

## AUTHOR COMMENTS

### GENERAL COMMENTS

The authors would like to thank the three anonymous referees for their helpful comments and suggestions. We have addressed all comments which we believe significantly improved the revised manuscript.

Two main concerns raised by the referees were (1) the effect of losses of semi-volatile vapors to the Teflon® chamber walls on our data and their implications and (2) that the implications of our work to the atmosphere were not clear in the original version of the manuscript. We address these main concerns here and address the more detailed comments below.

#### (1) Losses of semi-volatile vapors to the chamber walls

We agree with the Referees that wall losses of semi-volatile species occur in environmental chambers such as the chamber used for this work, and we have added a discussion of these losses in the revised manuscript. The challenges resulting from these losses are not unique to our study but rather apply to all environmental chamber experiments. Currently, losses of semi-volatile species are poorly constrained, and there is no consensus on how to accurately account for them.

In all of the experiments described here, the condensation sink after particle formation was approximately 1/min, while the initial condensation sink to ammonium sulfate seeds in seeded experiments ranged between 0.6 and 1/min. The timescale for sulfuric acid vapor wall loss in the Carnegie Mellon chamber is approximately 0.1/min, as determined by chemical ionization mass spectrometer measurement of sulfuric acid loss (V. Hofbauer, personal communication). Thus, in all of the seeded experiments, condensing vapors encountered the seeds approximately 10 times before encountering the walls, while in nucleation experiments the suspended aerosol population quickly grew to a size where this was also true. Thus, while wall losses of semi-volatile vapors are a source of uncertainty, we have attempted to ensure that vapor-particle interactions at least dominate over vapor-wall interactions. It is therefore reasonable to expect that observed differences between experiments are not driven by interactions with the walls but instead by chemical processing of the organic aerosol.

#### (2) Implications of work to the atmosphere

We have modified the discussion and the conclusion section to more specifically offer conclusions and atmospheric implications of this work. Uncertainties remain and underline the need for additional studies, but our results do offer new insights as well as directions for future study. Contributions and implications of our work include:

- Confirmation that photochemical aging influences SOA, as evidenced by the observed relationship between exposure to OH and physicochemical properties of SOA formed from the oxidation of toluene and other small aromatic VOCs
- A measured relationship between changes in organic aerosol (OA) oxidation state and saturation vapor pressure
- A measured relationship between changes in (OA) oxidation state and hygroscopicity. We found that there is no significant correlation between oxidation state and

hygroscopicity, which is an important result and suggests that both properties need to be measured to more fully characterize the OA.

## SPECIFIC COMMENTS

All referee comments are addressed below. Referee comments are included in italics; author responses are written in plain text.

### Referee #1

*(1) It isn't clear what new scientific knowledge this paper adds to the literature and it is less clear what the implications of this work are for the atmosphere. The manuscript would be greatly improved if the authors can offer more definitive and clear conclusions and discuss what the atmospheric implications of this work are.*

This has been addressed in the revised manuscript and in the response to general comment (2) above.

*(2) The authors do not discuss irreversible wall loss of semi-volatile species, which has been shown to be substantial and important for this (and many other) chemical system. ... Other researchers have also concluded that faster chemistry (i.e., higher OH exposure) helps to minimize wall loss (e.g. (Kroll et al., 2007)) and that lower-volatility, more highly oxidized species are more likely to be lost (Matsunaga and Ziemann, 2010). Therefore, it seems plausible that the entirety of section 3.2 could/should be explained by variable wall loss driven by the different oxidation conditions. Figure 4 strongly suggests these effects, with lower yields found at similar aerosol mass loadings for the slower reacting, lower OH exposure experiment. Furthermore, the difficulty the researchers report in reproducing their observations during experiment designed to have identical oxidizing conditions (p 31458, second paragraph) suggests that wall loss is a contributing factor (probably the driving factor) to their measurements in these two experiments.*

As explained in our general comment (1) above it is reasonable to expect that observed differences between experiments are not driven by interactions with the walls but instead by chemical processing of the organic aerosol. We disagree with the Referee that the entirety of section 3.2 could be explained by variable wall loss driven by the oxidation conditions, and that Figure 4 strongly suggests this. To review, Expt. 7 is the lower OH exposure experiment and showed lower mass yields, a lower extent of oxidation and more volatile organic aerosol compared to Expt. 9. We note that the exposure to UV and OH in Expt. 7 (and therefore the time during which organic aerosol was formed) was only 10 minutes long, compared to 3 hours in Exp. 9. Thus, the time available for wall losses is much higher during Expt. 9 than during Expt. 7, and yet the OA mass yields for Expt. 9 are higher than the yields for Expt. 7. Furthermore, if more highly oxidized species are more likely to be lost, Expt. 9 would be more strongly affected

by wall losses. In summary, while there is one effect (slower reactions) that may increase wall losses in Expt. 7 compared to Expt. 9, there are two effects (time of OA formation and extent of oxidation of products formed) that would increase wall losses in Expt. 9 compared to Expt. 7. Thus, overall we do not expect wall losses to be higher in Expt. 7 compared to Expt. 9, and it is reasonable to assume that differences in the aerosol mass yields shown in Figure 4 are primarily due to differences in photochemical conditions.

Furthermore, our difficulty in repeating experiments with identical oxidizing conditions stemmed from our method of HONO injection, which we have found was not reproducible. We have since fixed this issue and are now using a more reproducible method of injection. Thus we believe that the different experiments designed to have the same oxidizing conditions actually had different oxidizing conditions because some HONO injections resulted in little or no HONO actually injected into the chamber.

**(3)** *The Materials and Methods section of the paper should be significantly shortened with much of the material either left out altogether or moved to the supplementary material*

We have moved a significant amount of material from the main manuscript to the supplementary material.

#### Technical and Editorial Comments

**(4)** *Title: Since the author don't separate aging from SOA formation and acknowledge this in the manuscript, shouldn't the title be changed to reflect this fact?*

We have modified the title. The revised title now reads "Formation and Aging of Secondary Organic Aerosol from Toluene: Changes in Chemical Composition, Volatility and Hygroscopicity"

**(5)** *P 31455, Lines 3-5. It seems very unlikely that the mean carbon oxidation state is three, 20 minutes into the experiment. This would require approximately 10 oxygen atoms being added to the molecule in 20 minutes. The authors should remove this statement from the manuscript or justify how this could be possible. It seems more likely that the unreasonably high oxidation state is a result of low S/N or some other artifact.*

Upon careful reconsideration of the data we have determined that this high initial oxidation state was indeed an artifact. First, we had made a mathematical error in calculating oxidation state from O:C and H:C values. Second, a small amount of background organic signal (equivalent to approximately  $0.2 \mu\text{g}/\text{m}^3$  see next comment) with very high oxidation state caused this high initial oxidation state. After subtracting the effects of this background organic aerosol on the oxidation state measurement, the oxidation state of the toluene SOA is approximately constant throughout the experiment as shown in the updated top panel of Figure 2. We have also updated the values of oxidation state in Table 1 and in the analysis of volatility and hygroscopicity for

this experiment (Figures 9 and 10), as well as the associated discussion. Organic aerosol data from the other experiments did not suffer from this background.

**(6)** *Figure 2, Experiment 2 panel: It appears that the organic aerosol concentration at the beginning of the experiment is not zero. Please comment on the source of the background aerosol.*

The small amount of organic aerosol ( $\sim 0.2 \mu\text{g}/\text{m}^3$ ) was also present on that day when a particle filter was connected to the inlet of the HR-AMS; it therefore appears to be an instrument artifact. According to the HR-AMS data analysis the oxidation state of the background organic signal is approximately 2. It could therefore be due to material of very low vapor pressure slowly vaporizing from the HR-AMS heater - organic material that does not flash-vaporize at  $600^\circ\text{C}$ .

**(7)** *P31455, lines 14-16 and 23-24. There is a contradiction here or else the message the authors are trying to convey is unclear. Lines 14-16 say that the aerosol oxidation state increased in experiment 9 and in all other experiments. A few lines later, experiment 3 is discussed and the oxidation state decreases during the experiment. Please correct this.*

We clarified this in the revised manuscript: In experiment 3 the oxidation state increases initially but decreases during the long overnight irradiation period.

**(8)** *Figure 8. I recommend moving this figure to the supplemental material. It isn't discussed in the text, is only mentioned in one sentence, and only shows the fitting routine is adequate.*

We have moved this figure to the supplemental material as suggested by the referee.

**(9)** *Figure 9. The trendline seems to be driven to a large extent by the single point at the upper left in the graph. How confident are the authors in this point? Without it, it appears that the fit would produce a very different slope and therefore conclusion.*

The oxidation state of the point at the upper left was influenced by background organic signal as explained in the response to comments (5) and (6) above. Upon correcting the data for this background signal the data point moved down (to lower oxidation state). This datapoint now does not anymore drive the trendline: including the point results in a slope of 0.28; removing the point results in a slope of 0.31. Thus, we conclude that a change in the oxidation state of about 0.3 units results in a change in volatility of about one order of magnitude.

Referee 2:

AMS analysis:

**(1)** *They attribute all NO/NO<sub>2</sub> observed in AMS to organic nitrate since “no inorganic nitrate is added to or expected to be formed” (Page 31448, line 20). However, they add HONO which is photolyzed to NO, which is oxidized to NO<sub>2</sub> and further to HNO<sub>3</sub>. The observed ratio of NO/NO<sub>2</sub> = 8 is not a unique indicator for organic nitrate. This ratio varies from AMS to AMS and depends on the structure of ON. It has to be compared to the one recorded during their calibration using NH<sub>4</sub>NO<sub>3</sub>.*

The NO/NO<sub>2</sub> ratio measured during calibrations using NH<sub>4</sub>NO<sub>3</sub> is 2.4. This implies that the HNO<sub>3</sub> formed in these experiments does not partition appreciably to the (neutral) aerosol present in these experiments, consistent with its high vapor pressure. We have added this information to the revised manuscript.

**(2)** *The measured O:C are rather high for the rather low OH exposures. The H:C seems to be very high, in some cases higher than 2 (exp 3, 9). The precursor toluene has a H:C of 1.14. Where does all that hydrogen come from? Could it be a problem of the AMS analysis?*

The AMS analysis in this manuscript is non-standard in that it determines the amount of H<sub>2</sub>O<sup>+</sup> attributed to organics so that the mass of water does not correlate with the mass of organics ( $R < 0.01$ ) as expected for these low relative humidity experiments. The ratios of organic H<sub>2</sub>O<sup>+</sup> to (<sup>13</sup>CO<sub>2</sub><sup>+</sup> + CO<sub>2</sub><sup>+</sup>) are provided in Table 2 and ranged from 0.3 to 2.4, higher than the ratio of 0.225 in the default fragmentation table but consistent with recent calibration experiments (Canagaratna et al., 2015). This results in higher O:C and H:C ratios than when using the standard constant factor.

Hydrogen atoms can be added to the carbon backbone in these experiments through OH addition or by the reaction of HO<sub>2</sub> and RO<sub>2</sub> producing peroxides. Considering that O:C values were near 1, even a doubling of the H:C ratio of the precursor molecule is possible.

**(3)** *They conclude that “the methyl carbon atom is about three times less likely than the aromatic carbon atoms to form organic acids” (page 31462, line 11). Can they show from seeded blank experiments that there is no background formation of SOA producing CO<sub>2</sub> from 12C?*

Small concentrations of background organic signal such as was discovered to be present during experiment 2 could influence this result. Furthermore, as noted by Referee 3 not all CO<sub>2</sub><sup>+</sup> is necessarily due to organic acids. Due to these complications we have decided to remove these data and associated discussion from the revised manuscript.

**(4)** *Experiment 2 shows extremely high OSc in the beginning. These values (~3) are unbelievable even considering the multiperoxide formation mechanism recently reported. This experiment is reported with the highest OSc and defines basically the correlation between OSc and volatility (Fig. 9). All other points would yield a different dependence. How sure are the authors about the analysis of experiment 2. In Table 2 the OSc is given as 0.45. From Figure 2 it seems to be even higher and in Figure 10 it is shown as -0.2. It is also puzzling to see in Table 2*

*that the H<sub>2</sub>O/CO<sub>2</sub> is completely different from all the other experiments. Is this real or an issue of data analysis? Figure 2 indicates a background aerosol. How much does this influence the result?*

The high OSc at the beginning of experiment 2 was the result of an artifact related to the background aerosol as explained in the response to Comment 5 of Referee 1. We have corrected the data, all Figures and associated discussion in the revised manuscript.

**(5)** *Although not being an AMS specialist I wonder why the collection efficiency is so low (0.25), even for organics?*

AMS collection efficiency (CE) can differ between instruments and is still subject of active research. Recent work at Carnegie Mellon suggests a collection efficiency of organics of 0.3 (E. Robinson et al., in preparation). We also note that our collection efficiency estimation, since it is based on comparison of data from another instrument, could potentially account and correct for factors other than particle bounce at the vaporizer, for example the estimated ionization efficiency. The discussion of CE has been moved to the supplemental material in response to Referee #1.

Other:

**(6)** *They do not find a general correlation between OSc and hygroscopicity as was found by others. Thus they speculate on surfactants playing a role. I assume that kappa was calculated using ZSR for the mixed aerosols. As mentioned above, the aerosol might also contain inorganic nitrate which is not considered here and could explain observations.*

As mentioned in response to the Comment 1 above, our AMS data do not provide evidence for the presence of inorganic nitrate. Hence we have not changed this discussion in the revised version of our manuscript. We also note that while a number of other studies have found a link between OSc and hygroscopicity, our study is not unique in not having found such a correlation.

**(7)** *In the conclusions the authors state “experiments with higher OH exposure showed higher SOA mass yields”. This is shown for exactly 2 experiments.*

In the conclusions of the revised manuscript we have clarified that this was only shown for 2 experiments. We have also removed “mass yields” from the title of the manuscript to reflect that the focus of this manuscript was not on SOA mass yields. Nevertheless, we choose to report the SOA mass yields for the two experiments (Expts. 7 and 9) for which these data are available.

**(8)** *Two experiments were performed with other aromatics as seen in Table 1. No other information is given in the manuscript.*

Additional discussion of these experiments has been added to the revised manuscript. Organic aerosol formed in experiments which included VOCs other than toluene did not exhibit significantly different properties (specifically, volatility and hygroscopicity), suggesting that other small aromatic VOCs appear to behave similarly as toluene. The choice of using toluene as a “model system” therefore appears appropriate.

#### Technical comments

**(9)** *P31450, line 15: here density is fixed to 1.5 gcm<sup>-3</sup>. In table S1 other densities are reported.*

We used the estimated densities (from Table S1) to convert between mobility diameter and aerodynamic diameter. What we intended to emphasize in this line is that the CE / density optimization routine is much less sensitive to density than to CE (and that CE does not change significantly when fixing density at 1.5). This discussion has been clarified and moved to the supplemental information in the revised manuscript.

*P31456, line 20: the ratio would be 1/7*

**(10)** We have removed these data from the revised manuscript.

**(11)** *P31457, line 2: Light is reported at 100% in Table 1 for all four experiments. Therefore there is not lower UV intensity.*

There was a typographical error in Table 1; only 1/3 of the lights were used in Experiment 7. This was corrected in the revised manuscript.

**(12)** *P31459, line 6: Table 1 reports 100% UV lights Table 1: correct units for OH exposure*

There was a typographical error in Table 1; only 1/3 of the lights were used in Experiment 7. This was corrected in the revised manuscript. The units for OH exposure were also corrected in the revised manuscript.

**(13)** *Figure 4: correct numbers for OH exposure*

This was corrected in the revised manuscript.

Referee 3:

**(1)** *Why was toluene (the only aromatic studied in any detail) chosen for these experiments? Is there something about the chemistry that makes it an interesting and important choice?*

Toluene is frequently used as a model system to study organic aerosol formation from small aromatic VOCs (Seinfeld and Pandis, 2006).

**(2)** *Page 31450, Second paragraph: How does OA density compare with values calculated using the parameterization developed by Kuwata et al. (2012), ES&T, 46, 787? This is a useful way of checking for significant errors.*

The OA density values agree reasonably well. The average density (averaged over all experiments) predicted using the parameterization developed by Kuwata et al. (2012) is 1.42, while the average density predicted using the Kostenidou et al. (2007) algorithm is 1.34. For nine out of the eight experiments, the density predictions differ by less than 10%; for experiment 2 the density predictions differ by 16%. In the analysis presented by Kuwata et al., their parameterization “has an accuracy of 12% for more than 90% of the 31 atmospherically relevant compounds used in the training set”. Thus, the densities predicted by these different algorithms appear to agree within the uncertainties of the algorithms.

**(3)** *Page 31450, bottom paragraph: The approach for correcting for vapor loss to walls ignores the uptake into the Teflon film walls, which has been shown recently to be significant. Zhang et al. (2014) PNAS, 111, 5802 have shown that vapor wall losses in studies of SOA formation from toluene oxidation lead to underestimates in SOA yields by factors of 2–4. This issue should be discussed here and its potential effects on results, such as SOA mass, O/C ratios (loss of oxidized products to the walls that prevents further aging), etc.*

We acknowledge that wall losses are important, and a discussion of these effects has been added to the revised manuscript and is provided in our general comment (1). As also discussed in our general comment wall losses do not appear to dominate effects observed in these experiments.

**(4)** *Page 31453, first paragraph: This is the first I have heard of “shifting factors” and imagine this will be the case for many other readers. It would help to give the reader a feeling for what a certain relative reduction in “volatility” (an imprecise term) means in this framework. Is it somehow related to a relative change in average SOA vapor pressure or saturation concentration? Without this insight it is difficult to know if these represent large or small changes in “volatility”.*

A shifting factor of 10 implies a reduction in the SOA saturation mass concentrations of 1 order of magnitude.

**(5)** Page 31455, whole page: *There is no discussion of the observation that SOA was higher with seed than without. Why? According to the PNAS paper referenced in Comment 3, this is likely due to reduced wall loss of vapors, which will affect the interpretation of SOA results and O/C ratios. I suggest discussing this.*

We only have data on hydrocarbon concentrations for experiments 7, 8 and 9, all of which were seeded experiments. We therefore cannot compute aerosol mass yields for the unseeded experiments and cannot compare yields in seeded and unseeded experiments. While the amount of organic aerosol formed is higher for the seeded than the unseeded experiment shown in Figure 2, this could be due to factors other than the seed effect, most notably a difference in the amount of toluene reacted.

**(6)** Page 31455, bottom line: *What compounds are expected to photolyze at significant rates in these experiments?*

Peroxides, which can form from photo-oxidation of volatile organic compounds (VOCs) have been shown to photolyze under similar conditions (Surratt et al., 2006). A reference regarding this has been added to the revised manuscript.

**(7)** Figures 2 and 3. *I suggest adding toluene time profiles to these figures so that one can determine the extent to which early-generation products are still being formed vs. more aged products. These profiles should also be discussed along with the other quantities.*

The toluene time series has been added to Figure 2 of the revised manuscript, and a discussion has been added to the text. Toluene data were not available during experiment 4 (Figure 3)

**(8)** Page 31456, lines 20-25: *I am not aware of a mechanism for forming organic acids under the high NO<sub>x</sub> conditions of these experiments. Please provide a reference of definitive evidence by others that acids are formed. Might the CO<sub>2</sub><sup>+</sup> ion instead come from acylperoxynitrates (PAN-type compounds with formula R–C(O)OO–NO<sub>2</sub>) formed by oxidation of aldehydes, which are well established products of toluene oxidation, in the presence of NO<sub>2</sub>? See Chan et al. (2010), ACP, 10, 7169. This would be consistent with the large nitrate content of the SOA.*

It is generally observed that organic acids, especially diacids, show very high CO<sub>2</sub><sup>+</sup> (Canagaratna et al., 2015). However, the point is well taken that organic acids are not the sole source of CO<sub>2</sub><sup>+</sup> after electron-impact ionization of 600°C aerosol vapors. A counter-indication to peroxyacylnitrates as dominant source of the observed CO<sub>2</sub><sup>+</sup> is that the “nitrate” (NO<sup>+</sup> and NO<sub>2</sub><sup>+</sup>) signal in the SOA mass spectra was relatively volatile while the CO<sub>2</sub><sup>+</sup> signal was not. For example, when heating and evaporating the SOA formed in Expt. 9 at 100°C in the TD, the

fraction of the total organic signal due to “nitrate” ( $\text{NO}^+$  and  $\text{NO}_2^+$ ) decreased by a factor of 3 while the fraction of the total organic signal due to  $\text{CO}_2^+$  increased by approximately 40 percent.

**(9)** *Page 31457, lines 14-22: The Chan et al. (2010) reference given in Comment 8 indicates that for systems that form significant aldehydes, such as the one studied here, that SOA yields increase with increasing  $\text{NO}_2/\text{NO}$  ratio. This is worth including in this discussion.*

During experiments with multiple HONO injections the concentrations of  $\text{NO}_x$  in the system exceeded the maximum calibrated concentration of the  $\text{NO}_x$  monitor (1 ppm). In addition, interference from organic nitrates, HONO and  $\text{HNO}_3$  would complicate the quantification of  $\text{NO}_2$  concentrations in this system. Thus,  $\text{NO}_x$  concentrations are not discussed in detail in this manuscript.

**(10)** *Page 457, bottom paragraph: With regards to acylperoxynitrates, it might be mentioned that they might still be mostly stable in the TD for the 15 s residence time. Thermal decomposition lifetimes range from about 20 min to 5 s for temperatures 40–100 C [Orlando and Tyndall (2012), Chem. Soc. Rev., 41, 6294].*

In the AMS, organic molecules are fragmented during flash vaporization and/or due to harsh electron impact ionization. Therefore, we are unable to determine the molecular identity of particle-phase organics and cannot comment on the presence of acylperoxynitrates in our experiments, nor their behavior in the thermodenuder.

**(11)** *Page 31459, lines 15–20. My recollection is that past TD measurements/modeling by the CMU group has indicated a mass accommodation coefficient for SOA of 0.01. Any idea what is so different here?*

Some modeling work has shown solutions for mass accommodation coefficients as low as 0.01 (Epstein et al., 2010) with relatively high enthalpy of vaporization based on a-priori assumptions but also a volatility distribution that we now know omits extremely low volatility organic carbon (ELVOC) in the SOA. A challenge in this modeling is always covariance between parameters such as accommodation coefficients and volatility, which both influence the kinetics of evaporation. However, experiments designed to isolate mass accommodation through equilibration timescale measurement (Saleh et al., 2013) consistently find mass accommodation coefficients exceeding 0.1.

**(12)** *Page 31460, lines 14–21: Can anything be said about what this 0.5 unit reduction in volatility corresponds to with regards to vapor pressure, and what the change corresponds to in carbon number or functional group composition (e.g., using the SIMPOL method)?*

The equation indicates that a reduction of 0.5 units of oxidation state is associated with an increase in saturation vapor pressure of 1 order of magnitude. Thus, the equation directly relates a change in functional group composition (as well as it can be estimated from AMS data on OA oxidation state) to a change in SOA saturation vapor pressure. We have added to this discussion in the text in order to clarify this point. In addition, a correction in the data analysis has changed the slope to 0.3, so indeed a reduction of 0.3 units of oxidation state is associated with an increase in vapor pressure (saturation mass concentration) of one order of magnitude.

**(13)** *Page 31461, bottom paragraph: What about the possibility that carbon chain length affects CCN activity? This is not accounted for in O/C ratio and oligomers eventually reach a solubility limit.*

We thank the referee for pointing out this possibility. We have included a discussion of this in the revised manuscript.

**(14)** *Page 31462, line 2: The attempt to generalize these results to “small aromatic VOCs” seems inappropriate, since although a few are listed in Table 1 as being added to toluene in 2 experiments, and there is no discussion of what effects they had, if any. In the absence of such results and discussion I suggest limiting the conclusions to toluene, with perhaps some comments on whether there is reason to believe that other small aromatics might behave similarly or differently and why. I also suggest changing the title from “small aromatic VOCs” to “toluene” for the same reasons.*

In the revised manuscript we have changed the title as suggested by the referee and focused our conclusions on toluene, while also commenting that other small aromatics appear to behave similarly.

**(15)** *Page 31462, Conclusions: It is stated in the Introduction: “A main objective is to connect the extent of oxidation and the changes in volatility of these experiments with the 2D-VBS framework.” Was that objective met satisfactorily? How do these results contribute to broader objectives? Do these results help to explain what anyone else has observed, or are they specific to this study?*

The equation given in section 3.3.1 directly relates changes in the OA saturation vapor pressure to changes in its oxidation state. As such, the objective of “connecting the extent of oxidation and the changes in volatility of these experiments with the 2D-VBS framework” was met satisfactorily. Additional studies will need to be conducted to explore whether different systems show different dependencies between oxidation state and vapor pressure. The method of analysis presented in this manuscript could be used in these further studies. The data presented here are some of the first to directly relate measurements of OA saturation vapor pressure and oxidation state and are as such valuable to the research community. This has been made clearer in the

revised manuscript.

**(16)** *Table 1: I suggest adding final concentrations of toluene and also the concentrations of other aromatics added.*

Gas-phase measurements were only available for three out of the nine experiments; all available data have been added to Table 1 of the revised manuscript.

**(17)** *Table 2: How was NO<sub>2</sub> measured? NO<sub>x</sub> analyzers measure NO<sub>2</sub> + organic nitrates, which can be significant.*

The NO and NO<sub>2</sub> data presented in Table 2 refer to measurements of the (particle-phase) NO<sup>+</sup> and NO<sub>2</sub><sup>+</sup> fragments measured by the HR-AMS. We did not attempt to quantify gas-phase NO<sub>2</sub>.

**(18)** *Table 2: Some additional description of how NO/NO<sub>2</sub> was determined would be useful. It is not obvious how this was done using linear regressions.*

Particle-phase NO was plotted versus particle-phase NO<sub>2</sub>, and a line was fit through the data to obtain the values presented in Table 2. This has been clarified in the revised manuscript.

**(19)** *Figure 8. It seems like the nice linear relationship here deserves a little more discussion than “Figure 8 shows a comparison of the modeled vs. the measured MFRs.” If it is so un-noteworthy perhaps just leave it out.*

Figure 8 shows that the fits work and is therefore noteworthy, but we nevertheless decided to move it to the supplemental material.

Technical Comments:

**(20)** *Page 31447, bottom line: I suggest using a term other than “molecular ions”, since this can be interpreted as non-fragmented ions formed from reaction products, whereas given their low mass these are probably all ion fragments. Perhaps use “ion masses”.*

“Molecular ions” was changed to “ion masses” in the revised manuscript.

## References

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