**Response to reviewers for the paper "Real-time measurements of secondary organic aerosol formation and aging from ambient air in an oxidation flow reactor in the Los Angeles area." – A. Ortega et al. ACPD, 15, 21907–21958, 2015**

We thank the reviewers for their comments on our paper. To guide the review process we have copied the reviewer comments in black text. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper (**in bold text**).

**Anonymous Referee #1**

R1.0. The authors report a study investigating the aging of ambient air masses using an oxidation flow reactor. By exposing the samples in real-time to high OH exposures, they replicate the equivalent oxidative aging of 0.8 days to 6 weeks. A clear day/night cycle is observed in the enhancement of organic aerosol formation, attributed to the depletion of short-lived VOC precursors during daytime photo-oxidation. High reactor exposures were associated with a decrease in the SOA formation enhancement as heterogeneous oxidation leading to fragmentation and evaporation becomes dominant. The study highlights the advantages and insights that may be made by application of traditionally laboratory-based instrumentation to a field campaign, which may provide crucial measurements to help constrain model predictions of SOA formation. The scope of the study is fully appropriate for publication in ACP.

Overall the manuscript is well-written and insightful. The following comments should be addressed to improve the clarity of the manuscript.

R1.1. The authors should make the outlet configuration in the text (p21915 lines 1-4) and in the experimental schematic clearer. How narrow is the residence time distribution using this method? Have the "plug-flow" conditions been verified, either experimentally or using fluid dynamics simulations?

The use of "plug flow" was not accurate, what we meant to say is that the residence time distribution should be narrower when the inlet plate is removed. We have rephrased this text to clarify these issues, and also added results of CFD simulations, as:

**"The configuration with the large inlet strongly reduces recirculation in the reactor and narrows the residence time distribution (RTD) (Fig. S1). To further reduce the width of the RTD, output flow was sampled from both a central stainless steel 1/4 inch OD tube at 2.0 L $min^{-1}$ for aerosol measurements and a 3/8 inch OD PTFE Teflon perforated ring with 14 cm diameter for gas-phase measurements at 2.4 L $min^{-1}$. In addition, Peng et al. (2015) has shown that variations in the residence time distribution in the OFR had limited impact on the estimated $OH_{exp}$."**

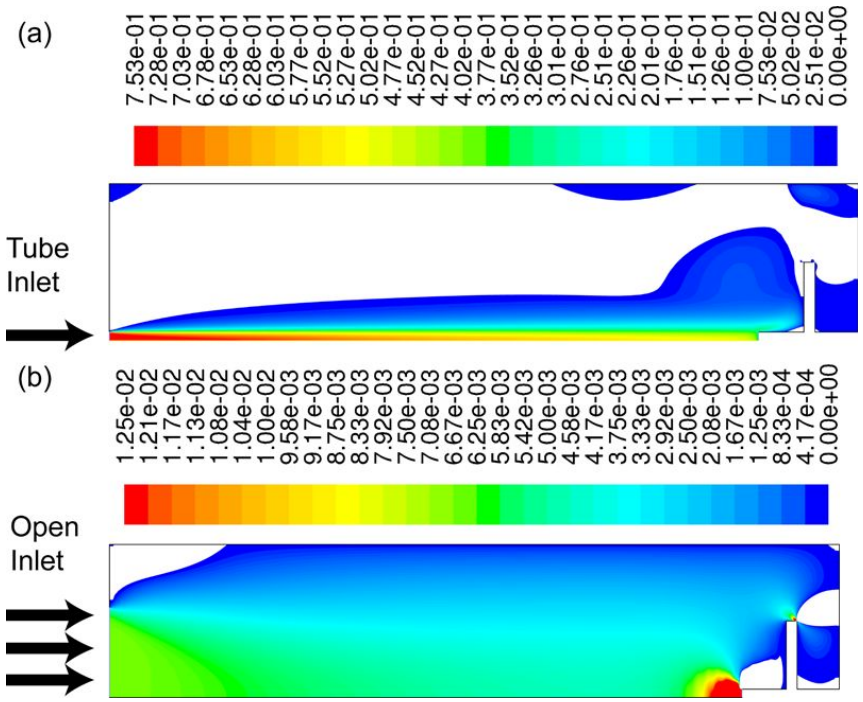



**Figure S1. Results of computerized fluid dynamics (CFD) simulations comparing two OFR configurations. (a) Tube inlet, similar to Lambe et al. (2011); (b) Large open face inlet (11.9 cm diameter) as used in this field study. Colors are contours of positive horizontal velocity. White regions involve negative horizontal velocities, i.e. recirculation regions. The extensive recirculation regions of case (a) are almost completely removed in case (b), resulting in a narrower residence time distribution. Simulations were conducted using the FLUENT software, using cylindrical symmetry, with air at 1 atm and 293 K.**

R1.2. Explain in more detail the particle loss correction. For instance, what does a “time varying way” mean in the context of applying the correction? A figure in the SI showing the uncorrected mass concentrations from the ambient and reactor sampling lines would help clarify. Further, might the temperature changes in the reactor with the lights on influence wall losses? Any temperature perturbation in the chamber should be reported.

The text describing the particle loss correction has been expanded to read:

**“To correct for the effect of particle losses we compared concentrations measured in the reactor output when UV lights are turned off with those measured through the ambient inlet. The loss of particle mass in this aluminum reactor is small, of the order of a few percent of the ambient concentrations (see also Palm et al., 2016). Losses in an OFR with a quartz body were observed to be ~35% in a previous study (presumably due to nearly complete loss of charged particles), which led to our use of the all-aluminum reactor. A time-dependent correction factor was estimated by comparing each reactor output measurement (for each period when the lights were off) with the average of the two ambient measurements immediately before and after. This correction is interpolated in**

**time and applied to all reactor output measurements with lights on. The resulting average correction was +5.8 %. Although losses may have some size dependence, given the broad distributions covering the same size ranges for both ambient air and OFR output, and the small magnitude of the correction, this effect has not been considered in detail."**

This correction seems too small and simple to warrant another supplementary figure.

We have added the following text to P21915/L18 to describe the second question:

**"The lights are housed in Teflon sleeves which are purged with $N_2$ gas to remove heat and avoid exposing the lamp surfaces to $O_3$ or other oxidants. When operated at full power the lights result in an increase of ~2°C above ambient conditions. Given the low volatility of ambient OA (Huffman et al., 2009; see also Fig. S12 in this paper and associated discussion below), very little OA evaporation is expected in the reactor due to this heating."**

R1.3. It seems the OH exposure is established in part by assuming the reactivity of the constituents. I'd be interested to see how an appropriate uncertainty placed on the assumed rate constant influences the inferred OH exposure.

OH exposure is calculated using a retrieval in which ambient OH reactivity is an input, as detailed in Li et al., (2015). During CalNex, an ambient direct measurement of total OH reactivity by the Stevens Group at the Indiana University was available, as stated on P21916/L9 of the ACPD manuscript. In this method, there is no assumption about the rate constants of different constituents. Other estimates of OH reactivity were available for the campaign, such as OH reactivity based on VOC measurements, but those values were not used due to the assumptions the reviewer highlights would be required. The following text has been modified to clarify this point:

**"The equation uses ambient $H_2O$ concentration, reactor output $O_3$ concentrations, residence time, and ambient OH reactivity from collocated measurements (total OH reactivity data measurement from the Stevens Group, Indiana University; in this method there is no assumption about the rate constants of different constituents)."**

R1.4. In section 2.4, the possible reasons for underestimating SOA are discussed, all consequences of the short residence time and high oxidant concentration – (ambient) aerosol condensation, wall condensation, further reaction with OH, or reactor exit. The discussion that follows on the correction for these is unclear. Is all loss of SVOC by condensation onto aerosol, rather than formation of SOA, corrected? For example, at an exposure of $10^{12}$ (note units on x-axis of figure S6), approximately half of the SVOC is lost by condensation onto aerosol. Thus, dividing by this gives a correction of a factor 2×, much larger than the 1.2× reported. There is some confusion here that should be made clear.

We are confused by the reviewer's question "Is all loss of SVOC by condensation onto aerosol, rather than formation of SOA, corrected?", since condensation onto aerosol and SOA formation are the same thing.

The following text is added to P21918/L9 to clarify:

**"The analyses leading to the correction terms were developed in Palm et al. (2016) and are applied here. As Palm et al. (2016) is now published in final form in ACP, we refer readers to that manuscript for the full details of the method."**

The magnitude of the correction is different at different $OH_{exp}$. The factor of x1.2 applies at the point of maximum SOA production, while larger corrections apply at higher ages. We have modified this text to give typical values as:

**"At $OH_{exp}$ lower than $1\times10^{12}$ molec $cm^{-3}$ s (~ 10 days) the dominant LVOC fate (50-75%) is condensation to the aerosol (see Fig. S7). At higher $OH_{exp}$, the fate of organic gases is dominated (>45%) by loss to reaction with OH rather than condensing on aerosol. LVOC lost to the walls (~7%) or exiting the reactor (~2%) play only small roles under the conditions of this study, due to the relatively high ambient aerosol surface area."**

R1.5. In Figure 3, the pie charts display average fractions – are these averages over the whole sampling period or just for the time shown in panel b? Why are the inorganic components enhanced in the reactor relative to ambient (nitrate in particular)? Does this suggest NOx chemistry in the reactor? Does this distribution change as a function of exposure in the reactor?

The pie charts are made from all data in panel (a), and this has been clarified in the figure caption. As stated in the figure caption the reactor data excludes dark reactor, "lights off" periods. I.e. periods are included only if $OH_{exp}$ > ambient. We have added the following text for clarification on P21920/L1:

**"The fact that the inorganic components are enhanced in the reactor is not surprising but expected. $SO_2$ and $NO_x$ in ambient air are expected to be oxidized to $H_2SO_4$ and $HNO_3$ by the OH in the reactor, and can then condense onto the aerosols (together with ambient $NH_3$ for $HNO_3$). See e.g. Kang et al. (2007) and Li et al. (2015) for further details."**

R1.6. The discussion of Ox species suggests the enhancement is brought about due to there being less Ox (as stated in reference to the "steep inverse relationship"). Ox results from photochemistry, and SOA result from photochemistry. It should be made clearer than Ox as discussed here is a proxy for ambient photochemistry, and that Ox itself is not playing a role in the reactor (unless I've misinterpreted the discussion, in which case I recommend clarifying it). Also, the plot in Figure 5 needs appropriate error bars.

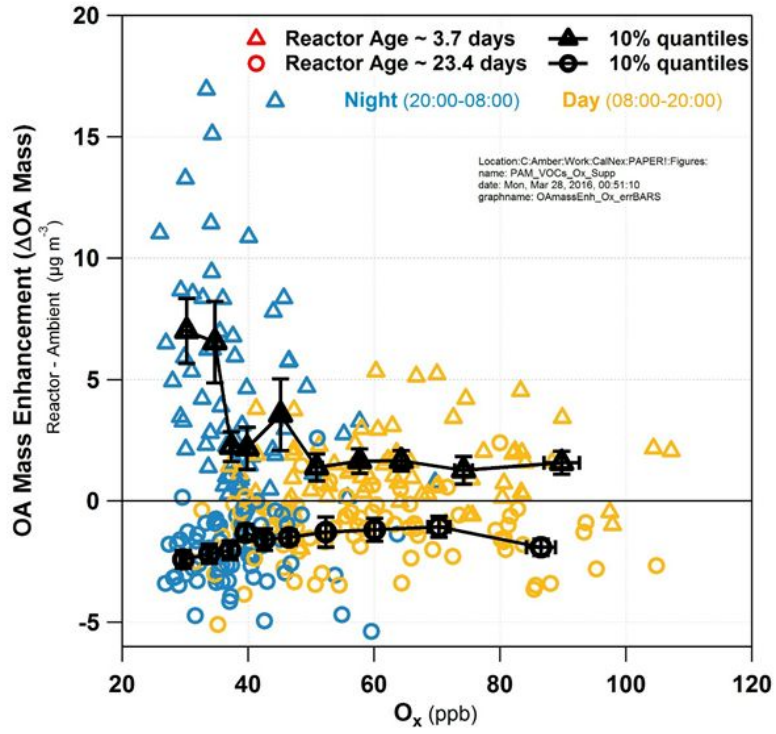
The reviewer's interpretation is correct. We note that the ACPD text reads (P21922/L7) "oxidants are generated internally and are not dependent on ambient Ox." To clarify the discussion, the following text has been added to P21922/L14:

”**As ambient $O_x$ is not itself playing a role in reactor aging, but rather is a proxy for ambient photochemistry, these results further confirm that as the degree of ambient photochemical processing of the sampled air increases (during daytime), […]**”.

We have also added the following text to the caption of Figure 5:

“**Note that ambient $O_x$ is not itself playing a role in reactor aging, but rather is a proxy for ambient photochemistry.**”

Figure 5 has been updated with standard error bars for the quantiles and noted in the figure caption. The updated figure is shown below:




R1.7. Please clarify line 14, starting “At the same…” on page 21925.

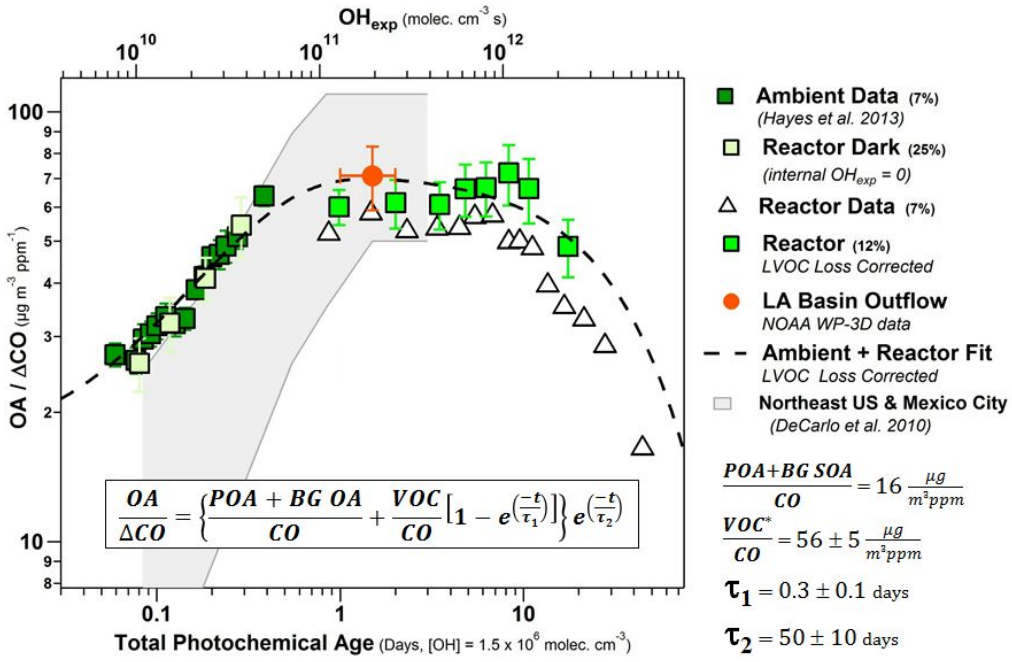
We have modified the text to include an example for clarity (P21925/L14) as:

**“At the same OH exposure, i.e. 8 days, higher $OS_C$ is observed (~1) for conditions of high reactor SOA production ($ER_{OA}$~2) compared to no net SOA production ($ER_{OA}$~1, $OS_C$~0).”**

R1.8. In Figure 9, the reactor data with wall loss correction and without are binned differently, and the uncorrected data spans a wider range on the x-axis. Why is this?

We note that, as stated in the legend and caption of the figure in the ACPD version,the figure is not “wall loss corrected”, but rather “vapor loss corrected” per the discussion in Section 2.4. We

have updated the figure legend and caption to say **"LVOC loss corrected"** to avoid confusion. The updated figure is reproduced below:




As discussed in Section 2.4 of the ACPD version, we state the LVOC loss correction cannot be applied when reactor OA is less than ambient OA. The range of LVOC loss-corrected data is thus smaller due to this fact. The number of bins was chosen to best illustrate trends of the data while not allowing too high an influence of noise, which is observed for high bin numbers. We have added the following text to the figure caption to avoid confusion:

**"Note that the LVOC loss correction can only be applied when reactor output OA is larger than ambient OA, which reduces the number of datapoints."**

R1.9. The errors bars used throughout do not appear to be representative of the variance in the data. Given that you are reporting on a single sample population, the standard deviation, rather than the standard error, is more appropriate.

The standard error is used when presenting quantile averages of data. For each quantile we calculate the average of the X and Y data in that bin. The quantity of most interest is how well those averages are known, i.e. the standard error. The full variability of the data can be seen from the full 2.5 min dataset in several figures (e.g. Fig. 4, 5, 12). Showing the standard deviation as another measure of the full variability of the data would be redundant, would clutter the figures, and would prevent showing the more relevant quantity. We have double-checked that the error bars are clearly explained as standard errors in all the relevant plots.

R1.10. On page 21930 line 20, a diameter of 285 nm is reported as the volume averaged value. From Figure S7, the average looks like it should be closer to 500nm. Please check this and

clarify any difference. Furthermore, for estimating the OH surface flux, the surface-weighted diameter should be used. How different are these values?

Perhaps the reviewer is confusing the two different diameters ($d_{va}$ and $d_{ve}$), which are clearly discussed in the main text and in the caption and X-axis label of Figure S8. To avoid confusion, the manuscript text has been updated with a reference to the key paper describing their relationship, as:

**"Heterogeneous oxidation calculations use surface-weighted diameter calculated from the peak of the mass distribution and estimated particle density from AMS components (DeCarlo et al., 2004) [...]."**

With a typical material density of 1.45 g $cm^{-3}$ estimated from the composition of this study, $d_{va}$ ~ density * $d_{ve}$ ~ 415 nm.

The value used in the calculation is an average of all size distribution observations, while only a subset of those is shown in (now) Figure S8 for clarity.

We have modified the calculation using the surface-weighted average diameter, with the results discussed in response to comment R3.9 below.

**Anonymous Referee #2**

R2.0. The authors present results from an experimental study in which the aging of ambient air is oxidized using a PAM reactor. This paper demonstrates of the PAM reactor as a tool evaluation of SOA formation during field studies. The study and the manuscript are well organized and documented and I recommend for publication. However, I have several comments (most minor and for my own curiosity) before this manuscript can be accepted for publication in Atmospheric Chemistry and Physics.

**Questions:**

Experimental Methods

R2.1. Page 21914: Line 10: The PAM reactor operates similar to a batch reactor giving you the spatial average of oxidized particles rather than with a traditional flow-tube you have particles with the same oxidative lifetime. Do you expect this to affect your results?

We are confused by this comment. The OFR (PAM reactor), at least as used in this study as described in the methods section, was used as a flow reactor with a short residence time. Thus its output corresponds to the processing of the air present at a given time at the field site, and not to a "spatial average." The relevant text of the methods section in the ACPD version is:

- (P21914/L15): "Ambient air was continuously sampled in an open flow-through configuration via a 14 cm diameter opening with coarse-grid mesh screen coated with an inert silicon coating (Sulfinert by SilcoTek, Bellefonte, PA)."
- (P21915/L6) "The total flow rate through the reactor was 4.4 L $min^{-1}$ corresponding to a residence time of 3 min."
- (P21915/L19): "Oxidant concentrations in the reactor were stepped in 20 min intervals, through six levels (including lights off, i.e. no added oxidants) comprising a two-hour cycle (Fig. 2). Only data from the last five minutes of each 20 min period are used, to avoid including reactor transient periods."
- (P21916/L4): "$OH_{exp}$ was estimated using a calibration equation developed by multivariate fitting of the output from a kinetic model of reactor (OFR185) operation, and verified against data from several field and laboratory experiments including CalNex (Li et al., 2015)"

Thus it is clear from the text already in the manuscript that the PAM is used here as a flow reactor and not a batch reactor. The use of a large inlet opening was also designed to narrow the residence time distribution, and this is a difference with how the reactor is run in laboratory studies.

See also the response to comment R1.1.

R2.2. Page 21914; Line 10: How long does it take the PAM reactor to reach equilibrium, in other words how long does the reactor need in order for complete replacement of particles? (I think this is 20 minutes if so please make it clearer in the text)

As stated in P21915/L6 of the ACPD version: "The total flow rate through the reactor was 4.4 L $min^{-1}$ corresponding to a residence time of 3 min." and (P21915/L19): "Oxidant concentrations in the reactor were stepped in 20 min intervals [...]. Only data from the last five minutes of each 20 min period are used, to avoid including reactor transient periods."

We have added the following text at that point to further clarify this issue:

**"Thus, five full residence times have elapsed after changes to the UV lights and before starting to sample reactor outputs, to allow full replacement of the contents of the reactor."**

See also response to R2.1, as well as Figure 2 in the ACPD manuscript.

R2.3. Page 21914; Line 10: Since the output of your photolysis lamps are 254 nm do you expect any significant photo-degradgation from any of your organic species of interest? Do you expect any of these reactions to lead to SOA formation?

The possibility of photolysis of gases or aerosols under the light conditions of the flow reactor during our specific study has been reported by Peng et al. (2016), which was submitted to ACPD shortly after this paper and is now published in final form in ACP. We have added the following text to summarize their findings at P21915/L13:

**"Peng et al. (2015) have investigated the possibility of photolysis of gases and aerosol species under the OFR conditions. OH reaction dominated the fate of all gases studied. Under most conditions in this study, photolysis was estimated to be responsible for only several percent of the fractional destruction of the gas-phase primary species most susceptible to it (aromatic species) even if photolysis quantum yield was assumed to be 1. The upper limit of the fractional destruction of possible oxidation intermediates was ~x2 that of primary species. Photolysis of SOA already present in the atmosphere may have played some role at the medium and high UV settings studied here when assuming upper limit quantum yields. However, photolysis e-fold decays in the reactor are estimated to be orders-of-magnitude lower than for the atmosphere for equivalent OH exposures."**

R2.4. Page 21915; Line 11: Do you expect loss of your compounds to be from ozonolysis rather than OH given that $O_3$ is being used as the precursor for OH? Were any experiments performed using HOOH? Were blank experiments performed to make sure there was not loss from photochemistry?

The reviewer may be confusing our experimental method (in which $O_3$ is NOT added to the reactor) with the method used in other applications of the PAM reactor, in which $O_3$ is added to

the reactor as the OH precursor. This was discussed in the experimental section, although perhaps not clearly enough. We have clarified the text on P21915/L7 to read:

**"The reactor was used to expose ambient air to high levels of OH and $O_3$, produced when UV light from two low-pressure mercury lamps (model no. 82-9304-03, BHK Inc., with discrete emission peaks at 254 and 185 nm) initiated $O_2$, $H_2O$ and $O_3$ photochemistry. This mode of operation is referred to as OFR185, and OH is formed from both $H_2O$ and $O_3$ photolysis (Li et al., 2015). In this mode, $O_3$ is formed in the reactor but is not added to the reactor, contrary to the OFR254 mode that has been used mainly in laboratory studies (Peng et al., 2015). Given that most known urban SOA precursors do not react with $O_3$ (e.g. Hayes et al., 2015), we expect OH to dominate the observed SOA formation. Consistent with this, no SOA was formed in test experiments during CalNex when ambient air was exposed to $O_3$ only without OH."**

To avoid the possibility of contamination and the possibility of incomplete mixing, we prefer to not add anything other than ambient air and UV light to the reactor, whenever possible. We have not explored using HOOH as an OH precursor, but that is not necessary given that high OH concentrations can be produced from ambient $H_2O$ photolysis and from the photolysis of $O_3$ formed in the reactor.

R2.5. Page 21916; Line 1: Is there a reason a gas-phase tracer (for example hexane) was not used to monitor your OH concentrations? This seems like it would be a more accurate method of quantification.

Using a gas-phase tracer is easy in a laboratory setting, but more difficult when adding to ambient air with a large inlet as used here. We have done so successfully on later field deployments, e.g. adding CO during the SOAS 2013 field study (Li et al., 2015), but during this initial field deployment of the reactor such a tracer delivery and detection system was not available.

It is actually preferable to use the decay of species already present in ambient air, which removes the need to mix a flow of the tracer species, thus diluting the ambient air and creating the possibility of contamination and additional leaks, as well as additional cost and complexity. During CalNex we used ambient $SO_2$ measured before and after the reactor to quantify $OH_{exp}$. This was only possible during periods of higher $SO_2$ concentrations (> 1 ppbv). The model-based $OH_{exp}$ estimation equation was fit to the $SO_2$ decay data from CalNex as well as to data from other studies, and used to estimate $OH_{exp}$ in our study. To clarify this detail we have revised the text on P21916/L4 to read:

**"$OH_{exp}$ was estimated using an equation developed by multivariate fitting of the output from a kinetic model of reactor (OFR185) operation, and verified against data from several field and laboratory experiments (Li et al., 2015). Data from the decay of ambient $SO_2$ in the OFR during CalNex, which was only reliable during periods with higher**

**ambient $SO_2$ concentrations (> 1 ppbv), was used to verify the $OH_{exp}$ estimation equation."**

R2.6. Page 21917; Line 15: Is there a reason why SVOC is not discussed in this manuscript? If there is could you please explain some of the issues of quantification of these species? (I assumed this will be a topic of an additional paper but this question is more out of curiosity)

Primary SVOC as precursors of the SOA observed to form in the OFR are discussed in the paper, see section 4.3 and Figure 10 (Fig. 11 in the revised version).

The formation of secondary SVOC in the reactor and their condensation to form SOA are not explicitly considered for several reasons. We have revised the text in P21917/L15 to clarify this point:

**"Semivolatile organic compounds (SVOC) will also be formed, but we focus this discussion on LVOC for several reasons. As shown in Figure S12 (discussed in Section 4.4), the volatility distribution of the SOA present during CalNex shows very limited importance of SVOCs as SOA constituents. Second, discussion and modeling of LVOC fate in the reactor is conceptually simpler. Third, the amount of SOA formed in the reactor is significantly higher than can be explained by the speciated precursors, consistent with other studies (Palm et al., 2016). The assumption of LVOCs results in higher SOA formation than if SVOC were assumed, and is thus a the most conservative assumption in terms of closure of measured vs. predicted SOA. Thus adding complexity to the loss model for species that are likely of limited importance was not a priority for our study."**

R2.7. Page 21918; Line 13: How much loss of LVOC did you measure on the walls or exiting the reactor? What is the percentage of wall loss?

In this study, LVOCs were not measured directly, as instruments such as CIMS were not available to us at the time. To clarify this detail, we have modified the manuscript (P21917/L26) to read:

**"To account for vapor losses, we follow the modeling method detailed in Palm et al. (2016)..."**

See also response to R1.5.

R2.8. Page 21918; Line 15: What are the rough percentages of LVOC fate of each pathway (condensation, wall loss, fragmentation) in each OH concentration regime (low, medium, high)?

See responses to R1.5 and R2.7.

Observations

R2.9. Page 21919; Line 5: It is explained later in the paper but it would help orient the reader if a brief discussion of the type of ambient precursors you might expect at your location?

We have added the following text to P21919/L9 to clarify this point:

**"The precursors that are expected to be important contributors to SOA at this location include aromatic VOCs and semivolatile and intermediate volatility species (mostly alkanes and aromatics), with low importance for biogenic species (Hayes et al., 2015)."**

R2.10. Page 21919; Line 25: What type of precursors for SOA do you expect to be depleted in the ambient air?

See response to R2.9, as well as sections 3.3.2 and 4.3 in the manuscript. We feel that repeating some additional details here would be confusing.

R2.11. Page 21920; Line 28: Could the loss of OA be due to the high OH concentrations that are forcing chemistry through channels that don't typically exist (ie, RO2 + RO2 chemistry)? How much of this OA loss do you expect to be through this pathway? (Reason I asked for rough percentages above).

We have investigated in detail some of the pathways that could lead to deviations between OFR chemistry and that relevant to the ambient atmosphere. The pathway that comes closest to playing a role in the OFR chemistry in this study, while still being of minor importance, is photolysis, as discussed in the response to R2.3 above.

Modeling results (unpublished) indicate that $RO_2$+$RO_2$ chemistry is typically unimportant in the reactor under the conditions of this study. $HO_2$ concentrations are also greatly enhanced in the reactor (Li et al., 2015) and the rate constants of its reactions with $RO_2$ are orders-of-magnitude higher than those of $RO_2$+$RO_2$. As a result, $RO_2$+$HO_2$ is faster than $RO_2$+$RO_2$ under most OFR conditions, and the main reaction channel of $RO_2$ is $RO_2$ + $HO_2$.

General Questions:

R2.12. Was NOx measured and if so was there any effect you would expect in SOA formation?

Ambient $NO_x$ was measured, but it was not measured after the reactor. Previously published results (Li et al., 2015) indicate that $NO_x$ is converted to $HNO_3$ very rapidly in the reactor. Thus it is not expected to play an important role in our results.

Figures:

R2.13. Page 21948: Please add part c to the figure which is a picture of the sampling site.

We have added the following picture of the sampling site as requested:

And added the following text to the caption of Figure 1:

**"(c) Photograph of the sampling site showing the different trailers and inlets. The OFR can be seen on top of the leftmost trailer, next to the AMS and SMPS ambient inlets."**

R2.14. Page 21949: What is the error in the concentration of O3 and OH in the reactor?

We have added the following text to P21914/L24:

**"The uncertainty in the $O_3$ measurement is +/- 1.5 ppb or 2% of the measurement, whichever is greater."**

We have added the following text to P21916/L12:

**"The uncertainty in the calculated $OH_{exp}$ is estimated to be a factor of 3 (Li et al., 2015; Peng et al., 2015)."**

R2.15. Page 21950: The differences in the reactor and ambient colors are really difficult to see. Is there a way that you could make this clearer?

We agree that this is a difficult figure, which is why the zoomed version in Figure 3b is essential. We have tried this figure with dashed lines for the reactor output as well as other alternatives, but they only complicated the visual appearance of this figure. As the five AMS species observed are the same for ambient and the reactor, and those colors are standardized within

the AMS community (and much of the larger community), showing the reactor in a lighter shade was the most intuitive option.

R2.16. Page 21951: Please explain where the error bars come from and whether they are 1s or 2s? Please put in the caption.

The figure caption already states “... with vertical error bars indicating standard errors.” Standard errors are a standard statistical metric, and are understood to be 1σ. Thus we feel that this is already clear enough. See also response to R1.9.

**Anonymous Referee #3**

R3.0. Ortega et al. report measurements of secondary organic aerosol generated by OH oxidation of ambient urban emissions in a PAM oxidation flow reactor during the CalNEX campaign. An aerosol mass spectrometer was used along with a scanning mobility particle sizer to obtain mass spectra, elemental ratios, and aerosol size distributions of the SOA. Selected VOCs were detected with a proton-transfer reaction mass spectrometer. The authors characterize organic aerosol enhancement factors as a function of OH exposure in the PAM reactor. The following results are obtained:

1. SOA formation peaks at an intermediate photochemical age in the reactor (~1-6 days' equivalent atmospheric OH exposure) prior to decreasing. This result is interpreted as a transition from functionalization- to fragmentation-dominated reactions.

2. SOA formation is largest during the nighttime. The authors interpret this result to suggest that the most SOA precursors have an atmospheric oxidation lifetime that is shorter than the source->receptor transit time (0.3 day) during the day, but not at night.

3. Campaign-average SOA oxidation state and Δ(SOA)/Δ(CO) emission factors are generally consistent with previous studies, although the magnitude and trend of observed Δ(SOA)/Δ(CO) emission factors is difficult to reproduce with conventional chemistry and transport models.

Overall, this manuscript addresses an important research topic regarding the characterization of ambient SOA formation and chemical evolution with oxidative aging. It demonstrates the unique capability of oxidation flow reactors to simulate in situ photochemical aging of air masses and complements previous studies through its application in an urban receptor location. I would support publication in Atmospheric Chemistry and Physics after incorporation of my comments below.

Main Comments

R3.1. P21914, L19-21: Please add data to the Supplement to support the claim that removal of the inlet plate reduces losses.

This text reads: "This configuration, with no inlet, was chosen because of the observation of reduced SOA formation when any inlet and/or an inlet plate was used in a previous experiment (Ortega et al., 2013)." The comparison of plate-on / plate-off SOA production was much easier to perform during the FLAME-3 study described in Ortega et al. (2013), as much higher concentrations of SOA precursors were maintained for several hours within a 3000 $m^3$ chamber. Thus the variations in SOA production were obvious and could be reproduced multiple times in a short period of time. In an ambient air study such as CalNex, SOA production is smaller, especially during the day when operators are typically present at the site, and the result of such short experiments is very noisy. Thus we have no direct evidence that this was true to CalNex,

but we did not state otherwise in the manuscript. We only stated that a decision was made to run without the plate because of the observations during FLAME-3.

R3.2. P21915, L1-4: Please add data (such as residence time distributions of tracer species) to the Supplement to support the claim that this flow configuration maintains plug flow characteristics.

See response to R1.1.

R3.3. P21915, L29: More information/clarification about the particle loss correction is needed. Specifically, it's not clear to me how the UV dependence to particle losses was determined if particle losses are measured with the lamps off. Also, shouldn't there be a size dependence to the magnitude of the particle losses?

The text "and accounting for variations in UV intensity" was erroneous and has been removed. We are not aware of any results or evidence that suggest that particle losses depend on UV light intensity.

See response to R1.2 for further details on the particle loss correction, including the size dependence.

R3.4. P21918, L3-4: "It is assumed that products after five oxidation steps with OH at kOH…." I found this sentence confusing. Couldn't you equivalently just state the OH exposure at which you assume that OH oxidation products no longer condense? For example, doesn't 5 oxidation lifetimes at kOH = $1*10^{-11}$ cm-3 molec sec correspond to an OH exposure of $5*10^{11}$ molec cm-3 sec? If so, the first sentence in the next paragraph states: "At OHexp lower than $1*10^{12}$ molec cm-3 sec … the dominant LVOC fate is condensation to the aerosol". While self-consistent, these two statements suggest a different OH exposure at which the transition to fragmentation-dominated reactions occurs (unless I am misinterpreting the method that is being applied). Please clarify.

5 oxidation lifetimes does approximately correspond to an $OH_{exp}$ ~ 5 x $10^{11}$ molec. $cm^{-3}$ s. However, because of the concatenation of exponential processes, at that $OH_{exp}$ only ~56% of the initial molecules have undergone the 5 generations of oxidation. After $OH_{exp}$ = $10^{12}$ molec. $cm^{-3}$ s, 97% of the initial molecules have undergone all 5 generations of oxidation. This explains the factor of 2 difference that the reviewer brings up. To clarify this point we have modified the text on P21918/L3 to read:

**"It is assumed that products after five consecutive oxidation steps with OH at $k_{OH}$ = $1\times10^{-11}$ molec $cm^{-3}$ $s^{-1}$ are lost (fragmented and too volatile to condense). We note that 56% (97%) of the initial molecules will have undergone five oxidation steps after an $OH_{exp}$= $5x10^{11}$ ($1x10^{12}$) molec. $cm^{-3}$ s."**

R3.5. P21918, L10-24: After reading this section, I found it difficult to come away with definitive conclusions about the relative importance of LVOC loss pathways as a function of OH

exposure. Figure S6 demonstrates the corrections that are used, but the information in this figure does not come across clearly in the text. I suggest moving this figure out of the supplement and into the main paper because it seems to be important for interpretation of results. Some suggested text to incorporate is provided below (paraphrase and update highlighted quantities as appropriate), which I think would make it clearer:

"The modeled fractional loss of LVOCs to condensation on pre-existing aerosols decreases from a maximum of 0.75 at OHexp = $1*10^{11}$ molec cm-3 sec to a minimum of 0.15 at OHexp = $1*10^{13}$ molec cm-3 sec. Over the OHexp range, the modeled fractional loss of LVOCs to gas-phase fragmentation reactions with OH increases from a minimum of 0.15 to a maximum of 0.83, and the fractional loss of LVOCs to the reactor walls and sampling line walls decreases from 0.10 to 0.02."

See the updated text in response to R2.7, which quotes the fraction of LVOCs undergoing the different fates, as also requested by reviewer #2.

We have considered moving Figure S6 from the supplementary information to the main paper as suggested. However, the primary paper describing those corrections was published recently in ACP (Palm et al., 2016), and thus we think it is more appropriate to refer readers to that publication for more detail, while documenting the application of the method to our study is suitable for the Supp. Info.

R3.6. P21919, L22-L24: I would be careful to avoid over-interpretation of a single event in claiming that the OFR can be used as a predictive tool. Figure 3b indicates that maximum nighttime OA concentrations ranging from 15 – 30 μg m-3 are observed at 6 separate intervals over 12 hours. Figure 2 shows a ~1.5 hr measurement cycle, suggesting that six OFR sampling cycles are conducted over this period. However, the corresponding OHexp at which these [OA] = 15 – 30 μg m-3 periods are attained is not discussed. If OHexp in the reactor is the same as the ambient OHexp during the following day (5-Jun-2010, peak OA ~ 25 μg m-3), over multiple days of the campaign (instead of just one day), then it might be appropriate to highlight "the reactor's potential for estimating the next day's OA concentrations." Otherwise, it is an interesting observation but (in my opinion) inconclusive. For example, Figure 2 suggests that maximum reactor OA concentration during a nighttime cycle on 2-Jun-2010 are observed at OHexp ~ $2*10^{12}$ molec cm-3 sec (15 days of equivalent atmospheric oxidation), which is presumably much higher than the ambient OHexp later that day.

Individual data points can be affected by noise and experimental uncertainties in both the X ($OH_{exp}$) and Y (SOA produced) variables. However, the results shown later in the paper in Figure 9 show that this statement is approximately true on the average. Note in Figure 9 that the amount of SOA produced after ~15 days $OH_{exp}$ and under the highest ambient $OH_{exp}$ is still similar. The wording at this point in the paper is more tentative ("suggesting"), since the latter evidence has not been shown. We have revised that text to read:

**"The nighttime reactor-aged OA mass peaks at approximately the same concentration as the following day's ambient OA concentration, suggesting the reactor's potential for**

**estimating the next day's OA concentrations. A more quantitative evaluation of this potential is discussed below (Sect. 4.1. and Figure 9)."**

R3.7. P21920, Section 3.2: The mean inorganic aerosol concentration is greater than the mean organic aerosol concentration (11 µg m-3 INORG versus 8.4 µg m-3 ORG in reactor, 8.2 µg m-3 INORG versus 6.8 µg m-3 ORG in ambient). However, aside from a brief mention in the Supplement relating to discussion AMS collection efficiency, the magnitude and OH exposure-dependent inorganic aerosol enhancements in the reactor are never discussed despite being comparable to the organic aerosol enhancements. This is especially evident from the nitrate time series in Figures 3a and 3b. There is likely valuable information here that complements the discussion of OA enhancements: Nitrate, sulfate, ammonium and chloride enhancements as a function of photochemical age. Are the trends the same or different as OA trends, and what does this reveal about their sources? Are nitrate and sulfate neutralized by ammonium in the reactor and in ambient? At the moment this information is buried in L21-L29 of the Supplement.

It is true that there are additional promising observations from this field deployment that are not reported in this manuscript. SOA formation was the topic of highest interest and resulted in a large paper already (12 figures in the main paper and another 12 in the Supp. Info, for a total of 35 figure panels). The formation of inorganic species in the OFR, together with other observations that we did not include in this manuscript either such as the variation of new particle formation with time, should be the focus of future publications. We have added the following text to the Supp. Info. (P1/L13) to briefly document these details:

**"Although the focus of this paper is OA formation and aging, a brief summary of the observed evolution of the inorganic species: (a) Sulfate formation proceeds as expected from the OH + $SO_2$ reaction. A quantitative analysis of sulfate formation is shown in Palm et al. (2016), which reports results from a similar experiment from our group, but in a forest environment. That analysis provides evidence that the corrections for losses of low volatility species developed in that work are appropriate. (b) Nitrate formation is more complex since OH + $NO_2$ is a fast reaction, but $HNO_3$ is semivolatile and the formation of $NH_4NO_3$ also depends on the availability of $NH_3$(g). (c) The aerosols in the output of the flow reactor during CalNex are neutralized, similarly to the ambient aerosols (Hayes et al., 2013).**

As an aside, as noted in Comment #13 below, the mean "total mass" listed in Figure 3c (22.4 µg m-3 in reactor, 14.9 µg m-3 in ambient) is not equal to the sum of the organic, nitrate, sulfate, ammonium and chloride components (19.4 µg m-3 in reactor, 15.0 µg m-3 in ambient). If this is a typo it should be fixed, if it is a real difference it should be explained.

This was a typo on the total mass, which has been corrected in the revised version.

R3.8. P21930, L12-L15. It is not clear how you distinguish gas-phase fragmentation of condensable species from heterogenous oxidation of SOA here because to first order, the timescales for gas-phase fragmentation of condensable species and heterogeneous oxidation of

SOA appear to be similar. Because this comparison is speculative and doesn't seem to add much to the discussion anyway, I would consider removing it.

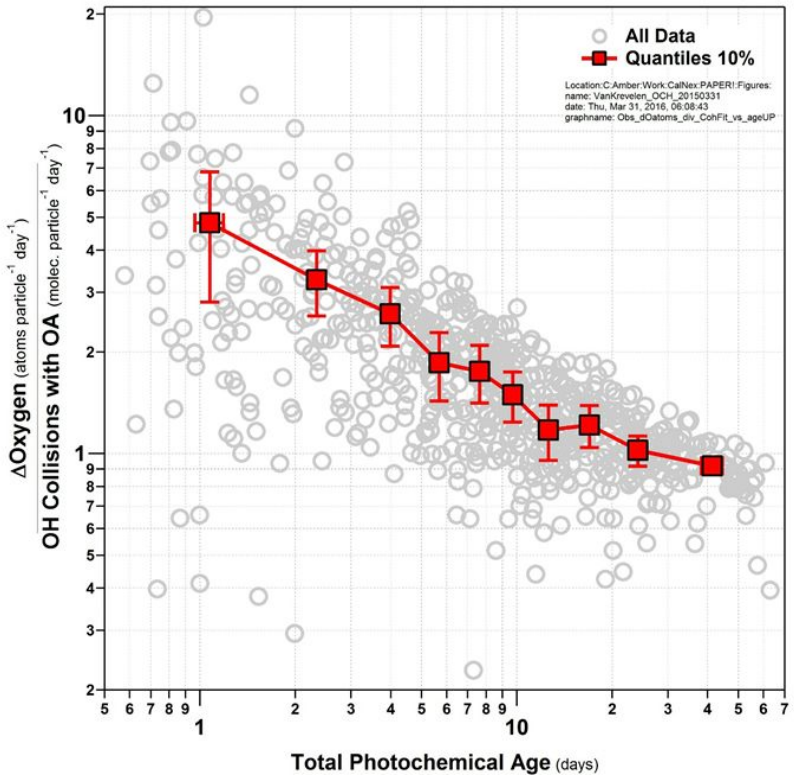
We have revised this text to clarify the point that we were trying to make:

**"Note that the George and Abbatt (2010) vs. Lambe et al. (2012) studies are qualitatively different, and thus the explanations of the decrease in OA at high ages may be different. George and Abbatt (2010) started their oxidation experiment with particles only, after removing gases with a denuder. Any decreases in OA in their study must result from heterogeneous oxidation. The Lambe et al. (2012) study started with gas-phase precursors only and no particles. Thus the reduction in SOA at high $OH_{exp}$ may be due to either gas-phase fragmentation of condensable species, so that SOA is never formed, or to formation of SOA followed by its heterogeneous oxidation and revolatilization. Results in Fig. S7 suggest that gas-phase oxidation would prevent the formation of SOA, and thus the second explanation is more likely."**

R3.9. P21930, L16-L29: To complement this discussion, I suggest adding a scatter plot of "measured oxygen added" versus "predicted oxygen added" to the main paper, and rephrasing the discussion accordingly. I am unable to draw this conclusion from Figure S10; I think this alternative figure would make the point a little clearer. Figure S10 could then be removed.

We have made a new figure illustrating this point that should be clearer. We have also updated this calculation to use the surface-averaged diameter, as detailed in response to comment R1.10. The new figure S10 is reproduced below, and the ACPD Figure S10 has been removed as suggested (now Fig. S11 in revised manuscript). The text in P21930/L16-29 has been revised to read:

**"To evaluate directly whether heterogeneous oxidation could explain the gain of oxygen observed in the aerosol, we follow the method outlined in appendix A of DeCarlo et al. (2008). Figure S11 shows the ratio of the gain of oxygen of OA observed in the reactor ($\Delta$Oxygen in OA = $O_{atoms,\ reactor} - O_{atoms,\ ambient}$) to the total number of OH collisions with OA in the reactor, plotted vs. total photochemical age. Heterogeneous oxidation calculations use surface-weighted diameter calculated from the peak of the mass distribution and estimated particle density from AMS components (DeCarlo et al., 2004), assume every collision results in reaction ($\gamma = 1$). If it is assumed that each OH collision with OA results in one O atom addition, the number of O atoms added is underpredicted by a factor of 5 at ages ~ 1 day, decreasing to a factor of 2 at ~ 10 days, and lower values at high ages (> 10 days). This analysis supports that heterogeneous oxidation is not dominant in contributing to SOA mass at low-to-intermediate ages, but it likely plays a role in OA evolution at the highest photochemical ages in the reactor."**




R3.10. P21932, L8-L29 and P21934-P21935, L28-2: In making the comparison with Tkacik et al. (2014), I would consider the following points in the discussion. High NO levels (>400 ppb) in Tkacik et al. might minimize the relative rate of RO2 + HO2 reactions in their reactor that would otherwise lead to multifunctional, condensable species (and possibly higher ΔOA/ΔCO). High NO and NH3 levels in Tkacik et al. result in nitrate and ammonium enhancements ~3x higher than the organic aerosol enhancements. Thus, while vehicle emissions presumably dominate SOA formation in both studies, the ensuing RO2 oxidation chemistry could be very different. Given that inlet losses of semivolatiles is pretty much discounted in this discussion, I would remove (or significantly shorten) that discussion and instead focus on the different photochemical conditions and how they might result in different secondary aerosol composition despite similar precursor makeup.The sum Δ(OA + Nitrate + Sulfate + Ammonium)/Δ(CO) would also be worth calculating and comparing between the two studies.

We have added the following text to the manuscript (P21932/L26) to clarify these issues:

**"(3) It may appear at first that the tunnel SOA may have been dominated by $RO_2$+NO, compared to $RO_2$+$HO_2$ for our ambient air results, thus making the results less comparable. However, while the initial NO levels in the tunnel may be high, the lifetime of NO under the conditions of the OFR is typically very low (Li et al., 2015). $O_3$ levels in OFR185 are typically 1-25 ppm, which result in NO lifetimes of 0.1-2 s. Since $HO_2$ levels are greatly enhanced by the reactor chemistry, the majority of the $RO_2$ radicals are still**

**expected to react via $RO_2$ + $HO_2$ under the tunnel conditions, similar to our study. The model of Peng et al. (2015) was used to estimate the fraction of $RO_2$ reacting with NO vs. $HO_2$ for the tunnel study. At the point of peak SOA production we estimate that 81% of the $RO_2$ radicals are reacting with $HO_2$ and 19% with NO. Therefore the chemistry of the OFR in the tunnel study is proceeding mostly through the $HO_2$ channel, similar to our ambient study."**

We have also added the following text to address a related point:

**"(4) A difference between the studies that may explain somewhat higher SOA formation in the tunnel study is the larger partitioning of semivolatile species, given the higher OA concentrations (~50 μg $m^{-3}$ in the tunnel vs ~15 μg $m^{-3}$ for our study). However, this effect is estimated to be a factor of ~1.5 for the aromatic and alkane precursors that are thought to dominate SOA formation from vehicle emissions (Barsanti et al., 2013), and it reduces the difference observed here, thus further supporting our conclusions."**

While the enhancements of the inorganic species are of some interest, those of sulfate are straightforward to explain (see response to R3.7), and those of nitrate depend on complex ways on $NH_3$(g) present which may be quite different in the two studies. Thus a comparison would be a complex subject that exceeds the scope of this paper.

In addition, during the revision process of Peng et al. (2015) we realized that there was an error on the inputs used for the simulation of $OH_{exp}$ for the tunnel study of Tkacik et al. (2014), as discussed in Peng et al (AMTD, 8, C3671 ; see response to comment SC.2 in http://www.atmos-meas-tech-discuss.net/8/C3671/2015/amtd-8-C3671-2015-supplement.pdf). Figure 12 has been updated to add the results using the correct inputs, which result in improved agreement between the ambient and tunnel observations. We have corrected the text on P21932/L28 to read:

**"Thus it is most likely that the observed difference between the tunnel and our study is due to overestimation of $OH_{exp}$ at lower ages in the tunnel study. We have used the model of Peng et al. (2015) to estimate the corrected $OH_{exp}$ under the tunnel conditions. The corrected curve is also shown in Fig. 12b, and shows much improved agreement with our urban air observations."**

The updated Figure 12b is shown below:

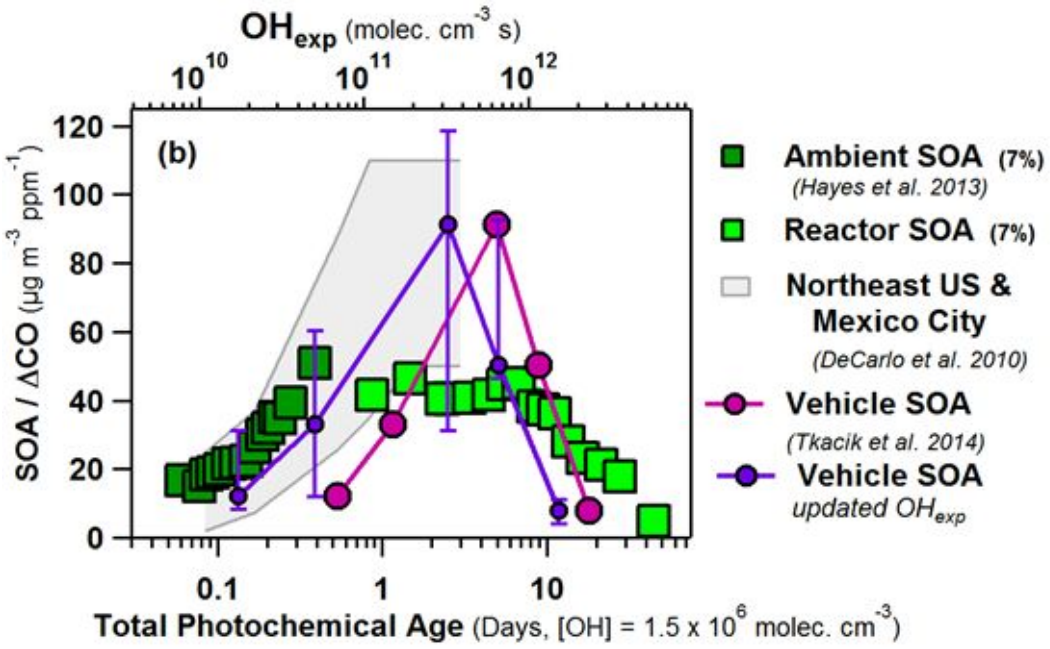



Figure Comments

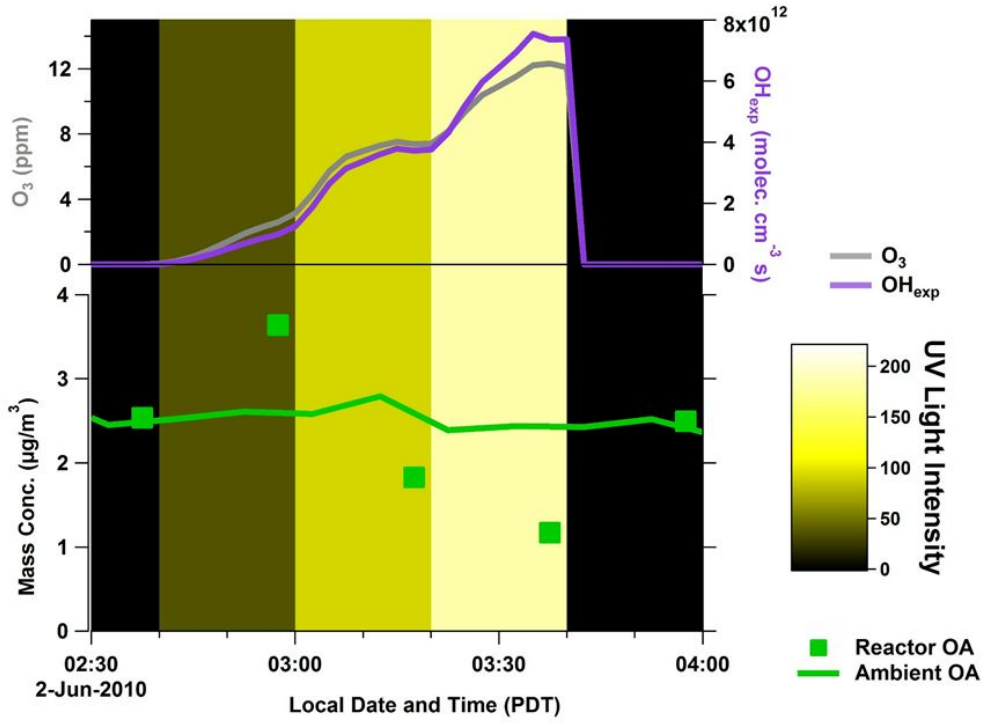
R3.11. Figure 1: This figure could be moved to the supplement.

We prefer to keep the figure in the main paper, since this was the first time that anyone demonstrated this type of reactor operation or our knowledge, and thus a visual reference for the experiment may help reduce confusion about our setup and results.

R3.12. Figure 2:

- Given the range of [O3] (up to ~16 ppm), I suggest plotting in parts per million instead of parts per billion.

We have made this change as suggested. The updated figure is shown below:




- I think it would be useful to have the colorbar scaled by the lamp voltages so that readers better the specific conditions that were used, especially if they want to reproduce the sampling protocols that were used here in their own work.

The UV light intensity colorscale was actually already the sum of the voltages applied to both lamps. We have added the following text to the figure caption to clarify this point:

**"The UV light intensity color scale corresponds to the sum of the AC voltages applied to the two lamps in the reactor. Only at the highest lamp setting are both lamps on, while at lower settings only one of the lamps is used."**

- In the caption, "oxidant cycle" is vague - something like "A typical OFR sampling cycle" would better describe the figure.

Figure caption text was changed to:

**"A typical OFR sampling cycle, including four steps in lamp intensity in the reactor."**

R3.13. Figure 3c: The "total mass" is not equal to the sum of the non-refractory components listed here (OA + Nitrate + Sulfate + Ammonium + Chloride): 22.4 µg m-3 stated versus 19.4 µg m-3 calculated (PAM reactor) 14.9 µg m-3 stated versus 15.0 µg m-3 calculated (ambient). This discrepancy should be explained or sorted out as appropriate. Also, is there a reason why the reactor" and ambient pie charts are different sizes?

The comment for the total mass is the same as R3.7, and it has been addressed in that response.

The following text has been added to the figure caption to explain the second point:

**"The pie chart areas are proportional to the total mass concentrations."**

R3.14. Figure 4: Analogous figures should be made for nitrate, sulfate and ammonium.

See response to R3.7.

R3.15. Figure 5: This figure could be removed or moved to the Supplement (see Comment #40)

See response to R1.6.

R3.16. Figure 6: It would make sense to show toluene here as well (rather than in Figure S8).

The VOCs highlighted in this figure were selected to serve as proxies for relative classes of reactivity. Thus, toluene has been left in supplemental as adding it would further complicate visually an already complex figure.

R3.17. Figure 7: I assume that symbols representing the PMF factors are the same in Figures 7a and 7b, but this should be made clear. The "ambient" and "reactor" symbols are also the same, but whereas they appear in two legends, the PMF factor symbols do not.

PMF factor symbols have been made larger and the legend now appears in both Fig. 7a and 7b.

R3.18. Figure 9:

- I suggest adding vertical lines at photochemical ages corresponding to one e-fold decay of 1,3,5-trimethylbenzene, toluene, and benzene, to illustrate the relevant range of kOH for important SOA precursors. This would convey the added information in Figure S9a in the main paper (and perhaps make that figure unnecessary in supplemental) more directly than the decay curves that are shown in Figure S9a.

This is an important figure for our conclusions and it is already pretty complex, and adding more lines would make its explanation more difficult. The issue of the VOC ages is already addressed also in Fig. 6, plus Fig. S9. Thus we prefer to keep Fig. 9 as is.

- Define "BG" as "background" and "POA" as "primary organic aerosol" in the figure caption.

The figure caption text has been adjusted as requested.

R3.19. Figure 10:

- The Hayes et al. 2014 ACPD citation shown in legend and caption is not in the listed references. Should this instead be Hayes et al. 2015?

Correct. The figure legend has been updated.

- In the figure caption, the text “This difference is due…photochemical ages less than 1.2 h” would probably be better in the main text.

We believe that this is a small detail, as it concerns a difference of 5 units in a graph with a scale up to 220. Thus we prefer to keep this text in the caption to facilitate the readability of the main text.

- Is there a reason why Figures 10a and 10b are different sizes?

Figure 10b was only meant as an inset. However we realize that the size difference may be distracting, and thus we have made both figures of the same size in the revised version (now Fig. 11).

R3.20. Figure S6: Move to main paper

See response to R3.5.

R3.21. In addition to (or instead of) Figure S10, Add a scatter plot of “measured oxygen added” versus “predicted oxygen added” to the main paper.

See response to R3.9.

Minor/technical comments

R3.22. P21909, L6: Define the “CalNEX” acronym (it is not definied until the last paragraph in the Introduction).

The Abstract text has been adjusted to, “An Oxidation Flow Reactor (OFR) was deployed to study SOA formation in real-time during the **California Research at the Nexus of Air Quality and Climate Change (CalNex)** campaign in Pasadena, CA, in 2010.”

R3.23. P21909, L7: Might it be useful to spell out “California” and indicate it’s in the United States?

Now, spelled out in the CalNex acronym definition.

We believe the fact that California is in the United States is already known for anyone who could be interested in our paper.

R3.24. P21909, L11-13: “OH radical concentration was continuously stepped […] 0.8 days – 6.4 weeks”. This sentence seems superfluous with the preceding sentence.

We have consolidated the text in L9-13 to read:

**"The reactor produced OH concentrations up to 4 orders of magnitude higher than in ambient air. OH radical concentration was continuously stepped, achieving equivalent atmospheric aging of 0.8 days–6.4 weeks in 3 min of processing every 2 hrs."**

R3.25. P21909, L19: Define LA-Basin

We have replaced "LA-Basin" with **"greater Los Angeles area."**

R3.26. P21909, L25-28: "The mass added […] fragmentation/evaporation." I'm not certain if the abstract is the best place for this text.

We believe that this is an important scientific contribution of our work, and thus that it should remain in the abstract.

R3.27. P21911, L12: Quantify "long" aging timescales.

Text has been modified to read, "SOA at long aging times **(>1 day).**"

R3.28. P21911, L19-21: "In order […] changing air masses." This sentence is unclear.

The sentence has been modified to read:

**"In order to characterize the SOA formation potential of urban emissions, a rapid field deployable experimental method is needed, so that rapid changes of ambient SOA formation potential can be captured."**

R3.29. P21913, L12-14: "By combining results from the ambient aerosol and aged ambient aerosol measurements, we provide a stronger test of current SOA models." Instead of 'stronger', I suggest "more rigorous." Also, explain why the combination of ambient and PAM-oxidized ambient measurements is a better test of SOA models.

The text "stronger**"** has been changed to **"more rigorous"** as suggested.

The last sentence of the paragraph has been updated to read:

**"By combining results from the ambient aerosol and aged ambient aerosol measurements, we provide a more rigorous test of current SOA models, since they can now be compared with data from a much wider range of photochemical ages."**

R3.30. P21915, L23: Add "and" between "reactor" and "resultant"

The text has been modified as requested.

R3.31. P21916, L8: Isn't residence time the governing parameter here (rather than flow rate)?

Correct. The text has been modified accordingly.

R3.32. P21916, L18-19: “OH concentrations averaged up to $4*10^6$ cm-3 during the daytime.” This sentence is confusing - was the mean daytime OH concentration $4*10^6$ cm-3 ? If so, delete “up to”.

This text has been modified, replacing “up to” with “**as high as.**”

R3.33. P21916, L19-22: “Since a significant part of SOA formation … peak OH observed during CalNex.” This sentence is unclear; please clarify or rephrase. Also, “peak OH” should be “peak [OH]” or “peak OH concentration”.

The text has been modified to read:

**“Since a significant part of SOA formation happens during the first few hours after emission, the 0.8 day minimum photochemical age probed with the reactor would correspond to ~0.3 days of transport age at the peak OH concentration observed during CalNex.”**

R3.34. P21918, L24: This is the first instance of “EROA” in the manuscript, so it needs to be defined here.

This text has been modified to read:

**“Thus, correction is applied when reactor-measured OA is greater than ambient OA (relative OA enhancement ratio, $ER_{OA}$ = reactor OA / ambient OA, $ER_{OA}>1$; and the absolute OA enhancement factor, ΔOA Mass = reactor OA – ambient OA, ΔOA Mass>0, Sect. 3.2).”**

Text in Section 3.2 has been adjusted to remove the definition.

R3.35. P21919, L17: Typo (“attributes”->”attribute”)

Text has been modified as requested.

R3.36. P21919, L25: Replace “indicating” with “suggesting”

Text has been modified as requested.

R3.37. P21919-21920, L26-1: “At the peak of…removal by photochemical oxidation and condensation”. Delete, this is repetitive with the previous sentence.

Text has been modified as requested.

R3.38. P21921, L4-6: The last sentence of this paragraph is confusing.

Text has been modified to read:

**"A smaller enhancement is observed during the day ~2 μg $m^{-3}$, or a factor of 1.2x of ambient, while at > 2 weeks of aging, day and night observations closely overlap, with a decrease up to ~2.5 μg $m^{-3}$, or a factor of 0.5x of ambient."**

R3.39. P21921, L14: Please provide a reference for the stated 0.5 day transit time from downtown Los Angeles to Pasadena.

Reference has been added to Washenfelder et al. (2011).

R3.40. P21922, Section 3.3.1 and Figure 5: In my opinion this section is somewhat self evident because the oxidant exposures attainable in the reactor are much higher than the ambient photochemical age. I don't think it adds much to the paper and would delete or move to the Supplement.

See response to R1.6.

R3.41. P21922, L19-20: I suggest a slight modification to the title of Section 3.3.2: "Further constraints on urban SOA formation timescales from OH reactivity of measured VOCs."

Text has been modified as requested.

R3.42. P21923, L6: Typo ("moelcule"->"molecule")

Text has been modified as requested.

R3.43. P21923, L14: Typo ("theses"->"these")

Text has been modified as requested.

R3.44. P21923, L24-25: Somewhere in the paper S/IVOCs should be briefly defined. This sentence could be explained slightly to point out why these species are not often measured.

The definition of S/IVOCs is given here, and the following text has been added to the end of the sentence:

**"due to the difficulty in measuring these compounds."**

R3.45. P21924, L6: f43, f44, H:C and O:C are never defined.

The text on p. 21917, line 3 was modified to define O:C and H:C:

**"The elemental analysis of OA (resulting in oxygen-to-carbon ratio, O:C, and hydrogen-to-carbon ratio, H:C)."**

The text was also modified to define $f_{43}$ and $f_{44}$ as:

**"$f_{44}$ is a tracer for aged OA (fractional organic contribution at *m/z* 44, mostly $CO_2^+$), while $f_{43}$ (fractional organic contribution at *m/z* 43, mostly $C_2H_3O^+$), due to non-acid oxygenates,**

**with some contribution from $C_3H_7^+$) is a tracer of POA and freshly formed SOA (Ng et al., 2011a).”**

R3.46. P21924, L10: Rather than “move up and to the left”, I suggest “f44 increases and f43 decreases.”

Text has been modified as requested.

R3.47. P21924, L13: Typo (“lay”->”lie”)

Text has been modified as requested.

R3.48. P21924, L17-L18: “The Van Krevelen diagram … demonstrates results that are very consistent to those of the previous plot”. The connection between f44 – O/C and f43 – H/C has been documented in previous papers (e.g. the Ng et al. 2011b ref, among others), but is never made in this paper. Readers might not make this connection themselves. I suggest doing so here if you want to relate Figures 7a and 7b.

We respectfully disagree. Both diagrams have been used in many publications, and we believe that our discussion and referencing (e.g. the Ng et al. citation) are sufficient to explain these figures.

R3.49. P21925, L12-13: “While ambient OSc is within the range of …urban/anthropogenic OA”. Please provide reference(s).

Reference is provided at the end of the sentence to Kroll et al. (2011).

R3.50. P21925, L21: I suggest a modification to the title of Section 4.1: “Evolution of OA/ΔCO with photochemical age”

We have changed the title to read:

**“Evolution of urban OA with photochemical age”**

R3.51. P21926, L8-L19 and PL22-23: “Ambient photochemical age … Fig. S9a for reference” and “Reactor data are shown… vapor loss-correction applied (see Sect. 2.3)”. Can this text be deleted or shortened significantly? Most of it is already in the Figure 9 caption or self-evident from viewing the figure, and it breaks up the flow of discussion of data in Figure 9.

We have moved the following text to the figure caption, deleting duplicated text when necessary:

- L8-11 , “Ambient photochemical age [...] and reactor age.”
- L16-19: “Figure 9 [...] for reference.”
- L22-23: “Reactor data [...] applied.”

R3.52. P21926, L27: “To further illustrate the lifetimes of important urban SOA precursors”. This sentence confuses the point. Benzene, toluene, and 1,3,5-trimethylbenzene are not important urban SOA precursors. Rather, their OH oxidation lifetimes – in conjunction with timescale over which OA/ΔCO increases -- constrain the range of OH reactivity (kOH) of important urban SOA precursors: 5*10-12 < kOH < 5*10-11 cm-3 molec sec. This should be clarified here and elsewhere in the discussion.

While those specific species are not unimportant (e.g. see Hayes et al., 2015), this text was trying to make the same point that the reviewer is indicating. We gather that was not clear, and we have reworded this text as:

**“To constrain the lifetimes of the important urban SOA precursors, the OH decays of three example gas-phase species (benzene, toluene, and 1,3,5-trimenthylbenzene (TMB)) are shown are overlaid in Fig. S10, together with data from Fig. 9 that illustrates the timescale over which OA/ΔCO increases. The correlation of different VOCs with maximum SOA formation in the reactor is shown vs. their reaction rate constants with OH ($k_{OH}$) in Figure 10. This analysis constrains the rate constants of the most important urban SOA precursors to the approximate $k^{OH}$ ~ 3-5x$10^{-11}$ $cm^3$ $molec.^{-1}$ $s^{-1}$. This constraint suggests that polyalkyl monoaromatics (such as TMB), substituted polyaromatics such as alkyl naphthalenes (Phousongphouang and Arey, 2002), or large alkanes with ~23 or more carbons (Calvert et al., 2008), or branched / cyclic species of similar size are (as a group) important contributors. The latter species are semivolatile and intermediate volatility species (S/IVOCs), and thus our results suggests a very important role for such species in urban SOA formation. ”**

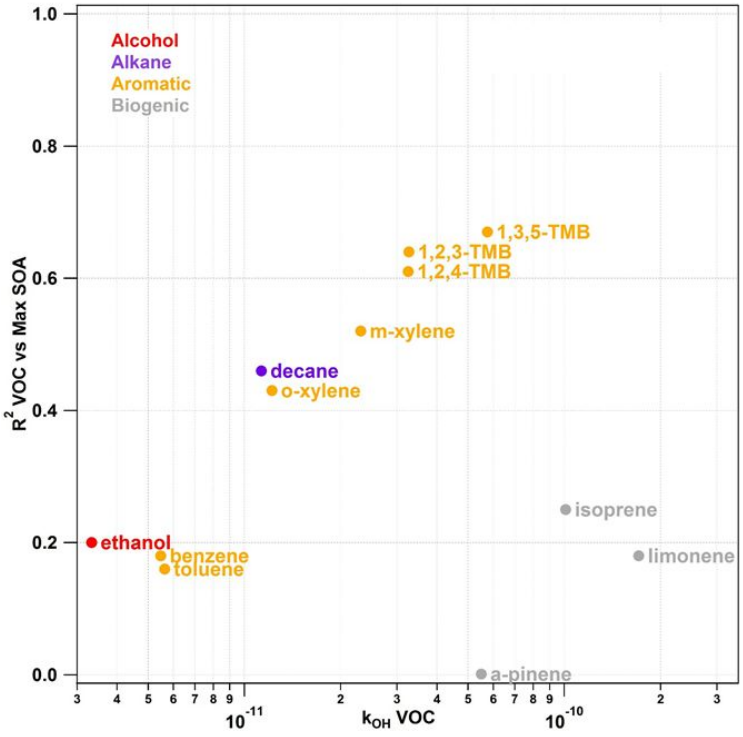



**Figure 10: $R^2$ between the concentrations of different VOCs and the maximum amount of SOA formation in the OFR, plotted vs. the reaction rate constant of each VOC with OH ($k_{OH}$).**

We have also modified the abstract to reflect this updated result as:

"**Reactor SOA formation was inversely correlated with ambient SOA and Ox, which along with the short-lived VOC correlation, indicates the importance of relatively reactive (OH ~0.3 day) SOA precursors (most likely semivolatile and intermediate volatility species, S/IVOC) in the greater Los Angeles Area.**"

R3.53. P21927, L15: I suggest a modification to the title of Section 4.2: "Fit to the observed ambient and reactor OA/ΔCO evolution" or perhaps "Parameterization of timescales for SOA functionalization and fragmentation processes."

We have modified the section title to:

**"Parameterization of the Amount and Timescale for Urban SOA Formation**"

R3.54. P21927, L22: "However, the evolution…": Evolution of OA/ΔCO?

Text has been modified as requested.

R3.55. P21928, L22: Isn't it implicit in the discussion that IVOCs and SVOCs are primary emissions? I suggest: "The second model variant represents SOA formation from IVOCs and SVOCs in addition to VOCs".

Text has been modified as requested.

R3.56. P21930, L6: Define "TPOT".

Definition added as requested.

R3.57. P21933, L14-L15: Didn't the George and Abbatt (2010) and Tkacik et al. (2014) studies that are already cited here also use an oxidation flow reactor to perturb ambient urban air?

Tkacik et al. (2014) was not a study of ambient urban air but a study of oxidation of vehicle emissions in a tunnel study. The George and Abbatt (2010) study used a denuder to remove VOCs and thus only studied heterogeneous oxidation. The latter point was not clear in the sentence that the reviewer is referring to, so we have updated that text to read:

**"This work represents the first application of an oxidation flow reactor to investigate SOA formation from ambient urban air, to our knowledge."**

**References**

Barsanti, K. C., Carlton, A. G., and Chung, S. H.: Analyzing experimental data and model parameters: implications for predictions of SOA using chemical transport models, Atmos. Chem. Phys., 13, 12073-12088, 10.5194/acp-13-12073-2013, 2013.

DeCarlo, P. F., Slowik, J. G., Worsnop, D. R., Davidovits, P., and Jimenez, J. L.: Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part 1: Theory, Aerosol Sci Tech, 38, 1185-1205, 2004.

George, I. J., and Abbatt, J. P. D.: Heterogeneous oxidation of atmospheric aerosol particles by gas-phase radicals, Nat Chem, 2, 713-722, 2010.

Hayes, P. L., Carlton, A. G., Baker, K. R., Ahmadov, R., Washenfelder, R. A., Alvarez, S., Rappenglück, B., Gilman, J. B., Kuster, W. C., de Gouw, J. A., Zotter, P., Prévôt, A. S. H., Szidat, S., Kleindienst, T. E., Offenberg, J. H., Ma, P. K., and Jimenez, J. L.: Modeling the formation and aging of secondary organic aerosols in Los Angeles during CalNex 2010, Atmos. Chem. Phys., 15, 5773-5801, 10.5194/acp-15-5773-2015, 2015.

Kang, E., Root, M. J., Toohey, D. W., and Brune, W. H.: Introducing the concept of Potential Aerosol Mass (PAM), Atmos. Chem. Phys., 7, 5727-5744, 10.5194/acp-7-5727-2007, 2007.

Kroll, J. H., Donahue, N. M., Jimenez, J. L., Kessler, S. H., Canagaratna, M. R., Wilson, K. R., Altieri, K. E., Mazzoleni, L. R., Wozniak, A. S., Bluhm, H., Mysak, E. R., Smith, J. D., Kolb, C. E.,

and Worsnop, D. R.: Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol, Nat Chem, 3, 133-139, 2011.

Lambe, A. T., Onasch, T. B., Croasdale, D. R., Wright, J. P., Martin, A. T., Franklin, J. P., Massoli, P., Kroll, J. H., Canagaratna, M. R., Brune, W. H., Worsnop, D. R., and Davidovits, P.: Transitions from Functionalization to Fragmentation Reactions of Laboratory Secondary Organic Aerosol (SOA) Generated from the OH Oxidation of Alkane Precursors, Environmental Science & Technology, 46, 5430–5437, 10.1021/es300274t, 2012.

Li, R., Palm, B. B., Ortega, A. M., Hlywiak, J. A., Hu, W., Peng, Z., Day, D. A., Knote, C., Brune, W. H., de Gouw, J. A., and Jimenez, J. L.: Modeling the Radical Chemistry in an Oxidation Flow Reactor: Radical Formation and Recycling, Sensitivities, and OH Exposure Estimation Equation, The Journal of Physical Chemistry A, 10.1021/jp509534k, 2015.

Ortega, A. M., Day, D. A., Cubison, M. J., Brune, W. H., Bon, D., de Gouw, J. A., and Jimenez, J. L.: Secondary organic aerosol formation and primary organic aerosol oxidation from biomass-burning smoke in a flow reactor during FLAME-3, Atmos. Chem. Phys., 13, 11551-11571, 10.5194/acp-13-11551-2013, 2013.

Palm, B. B., Campuzano-Jost, P., Ortega, A. M., Day, D. A., Kaser, L., Jud, W., Karl, T., Hansel, A., Hunter, J. F., Cross, E. S., Kroll, J. H., Peng, Z., Brune, W. H., and Jimenez, J. L.: In situ secondary organic aerosol formation from ambient pine forest air using an oxidation flow reactor, Atmos. Chem. Phys., 16, 2943-2970, 10.5194/acp-16-2943-2016, 2016.

Peng, Z., Day, D. A., Ortega, A. M., Palm, B. B., Hu, W. W., Stark, H., Li, R., Tsigaridis, K., Brune, W. H., and Jimenez, J. L.: Non-OH chemistry in oxidation flow reactors for the study of atmospheric chemistry systematically examined by modeling, Atmos. Chem. Phys. Discuss., 2015, 23543-23586, 10.5194/acpd-15-23543-2015, 2015a.

Peng, Z., Day, D. A., Stark, H., Li, R., Lee-Taylor, J., Palm, B. B., Brune, W. H., and Jimenez, J. L.: HOx radical chemistry in oxidation flow reactors with low-pressure mercury lamps systematically examined by modeling, Atmos. Meas. Tech., 8, 4863-4890, 10.5194/amt-8-4863-2015, 2015b.

Ryerson, T. B., Andrews, A. E., Angevine, W. M., Bates, T. S., Brock, C. A., Cairns, B., Cohen, R. C., Cooper, O. R., de Gouw, J. A., Fehsenfeld, F. C., Ferrare, R. A., Fischer, M. L., Flagan, R. C., Goldstein, A. H., Hair, J. W., Hardesty, R. M., Hostetler, C. A., Jimenez, J. L., Langford, A. O., McCauley, E., McKeen, S. A., Molina, L. T., Nenes, A., Oltmans, S. J., Parrish, D. D., Pederson, J. R., Pierce, R. B., Prather, K., Quinn, P. K., Seinfeld, J. H., Senff, C. J., Sorooshian, A., Stutz, J., Surratt, J. D., Trainer, M., Volkamer, R., Williams, E. J., and Wofsy, S. C.: The 2010 California Research at the Nexus of Air Quality and Climate Change (CalNex) field study, Journal of Geophysical Research: Atmospheres, 118, 5830-5866, 10.1002/jgrd.50331, 2013.

Tkacik, D. S., Lambe, A. T., Jathar, S., Li, X., Presto, A. A., Zhao, Y., Blake, D., Meinardi, S., Jayne, J. T., Croteau, P. L., and Robinson, A. L.: Secondary Organic Aerosol Formation from in-Use Motor Vehicle Emissions Using a Potential Aerosol Mass Reactor, Environmental Science & Technology, 48, 11235-11242, 10.1021/es502239v, 2014.

Washenfelder, R. A., Young, C. J., Brown, S. S., Angevine, W. M., Atlas, E. L., Blake, D. R., Bon, D. M., Cubison, M. J., de Gouw, J. A., Dusanter, S., Flynn, J., Gilman, J. B., Graus, M., Griffith, S., Grossberg, N., Hayes, P. L., Jimenez, J. L., Kuster, W. C., Lefer, B. L., Pollack, I. B., Ryerson, T. B., Stark, H., Stevens, P. S., and Trainer, M. K.: The glyoxal budget and its contribution to organic aerosol for Los Angeles, California, during CalNex 2010, Journal of Geophysical Research: Atmospheres, 116, D00V02, 10.1029/2011jd016314, 2011.