Response to Reviewer 1 Comments

Note: the first reviewer provided 3 general comments (not numbered) and 6 specific comments (numbered 1-6). In our response to this reviewer's comments, we have listed the general comments as comments A-C and the specific comments as comments #1-6.

A. In my mind the unfortunate complexity, which is clearly described in this study, is the broad somewhat complex residence time distribution (RTD) for these reactors. As the authors clearly show, both flow tubes do not have RTD's that resemble plug or laminar flow reactors. In fact the overall form of the RTD's more closely resemble a continuous flow stirred tank reactor (CFSTR) or a PFR with significant dead zones (long tail), bypass or channeling flows (Folger 2010). Are the authors sure that these reactors are not inadvertently behaving as CFSTR's and as a result subsequent analysis should utilize flow equations for this reactor type?

In our analysis, we compared the flow tube RTDs with the RTD for an ideal Continuous Stirred Tank Reactor (CSTR; which has a continuous flow of products and reactants), an ideal Plug Flow Reactor (PFR), and an ideal Laminar Flow Reactor (LFR). We concluded that a CSTR was not the best model for a couple reasons. First, the RTD of an ideal CSTR is characterized by an exponential decay of tracer starting at time $t = 0$, whereas the flow tube RTDs are characterized by a rise in tracer at time $t > 0$ followed by an exponential decay. Second, the tails of the flow tube RTDs were much longer than for an ideal CSTR (i.e. single exponential decay). Our interpretation of this behavior is that large-scale dispersions (i.e. turbulence) were affecting the flow tube RTDs. This, in conjunction with the laminar flow characteristics of the TPOT and PAM (Re = 15 and Re = 55; see reply to reviewer #2 comment #3 below) led us to model the flow tubes with the Taylor dispersion in laminar flow model presented in Appendix A. As we show in the manuscript, this model appears to account for the observed RTD's from the TPOT and PAM, including the observed dispersions, but does not provide insights into what the reasons behind the non-ideal flow behavior (i.e. dead volumes, channeling, and convection).

B. In any case, it seems as the RTD's introduce many uncertainties since particles or gas phase species exiting the flow tube will have sampled a broad distribution of oxidizing environments. This could impact for example, how the OH exposure axis is determined. The authors need to provide more details about how OH exposure was computed using SO2. Was this a relative rate measurement or a one time calibration? What is the major sink for OH in the flow tubes for each experiment? Walls? Particles? VOC's etc.? At what residence time was the decay of SO2 measured? What kinetic modeling is necessary to extract an OH exposure, do the authors need to know wall losses since SO2 is the most sticky of gases used in these experiments? Given the anomalous behavior of SO2 (relative to CO2) in the flow tubes, this gas seems like a poor choice for determining OH. Nevertheless, the authors need to show that extracting an OH exposure from reactors that do not behave as idealized plug flow, batch or continuous flow stirred tank (CFSTR) reactors is reliable. For example, Che et al. (2009) worked out the mathematical framework for quantifying OH in a CFSTR. In this case, rate coefficients measured in a CFSTR using a relative rate technique but analyzed assuming a reaction in a PFR, which neglects flow dynamics of a CFSTR, would yield incorrect results.

We agree that the gas and particles exiting the flow tubes have sampled broad distributions of oxidizing environments, which is the case in any real flow tube system. Knowing this would be the case, we invested a significant effort to directly measure the RTD's of the tubes and place reasonable uncertainties on our measured OH exposure axis. The measured RTD's provide reasonable uncertainties in the measured OH exposures.

The method we used for determining the time averaged OH exposure is via the gas phase reaction of SO2 with OH radicals under the same conditions (i.e. flow conditions, relative humidity, O3 concentrations, and lamp intensities) as our experiments with other reactants. This method assumes that the loss of SO2(g) is due to OH radicals and has been successfully used in other flow tube experiments (e.g. McNeill et al., 2008). We added a section to the appendix describing the OH exposure calibration procedure, explained why SO2 was acceptable to use, and described the kinetic modeling used to extract an OH exposure. Specifically, we note the advantages of this calibration in the appendix, "First, any potential bias resulting from SO2 wall losses cancels out. Second, no assumptions about SO2 residence times need to be made, since the time averaged OH exposure (product of the OH concentration and average residence time) is determined directly from the initial and final SO2 concentrations."

Finally, in a new design of the TPOT, we have subsequently compared the OH exposures calculated by looking at steady state losses of SO2 to those calculated by looking at loss of methyl ethyl ketone (detected by PTR-MS), and we find them to be the same to within experimental error. We feel this illustrates that any potential wall issues associated with SO2 are negligible.

C. The authors need to discuss as much as possible how having a distribution of aging times might impact their results. For example, in an ideal PFR reactor every BES or SOA particle has the same age. Would the CCN properties or O/C of an aged BES particle from a PFR be the same as the average of the distribution of aged particles from the PAM or TPOT? One could image that somehow particles at the tail end of the RTD (highly oxidized) might disproportionately contribute to O/C or CCN activity? In general, I agree with the authors when they say, in the conclusion section, developing reactors that have well behaved and mathematically tractable flow dynamics could be a better option for investigating both heterogeneous and gas to particle oxidation reactions.

We agree with the points raised by the reviewer. Having responded to comment #3 raised by the second reviewer, we feel we have addressed as many of these points as possible without adding significant speculation and length to the paper.

1. For SOA yield, how was the precursor gas concentration reacted determined (pinene, xylene)?

p. 5220, line 17, added: **"We estimated the mass of precursor gas reacted from the bimolecular rate constants of m-xylene + OH, a-pinene + OH, and a-pinene + O3**

(Atkinson, 1986). These calculations suggested that about 40% - 100% of the m-xylene and 80% - 100% of the a-pinene reacted, depending on the flow tube OH exposure."

2. Why is the measured O/C for BES so inaccurate (measured = 0.04 vs. expected = 0.15). Is this a simple linear offset? Can the trend of O/C with OH exposure be corrected by this simple offset?

Aiken et al., (Analytical Chemistry, 2007, 79, 8350-8358) measured the elemental composition of 35 pure organic compounds (including BES) using a high-resolution ToF-AMS. They obtained a measured O/C = 0.05 for BES, compared to the atomic O/C = 0.15, and found that on average the measured O/C for pure compounds underpredicted the atomic O/C by about 40% (Fig 3 of Aiken et al.), with significant compound-to-compound variability. Therefore, the bias between measured and atomic O/C for BES in this work is consistent with previous literature. As suggested by Aiken et al., a possible reason for the discrepancies observed (including for BES) is that fragments with electronegative elements, such as oxygen, tend to become neutral during unimolecular ion decomposition and thus AMS derived O/C ratios are lower limits on the true O/C ratio. Finally, Aiken et al. results suggest that AMS-derived O/C ratios may be reasonable on average (or for an ensemble of organic compounds), but not necessarily for single organic compounds. To address this point, we added the following:

p. 5225, lines 25-27: "The measured O/C ratio of unoxidized BES was 0.04, compared **to a measured O/C ratio of 0.05 by Aiken et al. (2007)** and an **atomic** O/C ratio of 0.15 ($C_{26}H_{50}O_4$.)"

and added this citation to the list of references:

Aiken, A. C., DeCarlo, P. F., and Jimenez, J. L.: Elemental analysis of organic species with electron ionization high-resolution mass spectrometry, Anal. Chem., 79, 21, 8350-8358, 2007.

3. The term "Convection currents" used throughout the manuscript suggest thermal gradients in the flow tubes? Have these been measured? Would convection currents vs. dead volume impact the RTD in distinctly different ways? What is the average temperature of the gas exiting the TPOT and PAM?

The reviewer raises a good point. The nonideal flow behavior we observe in the TPOT and PAM reactors may be due to several potential issues, such as thermally induced convection, dead volumes, and channeling. As we point out in our response to comment A, we applied a laminar flow model with Taylor dispersion and obtained reasonable fits to the measured RTD's; however, this model does not help identify the specific issues for the observed nonideal flow. The initial size and location of eddies formed from convection currents and from dead volume will be different, but the cascade of eddies to smaller sizes will be similar. Both result in complex motion that broadens the RTD. Without doing a detailed flow dynamics analysis that includes the eddies generated by the chamber shape (i.e., dead volume) and generated by convection, it is not possible to distinguish between their effects on flow tube RTDs. We think such an analysis is beyond the scope of this paper.

We did not measure thermal gradients inside the flow tubes, nor did we measure the temperature of the gas exiting the TPOT and PAM; we did measure the temperature inside the PAM chamber (p. 5220, lines 19-22).

We edited the text in the appropriate places as follows (changes bolded):

p. 5215, line 20: "…however, the larger volume of the PAM may facilitate more convection **or dead volume**"

p. 5222, lines 7-8: "…aerosol expansions and contractions in the flow tube designs that are not accounted for in the simple theory and may induce convection **or dead volume** in the flow tubes"

p. 5224, lines 12-13: "…a secondary component that is slower and more diffuse due to convection-induced recirculation **or entrainment in dead volumes** within the reactors"

p. 5225, lines 1-2: "greater fractional particle losses for particles entrained in convection currents**/dead volumes**…"

p. 5235, line 12: "These results suggest that less dispersion **~~(i.e., convection)~~** causes narrower RTDs in the TPOT than in the PAM, as expected."

4. Fig 2 and Fig 3 captions are incorrect (they are reversed)
Fixed.

5. The authors should show H/C ratios as well as O/C ratios for each system. This gives a more complete picture of the elemental composition of the particles?
We added subpanels to Figures 4 and 5 showing the H/C ratio as a function of OH exposure for oxidized BES, m-xylene SOA, and a-pinene SOA in the PAM and TPOT. We did not add H/C ratios for the smog chamber SOA because the smog chamber AMS data consists of unit mass resolution measurements, and to our knowledge there is no published method relating H/C to UMR measurements analogous to the Aiken et al. manuscript (ES&T, 2008) relating O/C to m/z = 44. We also edited the text in the following places (changes bolded):

p. 5220, lines 1-3: "Elemental analysis (Aiken et al., 2008) was performed on the HR-ToF-AMS data to determine the aerosol **hydrogen-to-carbon (H/C)** and oxygen-to-carbon (O/C) ratio**s**, **the latter of which was** used as a proxy for …"

p. 5225, line 22: "3.4.1. O/C **and H/C** ratio**s**

p. 5225, line 23: "Figure**s** 4a and **4b** shows the evolution of the aerosol oxygen-to-carbon (O/C) and **hydrogen-to-carbon (H/C)** ratio**s** for BES particles…"

p. 5225, lines 26-27: “The measured O/C **and H/C** ratios of unoxidized BES **were 0.04** and **1.96**, compared with … molecular formula O/C **and H/C** ratios of 0.15 **and 1.92** (C26H50O4)”.

p. 5225, line 27 – p. 5226, line 1: “As the OH exposure was increased, the measured O/C ratio increased to 0.20 in the TPOT and PAM. **The corresponding H/C ratios decreased to 1.78 in the flow tubes.**”

p. 5227, line 6: “O/C **and H/C** ratios”

p. 5227, line 7: “Figure 5 shows the O/C and **H/C** ratios**”**

p. 5227, lines 10-12: “As shown in Fig. 5a at low OH exposure (< 1011 molec cm−3 s), the O/C ratio for m-xylene SOA generated in the flow tubes was 0.63 ± 0.03 in the TPOT and 0.60 ± 0.01 in the PAM. **The corresponding H/C ratios were 1.46 ± 0.06 in the TPOT and 1.43 ± 0.07 in the PAM (Fig. 5b)**.”

p. 5227, lines 15-18: “As the OH exposure was increased from ~1011 to ~1012 molec cm−3 s, the O/C ratio of m-xylene SOA increased to 0.77 ± 0.05 in the TPOT and 1.24 ± 0.07 in the PAM. **These increases in O/C were accompanied by the H/C ratio decreasing to 1.38 ± 0.06 in the TPOT and 1.10 ± 0.05 in the PAM, indicating that the PAM-generated SOA was more oxidized**. Differences in the O/C and **H/C** ratios of m-xylene SOA…”

p. 5227, lines 26-27: “In Fig. 5**c**, the O/C ratio for α-pinene SOA generated in both flow tubes was 0.45 ± 0.02 at low OH exposures. **The corresponding H/C ratios were 1.51 ± 0.09 in the TPOT and 1.45 ± 0.07 in the PAM (Fig. 5d).”**

p. 5228, lines 1-2: **“**At high OH exposures, the O/C ratio of α-pinene SOA increased to 0.70 ± 0.12 in the TPOT and 0.90 ± 0.05 in the PAM, **with corresponding H/C ratios of 1.45 ± 0.07 in the TPOT and 1.17 ± 0.06 in the PAM.”**

p. 5228, line 9**: “This is captured by the different evolution of O/C and H/C with OH exposure in the TPOT and PAM, which may illustrate the formation of different functional groups as a result of oxidation (Heald et al, 2009).”**

We also edited the Figure 4 and Figure 5 captions accordingly, and added this citation to the References section:

Heald, C. L., Kroll, J. H., Jimenez, J. L., Docherty, K. S., DeCarlo, P. F., Aiken, A. C., Chen, Q., Martin, S. T., Farmer, D. K. Farmer, and Artaxo, P.: A simplified description of the evolution of organic aerosol composition in the atmosphere, Geophys. Res. Lett., 37, L08803, 2010.

6. Page 5214 line 10. References to flow tube studies of organic particles needs to be expanded to accurately represent the larger number of groups conducting these kinds

of studies. For example, J. D. Hearn and G. D. Smith, Geophysical Research Letters, 2006, 33. J. D. Smith, J. H. Kroll, C. D. Cappa, D. L. Che, C. L. Liu, M. Ahmed, S. R. Leone, D. R. Worsnop and K. R. Wilson, Atmospheric Chemistry and Physics, 2009, 9, 3209-3222. V. F. McNeill, R. L. N. Yatavelli, J. A. Thornton, C. B. Stipe and O. Landgrebe, Atmospheric Chemistr y and Physics, 2008, 8, 5465-5476.

We added the references suggested by the reviewer.

Response to Reviewer 2 Comments

Note: the second reviewer provided 19 specific comments (numbered 1-19) and 3 technical corrections. In our response to this reviewer's comments, we have listed the specific comments as comments #1-19 and the technical corrections as comments #20-22.

1. Page 5213, lines 19-21: Here and throughout the paper statements that particles had similar chemical composition cannot be made based on AMS measurements. Similar chemical composition means the particles are composed of similar chemical compounds, but the AMS does not measure chemical compounds. It measures a simple, highly fragmented mass spectrum that is influenced by chemical composition, but the information it gives is not chemical composition but a measure of oxidation state. This is why one can correlate m/z 44/43 ratios with O/C ratios. Instead of stating that measurements of chemical composition were made with the AMS, the authors should state that measurements of aerosol mass spectra and O/C ratios were made, which is technically correct. Furthermore, I suggest the authors note that when particles in different systems had similar AMS mass spectra or O/C ratios it does not necessarily mean they had similar chemical composition. Conversely, differences in mass spectra and O/C ratios are clear indications that two aerosols have different chemical composition.

At the reviewer's suggestion, we made the following revisions (bolded):

p. 5213, line 11: "(4) **aerosol mass spectra, oxygen-to-carbon (O/C) ratios** and cloud condensation nuclei (CCN) activity"
p. 5213, line 12: "(5) **aerosol mass spectra, O/C ratios,**"
p. 5213, lines 19-21: "Oxidized BES particles had similar **O/C ratios** and CCN activity at OH exposures greater than 10^{11} molec cm^{-3} s, but different CCN activity at lower OH exposures. The **O/C ratios**…"
p. 5215, lines 25 – 27: "(4) **Aerosol mass spectrometer (AMS)** and cloud condensation nuclei (CCN) activity measurements of BES particles exposed to OH radicals, and (5) **AMS**, CCN activity, and…"
p. 5219, line 25: "**Bulk chemical composition** of the aerosol was measured with an Aerodyne…"
p. 5225, line 21: "**O/C ratio** and CCN activity"
p. 5225, line 22: "3.4.1. **O/C ratio**"
p. 5227, line 1: "3.5 **O/C ratio**, yield…:
p. 5227, line 6: "3.5.1. **O/C ratio"**
p. 5228, line 8:" "Differences in a-pinene SOA **O/C ratio**…"
p. 5229, line 15: "As is evident in Figs. 6 and 7, at comparable OH exposures, the SOA **O/C ratio**…"
p. 5231, line 10: "Third, **O/C ratio** and CCN activity…"

p. 5231, lines 11-12: "Fourth**, O/C ratio**…"
p. 5231, line 25: "Under similar oxidizing conditions, the **O/C ratio**…"
p. 5231, line 28: "SOA O/C ratio…"

2. Page 5213, lines 24-26: Is this the only possible explanation? Given the complexity of SOA formation and the limited amount of information gained from the measurements, the authors are more definitive than I would be.
We think this is the most likely explanation, but the reviewer's point that there could be other explanations is well taken. We changed this statement to read:

Page 5213, lines 24-26: At comparable OH exposures, flow tube SOA was more oxidized than smog chamber SOA**, possibly** because of faster gas-phase oxidation relative to particle nucleation."

3. I suggest that the authors write a short section on the similarities and differences one might expect to see in the results obtained from the two flow tubes and smog chamber. This could be placed at the beginning of the Results & Discussion section. The authors have sufficient knowledge about how differences in the reactor designs might influence wall loss, aerosol chemical composition, sulfuric acid and SOA yields, and CCN activity. This would allow the authors to educate readers in a clear and systematic way about the proper ties of these different systems before overwhelming them with their results, many of which have rather speculative explanations. This approach also gives the reader the sense that this is hypothesis-driven research, since some plausible expectations are presented first, followed by results.

Beginning of Results and Discussion, added: "This study provides intercomparison measurements of aerosol chemical composition, aerosol CCN activity, and secondary aerosol yields. We expect that two fundamental properties of the different systems will most strongly affect aerosol measurements: (1) wall interactions and (2) residence time distributions (RTDs) of gases and particles in the reactors. Wall interactions (gas and particle) are influenced by a combination of reactor SA/V ratio and average residence time and influence the measured yields of oxidation products. The PAM is designed to minimize wall interactions, as compared with the TPOT. Specifically, the PAM has a SA/V ratio ~10× lower than the TPOT while the average TPOT and PAM residence times are similar, the PAM has a larger radius which minimizes interactions with the walls due to diffusion, and the PAM subsamples flow from the center of the tube whereas the TPOT samples the total flow. Flow tube transmission efficiency measurements in Sections 3.1 and 3.2 show the effects of wall interactions on measured gas and particle yields. RTDs are influenced by reactor geometry and flow rate, as characterized by the Reynolds number (Re). Flow is laminar in both the TPOT (Re = 15) and PAM (Re = 55); however, nonideal flow behaviors in the two systems are expected to produce flow instabilities that broaden the RTD's. Consequently, a precursor input to the reactors in the presence of oxidants may sample a range of OH exposures. This may affect the measured chemical composition and CCN activity of SOA particles generated in the flow tubes and compared with the chamber. Measurements of gas and particle RTDs are presented in Section 3.3. The influence of these two factors on the PAM and TPOT SOA chemistry, CCN activity, and SOA yields are presented in Sections 3.4 and 3.5. Finally, the Caltech smog chamber SA/V ratio is much lower than in the TPOT and PAM, while the average residence time is much longer. Flow tube - smog chamber intercomparison measurements presented in Section 3.5 provide insight into the relative importance of the two factors in influencing SOA chemistry and yields."

4. Page 5218, lines 8-10: Please provide a more detailed description of the PAM design features that reduce wall loss. This is not clear from this simple sentence or the figure. One should not force the reader to go to another reference for this information. It is sufficiently important for this paper that it justifies a stand-alone explanation.

We have added the following detailed descriptions of the PAM design features that help reduce wall effects.

IN INTRO:

In this paper, we compare two flow tube reactors of different designs. One is a glass flow tube of conventional dimensions (34 cm length x 7.3 cm diameter) developed at the University of Toronto for controlled heterogeneous oxidation studies of particles (George et al., 2007). The other flow tube developed at the Pennsylvania State University has a significantly larger volume (46 cm length x 22 cm diameter), providing a smaller surface-to-volume (SA/V) ratio (Kang et al.,2007). The two flow tubes are designated as the Toronto Photo-Oxidation Tube (TPOT) and Potential Aerosol Mass(PAM) reactors, respectively. An important distinction between the two flow tubes is that attempts were made to minimize wall interactions in the PAM **(e.g. large radial/axial ratio and flow is subsampled from the center of the reactor while flow near the walls is dumped),** whereas no such attempts were made with the TPOT. The TPOT was designed to generate high OH concentrations for heterogeneous oxidation experiments. The PAM was designed for the study of gas-to-particle formation processes, and was adopted for aerosol kinetic studies by the Boston College – Aerodyne Research research group. The speed of flow through both flow tubes was slow: 0.35 cm s^{-1} in the TPOT and 0.37 cm s^{-1} in the PAM. The SA/V ratio is significantly smaller for the PAM (0.23 cm^{-1}) than for the TPOT (2.8 cm^{-1}); however, the larger volume of the PAM may facilitate more convection or dead volume. Results are compared to smog chamber data where applicable.

SECTION 2.2.2

"The Potential Aerosol Mass (PAM) reactor is a horizontal 15 L glass cylindrical chamber that is 46 cm long x 22 cm ID. **In an effort to reduce wall effects on the photochemistry, the PAM flow reactor was designed with a larger radial/axial dimension ratio and a smaller surface area to volume ratio relative to other flow reactors (e.g. TPOT) and the sample flow (87% of total flow) is subsampled from the center of the reactor, with a secondary flow (13% of total flow) diverted at the exit through an internal perforated ring that dumps air near the reactor walls. The current PAM design** is different from the PAM reactor used in Kang etal. (2007), which was a vertical 19 L Teflon bag with the flow entering the top and a length of 60 cm. Carrier gas flows of 8.5 lpm N2 and 0.5 lpm O2 were used, with 8.5 lpmof flow pulled through the PAM and 0.5 lpm of excess flow removed prior to the reactor. At these flow conditions, the τplug was 106 s, compared to a τplug of 240 s used by Kang et al. (2007). Four mercury lamps (BHK Inc.) with peak emission intensity at λ = 254 nm are mounted in teflon-coated quartz cylinders inside the chamber. The lamp-mounting cylinders were continually purged with N2 to prevent O3 formation and remove outgassing compounds. Unlike the TPOT and the PAM chamber in Kang et al. (2007), the OH exposure in the PAM was varied by changing the UV light intensity via stepping the lamp voltages between 0 and 110V."

5. Page 5222 and Figure 3. I suggest adding results of the Hinds-type calculations of particle transmission efficiencies to the figure so that the reader can get a better sense of discrepancies.
Per the reviewer's suggestion, we added to Figure 2 the theoretical, size-dependent particle transmission efficiency if governed by diffusional and gravitational losses through a tube under laminar flow conditions. Also, we added the following to the discussion (changes bolded):

Page 5222, lines 4-6: "The particle transmission efficiencies for the two systems shown in Figure 2 have increasing size-dependent trends as simple theory predicts (Hinds, 1999); however, the magnitudes of **measured** particle losses are **significantly** greater than predicted by theory."

6. Page 5222-5223, section 3.2: I suggest explicitly differentiating between H2SO4 vapor and H2SO4 particles in this discussion. As it is now I think H2SO4 refers sometimes to one or the other, and yet it is only the H2SO4 in particles that is measured.
At the reviewer's suggestion, we explicitly differentiated between H2SO4 vapor and particles in the appropriate locations. The text in Section 3.2 now reads as follows (changes bolded):

"However, it may not be a perfect surrogate […] because the wall loss behavior of the product gases (i.e., H2SO4 **vapor** and semivolatile organic compounds) may differ. The transmission efficiency of H2SO4 **particles** was calculated from the ratio of the measured aerosol mass to the theoretical H2SO4 **aerosol** yield from the known SO2−OH reaction
[…]
Two trends were observed […] increasing the SO2 concentration increased the transmission efficiency of H2SO4 **particles** because a smaller fraction of SO2 and H2SO4 vapor was required to passivate the walls ~~**leaving more SO2 to form H2SO4 vapor**~~. Second, H2SO4 **particle** transmission efficiency was affected by the OH concentration. At low OH concentration, […] H2SO4 **aerosol** yield was more affected by SO2 and/or H2SO4 **vapor** wall loss. At high OH concentration […] H2SO4 **aerosol** yield was less affected by **losses of SO2 and H2SO4 vapor to the walls**. As the OH exposure was increased […] in the TPOT […] the **particle** transmission efficiency increased […]. Over a similar OH exposure range in the PAM, the […[**particle** transmission efficiency increased […]. **Assuming typical experimental conditions of 10^5 particles cm^{-3} with a mean diameter of 75 nm and a gas-phase diffusion coefficient of 0.1 cm^2 s^{-1} , the characteristic timescale for condensation of H2SO4 vapors onto preexisting particles was ~50 sec. Timescales for gas-phase diffusional wall losses were ~70 sec in the TPOT and ~600 sec in the PAM. These calculations indicate that flow tube walls were competitive with H2SO4 particles as a sink for H2SO4 vapors in the TPOT and significantly less competitive with H2SO4 particles in the PAM.**

Average H2SO4 **particle** transmission efficiencies in the TPOT and PAM are plotted in Fig. 2 […] The **particle** transmission efficiencies through the flow tubes are shown to be similar for BES and H2SO4 **particles**. For the test conditions here, the yields for SO2 oxidation (H2SO4 particle formation) saturate at **particle** transmission efficiencies of ~0.5 due to size-dependent particle losses in the flow reactors."

7. Page 5222-5223, section 3.2: My interpretation of the discussion is that loss of H2SO4 particles to the walls is considered but not loss of H2SO4 vapor. This can also be estimated using Hinds-type calculations. How does the timescale for this loss of vapor to the walls compare with the timescale for condensation onto the particles? The discussion focuses entirely on loss of SO2, so I get the sense that the authors are assuming that H2SO4 instantly condenses onto particles.

We calculated relevant time constants for condensation of H2SO4 vapor on the walls of the TPOT/PAM flow tubes versus condensation onto the particles (assuming typical conditions of 75nm diameter H_2SO_4 particles with a number concentration of 10^5 cm^{-3}). We considered diffusion limitations in these calculations (assuming a diffusion coefficient of 0.1 cm^2 s^{-1}). In both flow tubes, the timescale for condensation onto the particles is 50 sec. In the TPOT, the timescale for loss of vapor to the walls was about 70 sec, compared to a timescale of 600 sec in the PAM. These are "back-of-the-envelope" type calculations, but nonetheless indicate the relative importance of the walls in both flow tubes. As a result, we modified the text in Section 3.2 as shown in our reply to comment #6.

8. Page 5223-5224, section 3.3: Please provide the Reynolds Numbers for the TPOT and PAM flow conditions.
In responding to comment #3 from reviewer #2, we provided the Reynolds numbers for the TPOT (15) and PAM (55) at the beginning of the Results and Discussion section. This information is also included in section A3 of the Appendix.

9. Page 5225, lines 25-27: I would think that a factor of 4 difference between the measured AMS O/C ratio of BES of 0.15 and the true value of 0.04 would be cause for concern. I suggest some comments on the degree of confidence in the O/C measurements.
Please see our reply to comment #5 raised by reviewer #1.

10. Sections 3.4 and 3.5: I suggest that when comparing AMS results on OA in the PAM, TPOT, and smog chamber that at least in some cases mass spectra are shown, not just O/C ratios. This will allow readers to get a better feel for how similar or different the OA mass spectra are in these systems and the information that is being used to distinguish differences.
We agree with the reviewer that more information on chemical composition is needed than just O/C ratio (similar to comment #8 by the other reviewer). Our concern is that adding mass spectra has limited utility in this paper because in several cases, the different OA systems have poor overlap, especially at low OH exposure conditions. This makes a straightforward comparison difficult. Per the other reviewer's suggestion, we have added H/C ratio data for the three systems examined in this study, which, together with O/C

ratio, provides an additional amount of chemical insight, as shown in Heald et al (2009) when constructing van Krevelen diagrams that show H/C as a function of O/C. We think this addition addresses the general comment made by both reviewers that O/C alone is insufficient.

11. Section 3.5: I suggest providing some estimates for possible timescales for loss of organic vapors to walls in the flow tubes and flow chambers and gas-particle partitioning. This can be done assuming maximum possible diffusion-limited rates. It is not enough to compare differences in particle mass loadings and assume gas-particle equilibrium, since the particles are competing with the walls for vapors. These timescales can be used to improve the comparisons of SOA formation in the systems.
Per the reviewer's suggestion, we calculated maximum diffusion-limited timescales for loss of vapors to the flow tube walls assuming a diffusion coefficient of 0.1 cm2/s (see reply to comments #6 and #7). These calculations confirmed that wall losses were more significant in the TPOT and that different gas-particle-wall equilibria might have resulted in different organic aerosol composition. We agree that this is a more suitable explanation for observed trends than assuming gas-particle equilibrium and comparing mass loadings. As a result, we edited the text in Section 3.5 as shown below **(changes bolded):**

Page 5227, lines 17 – 25: "Differences in the O/C ratio of m-xylene SOA at ~10^{12} molec cm^{-3} s OH exposure may be related to different gas-phase residence time distributions (as discussed above), or to different organic aerosol concentrations (C_{OA}). **Assuming a diffusion coefficient of 0.1 cm^2 s^{-1} for oxidized vapors, characteristic vapor wall loss timescales were much shorter in the TPOT than in the PAM (Section 3.2) despite similar average residence times (Figure 2). This indicates that walls were a more competitive sink for vapors in the TPOT than in the PAM. In describing the effects of gas-wall partitioning on SOA formation, Matsunaga and Ziemann (2010) treated smog chamber walls as an effective organic aerosol concentration (Cw). If the sum of C_{OA} and Cw was larger in the TPOT than in the PAM,** the condensed-phase partitioning of semivolatile compounds with effective saturation concentrations (C∗; Donahue et al., 2006) similar to $C_{OA} + C_w$ would **increase**. This would enrich the aerosol with less-oxidized, higher-volatility products having lower O/C. ~~**For the most-oxidized m-xylene SOA, COA was higher in the TPOT (16–42 µg m^{-3}) than in the PAM (10 µg m^{-3}). If these m-xylene products had similar C∗, their phase partitioning would be strongly affected by the difference in COA.**~~**"**

p. 5228, lines 5-6: ~~Because COA for the most oxidized α-pinene SOA was similar in the TPOT (COA = 124 µg m−3) and PAM (COA = 116–141 µg m−3), the different O/C ratios of α-pinene SOA cannot be explained by COA.~~ **As was the case with m-xylene SOA**, differences in α-pinene SOA O/C **and H/C** ratios may be due to the different residence time distributions **or to different $C^*/(C_{OA} + C_w)$ ratios**, **as well as** to different flow tube designs."

12. Section 3.5: It should be kept in mind in this discussion that a major difference between the flow tubes and the smog chamber is that the much longer time available for reactions in the chamber will allow condensed phase oligomerization reactions to occur

to an extent that will not happen on 100 s time scales. For both the SOA systems studied here it is known that in smog chambers oligomers contribute large fractions of the mass.
We agree with this point raised by the reviewer, and added the following (bolded) to the discussion in Section 3.5.2:

p. 5229, lines 21-23: "Oxidation rate, **oligomerization reactions,** UV lamp intensity/ wavelength, and/or wall effects may have influenced SOA yield. Faster gas-phase oxidation relative to nucleation could explain lower yields in the flow tubes than in the smog chamber. **Longer oxidation timescales in the smog chamber could favor the formation of oligomers to an extent that is not possible in the flow tubes (e.g. Hallquist et al. (2009) and references therein).**

Along with the corresponding citation in the References section:

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffman, T., Iinuma Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5236, 2009.

13. Page 5226, section 3.4.2: Why not use Kappa values to quantify the CCN activity of these systems, since these values can be more easily compared to the literature? Sc seems like a less useful quantity.
We changed the y-axes in Figures 4b, 8a, and 8b to show kappa as a function of OH exposure (instead of critical supersaturation), and updated Figure 4 and Figure 8 captions accordingly.

Page 5220, line 14, added: "CCN activity was characterized in terms of the hygroscopicity parameter κ as defined by Petters and Kreidenweis (2007)."

Page 5226, lines 7 – 16 (changes bolded): "Figure 4b shows results of CCN activity studies expressed in terms of the **hygroscopicity parameter κ** of heterogeneously oxidized BES particles as a function of OH exposure. As expected, **κ increased** as the OH exposure and O/C ratio increased (Petters et al, 2006; Massoli et al., 2010). The **κ** values for particles with O/C > 0.08 were between **0.012–0.028**. At an OH exposure of ~1.4 × 10^{12} molec cm−3 s, the **κ** values measured with the two flow tubes were within **50%** of each other. However, at lower OH exposures for O/C < 0.08, the **κ** values measured in the two flow tubes diverged considerably, differing by as much as **100%.** Under the low oxidation levels with the large **κ** discrepancies, the CCN activation curves for both systems are broad (Fig. A2). The **κ** discrepancy and …"

Page 5230, lines 6-12 (changes bolded): "Figure 8 plots the **hygroscopicity parameter (κ)** of flow tube m-xylene and α-pinene SOA particles as a function of OH exposure. The TPOT and PAM measurements agreed within **30%** and **25%** for m-xylene and α-pinene

SOA, respectively. As with oxidized BES particles, **κ increased** with increasing OH exposure and corresponding O/C ratio. For particles generated at an OH exposure of ~1.5 × 10^{12} molec cm−3 s, PAM SOA had a slightly higher O/C ratio and **higher κ** than TPOT SOA. This is consistent with more highly-oxidized hydrophilic particles having higher water solubility **(Massoli et al, 2010).**

Added appropriate citation to References: "Petters, M.D., and Kreidenweis, S.M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos. Chem. Phys., 7, 1961-1971, 2007."

14. Page 5226, lines 24-26: Can't the explanation for the differences in CCN activity at low OH exposure be that there are significant differences in the chemical compositions of the oxidized BES particles (which is what determines CCN activity) that are not captured by a simple O/C ratio?
We agree – we added a closing sentence for this section (after lines 24-26 on p. 5226) stating: "This may be due to different chemical composition that is captured by the CCN measurements but not the O/C and H/C ratio measurements".

15. Page 5227, lines 27-28 through Page 5228, line 9: It seems that because the alpha-pinene reacts with O3 before exposure to OH in the TPOT that the largest discrepancy in O/C ratios between the TPOT and PAM should be at low OH exposure, since the oxidation history is the most different in this case.
The reviewer raises a valid point. Unfortunately, we were not able to collect TPOT data for this system at low OH exposure (e.g. < 5*10^{11} molec cm^{-3} s) to confirm this hypothesis. Extrapolating TPOT measurements between O3-only conditions and OH+O3 conditions implies that the discrepancy in O/C ratios at low OH exposure conditions will be small. As the reviewer pointed out in comment #1, similar O/C ratio does not necessarily imply similar chemical composition, as could be the case here.

16. Page 5228, lines 16-18: What is the evidence that the SOA yields differed because of gas-phase wall losses?
To the extent that oxidation product vapors are lost to the walls in a (qualitatively) similar manner as SO2 / H2SO4, the transmission efficiency measurements of SO2 and H2SO4 serve as indirect evidence of greater gas-phase wall losses. We clarified this point by rewriting:

p. 5228, lines 16-18: "SOA yields in the TPOT were lower than in the PAM and Caltech chamber. This is presumably because the higher TPOT SA/V ratio caused greater losses of gas-phase precursors and/or oxidation products to the walls, as was observed with SO_2 and H_2SO_4 (Sections 3.1.1 and 3.2)."

17. Page 5228, lines 25-27 through Page 5229, line 2: It seems like the SOA yields being compared here are not statistically different. Why speculate on causes for possible differences that may not exist?
We think the reviewer misinterpreted this section. We are comparing the maximum measured yields to yields measured at lower and higher OH exposures. We are not

comparing the yields measured at low OH exposures to the yields measured at high OH exposures. We rewrote this section to make the point more clearly (changes bolded):

p. 5228, lines 25-27 – p. 5229, line 2: For lower and higher OH exposures, yields of PAM α-pinene SOA were different (0.26 ± 0.04 and 0.19 ± 0.03) than the maximum measured yield **(0.38 ± 0.08)** at 3 × 10^{11} molec cm^{-3} s OH exposure. This was also the case for yields of PAM m-xylene SOA, which were 0.024 ± 0.005 at lower exposures and 0.022 ± 0.003 at higher OH exposures **compared to the maximum measured yield (0.17 ± 0.07).**

18. Page 5230, lines 17-19: Can the authors suggest possible materials that could be used instead of Pyrex that meet this criterion?

p. 5230, lines 17-19, added (changes bolded): "Replacing pyrex flow tube walls with a passivated conductive material **(e.g. Silconert-coated stainless steel or high nickel-alloy steel)** could increase particle transmission efficiency by minimizing electrostatic losses.

19. Page 5230, lines 23-25: Please be more specific about how to manipulate flows to avoid wall effects.

We added similar information as was used in replying to the reviewer's comment #4:

p. 5230, following line 25: "As an example, the primary sample flow from the PAM subsamples gas and particles from the center of the tube (minimizing diffusional interactions with the walls) and a secondary peripheral flow that removed air near the reactor walls."

20. Page 5223, line 9: Should be Fig. 3 not Fig. 2.

Fixed.

21. Page 5224, line 15: "are times" should be 'times are".

Fixed (this correction applied to page 5225, line 15).

22. Figure 2 and 3 images should be switched; the captions are all right.

Fixed.