out by our group (using reactors that employ either 254 nm only or both 254 + 185 nm wavelengths from mercury lamps to generate OH) suggests this "OH suppression" can reach 1-2 orders-of-magnitude for high $OHR_{ext}$ (100-1000 $s^{-1}$). Very high $OHR_{ext}$ were indeed used in the experiments described in this paper. With the information provided, it is impossible to know if the effects of OH suppression from high $OHR_{ext}$ were accounted for or not in this study. Several critical pieces of information include:

- Were the $SO_2$ decay measurements performed only "offline", i.e. in the absence of VOC? Or were they carried out "online" (in the presence of added VOC)?
- If offline, at what range of $OHR_{ext}$ (i.e. $SO_2$ concentrations)?
- What $H_2O$ concentrations were used for the calibrations and how do they compare to those used in the VOC experiments, if those were different experiments?

- What input $O_3$ levels were used for the $SO_2$ and VOC experiments?
- Were the calibrations and SOA experiments conducted close in time? Hg lamps age with time and the same light power setting may not correspond to the same UV flux if multiple months have passed.

**Response.** We have revised the text shown below (changes in response to Comment #1 are shown in bold/strikethrough; changes in response to Comment #2 are shown in red).

**P30581, L4-10**: "In the flow reactor, OH radicals were produced in the absence of $NO_x$ via the reaction $O(^1D) + H_2O \rightarrow 2OH$, with $O(^1D)$ radicals produced from the reaction $O_3 + h\nu \rightarrow O_2 + O(^1D)$. $O_3$ (15 – 30 ppm) was generated by $O_2$ irradiation with a mercury lamp (λ = 185 nm) outside the flow reactor. The $O(^1D)$ atoms were produced by UV photolysis of $O_3$ inside the flow reactor using four mercury lamps (λ = 254 nm). In offline calibrations, OH concentrations were varied by changing the UV light intensity **through stepping the lamp voltages between 0 and 110V**. $SO_2$ was added to the carrier gas, typically at mixing ratios ranging from 30 to 60 ppbv, and was used as an OH tracer. Calibrations were conducted at the same $H_2O$ and $O_3$ concentrations used in SOA experiments.

**At each lamp setting, OH exposures were quantified by measuring the steady-state $SO_2$ mixing ratio and normalizing to the $SO_2$ mixing ratio obtained with the lamps turned off. The corresponding OH exposure ($OH_{exp}$)** was quantified by ~~measuring the decay of $SO_2$~~ **normalizing the $SO_2$ mixing ratio with the lamps on to the $SO_2$ mixing ratio with the lamps off** and applying the known OH+$SO_2$ rate constant, $k_{SO_2}^{OH}$, (Davis et al., 1979)**, as shown in Equation 1:**

$$OH_{exp} = -\frac{1}{k_{SO_2}^{OH}} ln\left(\frac{[SO_2]}{[SO_2]_i}\right)$$

The concentrations ranged from approximately $2.0 \times 10^8$ to $2.2 \times 10^{10}$ molec $cm^{-3}$. The corresponding OH exposures ranged from $2.0 \times 10^{10}$ to $2.2 \times 10^{12}$ molec $cm^{-3}$ s or approximately 0.2 to 17 days of equivalent atmospheric exposure.

Additional $SO_2$ calibration measurements were conducted in the presence and absence of a subset of precursors (isoprene and JP-10) to investigate reductions in OH levels following addition of those precursors to the flow reactor at mixing ratios that were used in SOA experiments. No change in $SO_2$ decay was observed upon addition of isoprene, but addition of JP-10 decreased OH levels by approximately 10% (highest OH exposure) to 50% (lowest OH exposure) (Lambe et al., 2012). Reductions in OH exposure following addition of other VOCs will be investigated in future work using the methods of Li et al. (2015).

**P30607, Figure 5 caption: "**Yields of SOA produced from photoxidation of **(a)** isoprene, **(b)** α-pinene, and **(c)** tetracyclo[5.2.1.$0^{2,6}$]decane (JP-10) in environmental chambers and PAM reactor as a function of OH exposure. The OH exposure in Fig. 5c is corrected for reductions in OH levels upon JP-10 addition (see Section 2.1)."

3) $H_2O$ and $O_3$ concentrations will strongly affect both $OH_{exp}$ and degree of OH suppression for a given lamp setting. If calibrations were not conducted at relevant conditions or characterization of the effects of OH suppression estimated, a discussion of possible biases should be included in the manuscript, or (better) $OH_{exp}$ calibration experiments should be conducted under conditions

representative of the $OHR_{ext}$ of the experiments. If differences in OH suppression between calibrations and VOC experiments were corrected for, the details of such corrections should be thoroughly described in the paper.

**Response**. OH exposure calibrations were conducted at the same $H_2O$ and $O_3$ concentrations that were used during SOA formation experiments. In the present work, calibrated OH exposure data are shown for in Figure 5 for isoprene SOA, α-pinene SOA, and JP-10 SOA formation experiments. We conducted OH exposure calibrations in the presence and absence of isoprene (added at 462 ppbv mixing ratio) and did not observe changes in OH exposure upon isoprene addition, so no correction was applied. We have not measured OH exposure reductions upon addition of α-pinene. As suggested by Li et al. (2015), we will conduct OH exposure calibrations in the presence of α-pinene (and othere relevant VOCs) in future work. We conducted OH exposure calibrations in the presence and absence of JP-10 (added at 55 ppbv mixing ratio). A 10%-50% reduction in OH exposure was observed upon addition of 55 ppb JP-10; we initially reported this result in Lambe et al. (2012). Results shown in Figure 5c of the discussions manuscript accounted for this reduction in OH exposure and the revised manuscript mentions this correction.

4) Also, for conditions with high VOC concentrations, $RO_2$+$SO_2$ reactions may cause substantial decay in $SO_2$, not attributable to OH (Kan et al., 1981; Richards-Henderson et al., 2014). Therefore, if online calibrations were conducted (i.e. if the $SO_2$ was introduced at the same time as the VOC) this may cause a substantial overestimate in $OH_{exp}$. If additional high $OHR_{ext}$ calibrations/characterizations experiments are conducted, use of an additional compound that reacts with OH but not $RO_2$, such as CO, would help eliminate errors arising from that cause.

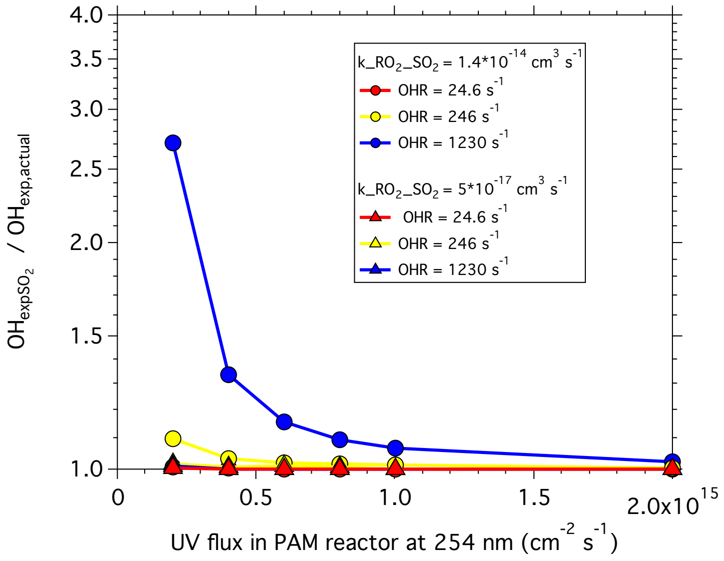
**Response**. The Kan et al. (1981) study measured a bimolecular reaction rate constant $k_{RO2}^{SO2}$ = $1.4*10^{-14}$ $cm^3$ $s^{-1}$ between $SO_2$ and methylperoxy ($CH_3O_2$) radicals. However, other studies have measured much slower $SO_2$ + $RO_2$ reaction kinetics. Sander and Watson (1981) reported an upper limit reaction rate $k_{RO2}^{SO2} < 5*10^{-17}$ $cm^3$ $s^{-1}$, a value that is more than 100 times lower than Kan et al. (1981). A computational study by Kurten et al. (2011) suggests an even lower upper-bound reaction rate constant $k_{RO2}^{SO2} < 5*10^{-21}$ $cm^3$ $s^{-1}$. JPL Evaluation 17 (2011) recommends the Sander and Watson result, as summarized below, with a possible experimental artifact in the Kan et al. (1981) result highlighted:

> *"This recommendation accepts the results from the study of Sander and Watson [1255]. These authors conducted experiments using much lower $CH_3O_2$ concentrations than employed in the earlier investigations of Sanhueza et al. [1259] and Kan et al. [765], both of which resulted in k(298 K) values approximately 100 times greater. A later report by Kan et al. [764] postulates that these differences are due to the reactive removal of the $CH_3O_2SO_2$ adduct at high $CH_3O_2$ concentrations prior to its reversible decomposition into $CH_3O_2$ and $SO_2$. They suggest that such behavior of $CH_3O_2SO_2$ or its equilibrated adduct with O2 ($CH_3O_2SO_2O_2$) would be expected in the studies yielding high k values, while decomposition of $CH_3O_2SO_2$ into reactants would dominate in the Sander and Watson experiments. It does not appear likely that such secondary reactions involving $CH_3O_2$, NO, or other radical species would be rapid enough, if they occur under normal atmospheric conditions to compete with the adduct decomposition."*

We simulated PAM reactor photochemistry over a range of conditions that are representative of the SOA formation experiments used in this work. The photochemical box model was developed by W. H. Brune and is a revised version of the model described in Li et al. (2015) that incorporates additional $RO_2$ + $SO_2$ reactions following the oxidation of added VOCs to form $RO_2$ radicals. The following inputs were used in the model:

Mean residence time = 100 sec
Flux254 ($cm^{-2}$ $s^{-1}$)= [2e14; 4e14; 6e14; 8e14; 1e15; 2e15]
Flux254 ($cm^{-2}$ $s^{-1}$)= [2e12; 4e12; 6e12; 8e12; 1e13; 2e13]
$[O_3]_i$ = 20 ppmv
$[H_2O]$ = 1.1 %
$[SO_2]_i$ = 60 ppbv
$[VOC]_i$ (ppbv) = [10; 100; 500]
k_OH_VOC = 10e-11 ($cm^3$ $s^{-1}$)
k_ro2_so2 = 1.4e-14 $cm^3$ $s^{-1}$ [Case 1; Kan et al. (1981)]
k_ro2_so2 = 5e-17 $cm^3$ $s^{-1}$ [Case 2; Sander and Walker (1981)]

The above range of UV intensities covers most of the experimental conditions used in our measurements. This range of conditions corresponds to "external" OH reactivities ($OHR_{ext}$) of 24.6, 246, and 1230 $s^{-1}$, respectively, which span the range of $OHR_{ext}$ for data presented in Table 2 and Figures 5-7. For example, the addition of 55 ppb JP-10 is equivalent to $OHR_{ext}$ ~ 31 $s^{-1}$ assuming k_OH_VOC = $2.3*10^{-11}$ $cm^3$ $s^{-1}$ (Lambe et al., 2012 supporting information). The addition of 41 to 100 ppb α-pinene corresponds to $OHR_{ext}$ = 54 to 113 $s^{-1}$ assuming k_OH_VOC = $5.33*10^{-11}$ $cm^3$ $s^{-1}$, and addition of 462 ppb isoprene corresponds to $OHR_{ext}$ = 1136 $s^{-1}$ assuming k_OH_VOC = $10^{-10}$ $cm^3$ $s^{-1}$ (Atkinson et al., 1986). Results of our model runs are shown in the figure below:



As is evident from the figure, application of the Kan et al. (1981) kinetic data (circles) suggests an overestimate of the OH exposure by up to factor of ~3 at Flux254 = $2*10^{14}$ $cm^{-2}$ $s^{-1}$ and $OHR_{ext}$ = 1230 $s^{-1}$, which is equivalent to the addition of 500 ppbv isoprene to the PAM reactor. At higher UV intensity and/or lower $OHR_{ext}$, the overestimate in OH exposure is a factor of 1.3 or less. Application of the Sander and Walker (1981) kinetic data at the same operating conditions (triangles) reveals no effect of $RO_2$ + $SO_2$ reactions on the measured OH exposure.

Because of the aforementioned issues with the Kan et al. (1981) data, it is not clear that $RO_2$+$SO_2$ reactions affect our OH exposure calibrations.

References:

Sander, S. P. and R. T. Watson, A kinetic study of the reaction of $SO_2$ with $CH_3O_2$, *Chem. Phys. Lett.*, 77, 473-475, 1981.

Kurten, T., J. R. Lane, S. Jørgensen, and H. G. Kjaergaard, A Computational Study of the Oxidation of $SO_2$ to $SO_3$ by Gas-Phase Organic Oxidants, *J. Phys. Chem. A*, 115, 8669-8691, dx.doi.org/10.1021/jp203907d, 2011.

5) This concern about uncertainties in the quantitative OH exposure relates to Referee 2's comment about the authors' interpretation of Fig 5 that "It is not evident to me from Figure 5 that SOA yields at comparable OH exposures are a factor of 2 to 10 lower in the flow reactor than in chambers." For Fig 5a and Fig 5b, it appears that a decrease in OH exposure on order of a factor of ~2 would make the yields between the chamber and PAM indistinguishable for overlapping $OH_{exp}$. Therefore, unless the authors can demonstrate that the uncertainty in $OH_{exp}$ is substantially less than a factor 2 with their methods, this statement should be removed from the paper (especially from the abstract and conclusions, where it appears in less quantitative terms), or possibly modified to reflect only the factor of 2-3 difference for isoprene SOA under the experimental conditions of these studies (and also probably the experimental agreement for the other compounds). Such low uncertainty of only a factor of 2 in $OH_{exp}$ is difficult to achieve in practice with a PAM in our experience, and in any case requires careful work on this topic, something that cannot be assessed from the current version of the paper.

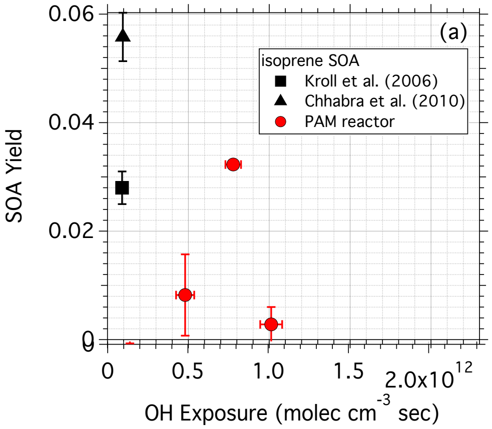
**Response**. Please see our response to Referee #2, Comment #5, where we revised the text as follows (changes in strikethrough):

**P30587, L21-22**: "1. SOA yields at comparable OH exposures are ~~a factor of 2 to 10~~ lower in the flow reactor than in chambers, whereas the mass spectra, O/C and H/C of SOA generated in the chambers and flow reactor are similar (Figs. 2–4)."

6) Meanwhile, only one chamber experiment from isoprene oxidation (in Fig 5a and Fig 6) was compared to the yield of isoprene in flow reactor experiments. However, isoprene SOA yields were also reported in other experiments, e.g., Kroll et al., (2006) found a yield range of 0.9%-3.6% for isoprene oxidation (low NO conditions) in chamber studies, which is lower than the chamber yield (~5.5%) used in this study and similar to the yield range in the PAM. A more comprehensive summary of published chamber yields should be included. Alternatively if there are reasons to exclude certain chamber studies, these should be given.

**Response**. For isoprene SOA, we are restricting the flow reactor/chamber comparison to data obtained without added $NO_x$ and where the integrated OH exposure is provided (or can be calculated based on available information), as is stated on P30587, L10-11 of the discussions manuscript: "Figure 5 shows yields of SOA as a function of OH exposure for isoprene SOA (no added $NO_x$)." To our knowledge Kroll et al. (2006) is the only other chamber experiment (in addition to Chhabra et al., 2010) where these criteria are satisfied; thus, we have revised Figure

5a as shown below.



7) On a related point, what do the one-sigma uncertainties represent in Fig 5? Please clarify. As is, they may lead readers to assume they represent the uncertainty in the OH exposure (which is almost certainly much larger). They more likely represent ONLY the propagated variability from the measurements used to calculate it (rather than uncertainty in the offline/online calibration and/or models use to estimate $OH_{exp}$). An uncertainty analysis should be conducted to characterize the true uncertainties in $OH_{exp}$, which would help clarify whether the differences in yield in Fig 5 really have meaning.

**Response**. The Figure 5 caption states "Error bars indicate ±1σ uncertainty in binned measurements." The absolute uncertainty of OH exposures is presumably larger. Li et al. (2015) suggest an average ±34% uncertainty in OH exposure as measured using $SO_2$ tracer decay in an extensive series of OH exposure calibrations. We have revised Figure 5 and 6 (and captions) to incorporate this average ±34% OH exposure uncertainty as suggested by Li et al.

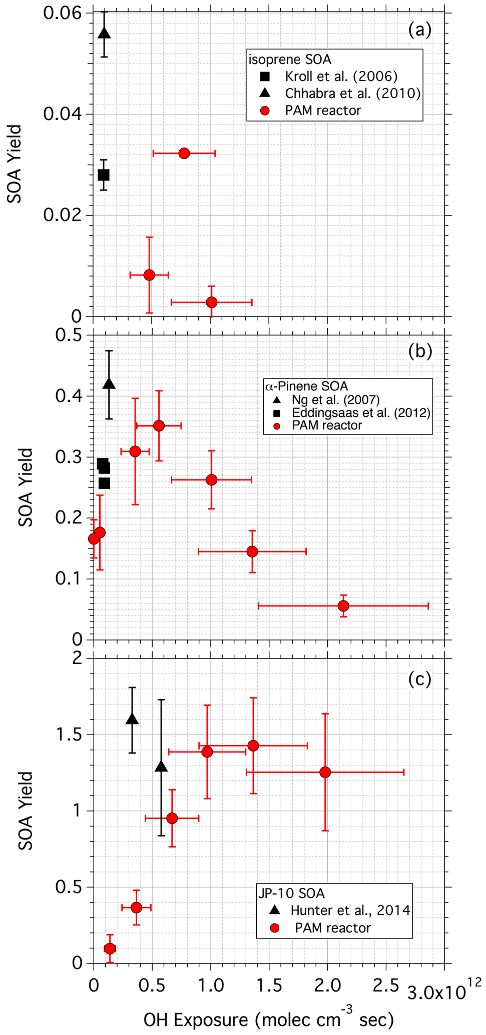


**Figure 5.** Yields of SOA produced from photoxidation of **(a)** isoprene, **(b)** α-pinene, and **(c)** tetracyclo[5.2.1.$0^{2,6}$]decane (JP-10) in environmental chambers and PAM reactor as a function of OH exposure. Error bars indicate ±1σ uncertainty in binned **SOA yield** measurements **and ±34% uncertainty in OH exposure values (Li et al., 2015)**. Black markers indicate data from **Kroll et al. (2006),** Chhabra et al. (2010), Eddingsaas et al. (2012), and Ng et al. (2007) obtained in the Caltech chamber and data from Hunter et al. (2014) ~~was~~ obtained in the MIT chamber.

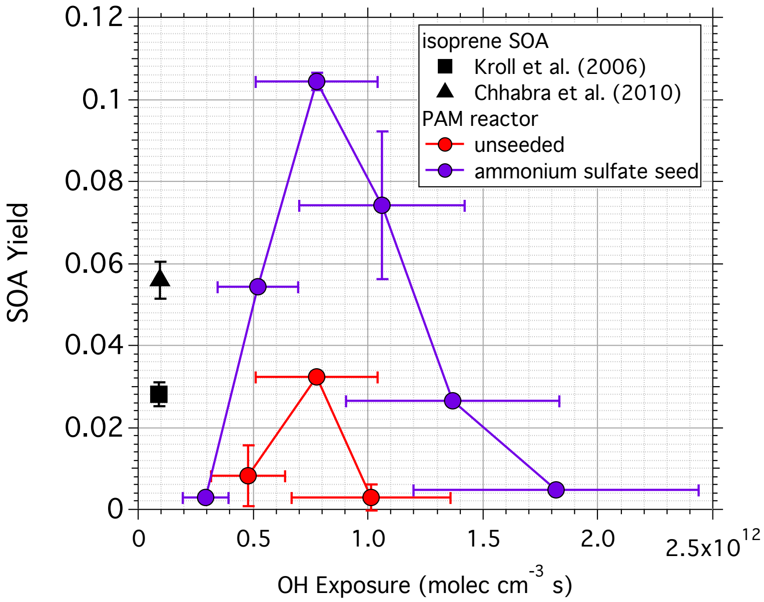


**Figure 6.** Yields of SOA produced from photoxidation of isoprene in the PAM reactor as a function of OH exposure in the presence of 20 µg m$^{-3}$ ammonium sulfate seed. Error bars indicate ±1σ uncertainty in binned **SOA yield** measurements **and ±34% uncertainty in OH exposure values (Li et al., 2015).**

8) Table 1 and Figs 1-4 show that 8 different compounds were studied, however the yields are only discussed for 3 compounds. Why? Given that the yield results will likely be of the most interest to the community from this study, it would seem useful to discuss those results. This would give a better sense of the variability in the agreement/disagreement and provide better support for any generalizations and conclusions. As is, a reader quickly skimming the abstract and figures will assume that the yield conclusions broadly apply to the relatively wide range of compounds studied, which in current form is not supported in the manuscript.

**Response**. The yield conclusions apply to the rest of the compounds that were studied; thus, to simplify the presentation we focused on a representative subset that covered a range of different SOA yield values (isoprene SOA = low; α-pinene SOA = midrange; JP-10 SOA = high). We have revised the text to clarify this point (**changes bolded**):

P30587, L21-23: "SOA yields at comparable OH exposures are lower in the flow reactor than in chambers, whereas the mass spectra, O/C and H/C of SOA generated in the chambers and flow reactor are similar (Figs. 2–4). **Flow reactor SOA yields are also lower in the flow reactor than in chambers for the other precursors studied that are not shown in Figure 5.**"

9) OA concentrations have a major effect on SOA yields (as the authors point out as background in Sect. 3.4). However, the OA concentrations in the PAM vs chamber experiments in Fig 5 are not discussed in terms of their effect on the measured SOA yields. At least some of the chamber studies report OA-dependent yields, and the chamber yields should be corrected to the same OA concentrations observed in the flow reactor experiments.

    **Response**. This is a fair point but in practice is difficult to identify overlap in OH exposure, precursor concentration reacted, and OA concentration. Our presentation in Figure 5 reflects the best overlap we could achieve. In our opinion even if it were possible to correct to the same OA concentration it would not alter the main conclusions of the figure and related discussion.

10) We suggest that Fig 7 should be plotted vs seed surface area, rather than mass, since condensation to seed aerosol or reactive uptake to an acidic seed aerosol would likely be a surface area-limited process.

    **Response**. This is a good suggestion that we cannot readily implement for the sulfuric acid experiments. To obtain as many yield measurements as possible, the isoprene mixing ratio input to the PAM reactor was kept constant while varying the $SO_2$ mixing ratio in order to vary the sulfuric acid concentration. Characterization of the $H_2SO_4$ surface area at each condition would necessitate separate measurements of the sulfuric acid size distribution in the absence of isoprene SOA, which are not available. This would further require making the assumption that isoprene oxidation products do not interact with sulfuric acid vapor in the formation of new particles, which may not be the case.

11) Furthermore, it seems from the manuscript that the sulfuric acid ($H_2SO_4$) seed aerosol was produced by oxidation of $SO_2$ concurrent to isoprene oxidation in the flow reactor, in contrast to the atomized ammonium sulfate seed. Nucleation and atomization likely produced very different size distributions and thus very different surface area/mass ratios, potentially affecting the yields of SOA from isoprene. Also the size distribution in the nucleation experiments may lead to a significant fraction of SOA mass being too small to be measured by the AMS. The SMPS measurements from these experiments may help answer these questions.

    **Response**. The SMPS mode volume-weighted diameter ranged from 122 to 217 nm in ammonium sulfate experiments and ranged from 195 to 241 nm in $H_2SO_4$ experiments. The AMS aerodynamic lens transmits particles with aerodynamic diameters ranging from about 60 to 600 nm with 100% efficiency, suggesting that most (if not all) of the mass is detected in the AMS. We added the following information to the text:

    **P30589-P30590, L26-4**: "At an OH exposure of $7.8 \times 10^{11}$ molec $cm^{-3}$ s and a sulfate seed particle concentrations of 20 $\mu g\ m^{-3}$, the yield of isoprene SOA increases from 0.032 to approximately 0.14 in the presence of ammonium sulfate seeds and 0.25 in the presence of sulfuric acid seeds. **SMPS size distributions of the mixed particles suggest that most of the particle mass is measured by the AMS (Jayne et al., 2000).** Increasing the seed particle concentration led to a continued increase in the yield, along with a decrease in the O/C ratio of the SOA as condensation of less-oxidized products was enhanced."

    The following citation was added to References:

J. T. Jayne, D. C. Leard, X. Zhang, P. Davidovits, K. A. Smith, C. E. Kolb, and D. R. Worsnop, Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles, Aerosol Science and Technology, 33, 49-70, 2000.

12) Comparison of the mass spectra in Fig 2 is very unclear. Larger log-log scatterplots, difference plots, or uncentered $R^2$ (Ulbrich et al., 2009) may be more useful. This topic was also alluded to by both referees.

    **Response.** Please see our response to Comment #2 raised by Referee #2.

13) Particle wall losses in the reactor are quoted as 32% +/-15%. This is much higher than in our experience, where these losses are typically 5% in mass, when using an aluminum wall chamber. We observed losses of ~30% when using a glass cylindrical chamber as used in this study. As reported in Ortega et al., (2013), we believe the increased loss is due to nearly complete loss of charged particles to walls made of insulating material such as glass, Pyrex, or Teflon. In addition, very different charged-particle loss corrections need to be used when generating (charged) particles from an atomizer or (uncharged) particles by nucleation. Freshly atomized particles tend to be highly charged leading to even higher losses, and this effect can be reduced by passing the particles through a sufficiently potent radioactive neutralizer. It should be stated whether such neutralization was done or not in this study, so that it can help compare the likely particle losses in the experiments reported here with other studies. We suggest that the authors discuss these issues in some detail, as otherwise other groups may not be aware of the difference and apply the wrong loss correction in the future, thus significantly over or underestimating these effects.

    **Response**. Atomized particles were not passed through a radioactive neutralizer. We revised the text to indicate this (changes bolded):

    **P30582, L9-L11**: "The particles were dried and introduced continuously into the flow reactor along with the gas-phase SOA precursor **without radioactive charge neutralization."**

14) Page 30588, lines 4-12. The authors briefly discuss the time required for condensation, noting timescales of 2000-20,000 seconds, while the residence time in the reactor is 100 s. If those timescales represent e-fold timescales, that would suggest only 0.5-5% of the condensable products would condense in the reactor, rendering the PAM useless without large seed surface areas, which is clearly not the case. For example, if the isoprene yield was corrected by that condensation efficiency, SOA yields of ~60-600% would be implied. A more detailed discussion (including explicit calculation of the condensation timescales) is needed.

    **Response**. We modified the text as follows (changes bolded).

    "One reason for the lower SOA yield in flow reactors may be the relative timescales for oxidation in the gas-phase vs. condensation onto pre-existing aerosols. **The timescale for condensation of a gas-phase molecule onto pre-existing seed particles ($\tau_{cond}$) can be calculated using Equation 1 (Seinfeld and Pandis, 2006):**

$$\tau_{cond} = \frac{1}{\alpha * A_p}\sqrt{\frac{2\pi M_W}{k_B T}} \quad [1]$$

**Where $M_w$ is the molecular weight of the condensing species, $\alpha$ is the mass accommodation coefficient, and $A_p$ is the particle surface area**. For example, over a representative range of particle surface area concentrations used in the flow reactor (10 to 100 μm$^2$ cm$^{-3}$), condensation timescales range from approximately 2000 to 20000 s assuming a mass accommodation coefficient of 0.1 (**α-pinene ozonolysis SOA;** Saleh et al., 2013) and an average SOA molecular weight of 150 g mol$^{-1}$. **A lower limit of $\tau_{cond}$ = 200 to 2000 s is calculated over the same range of $A_p$ assuming $\alpha$ = 1.** While our measurements do not constrain the mass accommodation coefficient, these timescales suggest that the residence time in the flow reactor (100 s) may not be adequate to allow complete condensation of semivolatile organic gas-phase species into SOA**, whereas residence times in environmental chamber experiments are typically 10000 sec or longer**."

We would like to reiterate that we did not constrain the mass accommodation coefficient in our measurements. As noted in the revised text, the $\alpha = 0.1$ result reported by Saleh et al. (2013) corresponds to α-pinene ozonolysis SOA; no literature values of accommodation coefficients for isoprene SOA are available, so this accommodation coefficient may or may not be representative of isoprene oxidation products.

The following citation has been added to references:

Seinfeld J. H. and Pandis S. N., Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 2nd edition, J. Wiley, New York, 2006.

15) Seed experiments were shown only for isoprene, which is the only compound with evidence for lower yields in PAM compared to a chamber experiment. However, the authors conclude at the end of Sect. 3.5 "these measurements suggest seed particles are required in flow reactor measurements in order to more closely simulate condensation conditions in environmental chambers." Such a general statement is not supported and should be modified accordingly.

**Response**. We revised the text as follows (changes bolded):

**P30590, L10-12**: "These measurements suggest seed particles are required in flow reactor measurements **of isoprene SOA (and potentially other types of SOA as well)** in order to more closely simulate condensation conditions in environmental chambers."