Response to Reviewer #1

# General comments:

**Q1:** This manuscript describes laboratory experiments aimed at measuring the yield and composition of SOA formed from the OH oxidation of toluene, in the presence of either initially deliquesced ("wet") or effloresced ("dry") ammonium sulfate (AS) seeds. This work extends the study by Faust et al. (2017), by examining the effects of toluene SOA yield/composition at different OH exposures. The authors certainly highlights an important point that SOA formed onto AS seed particles will lower the deliquescence RH (for initially dry AS) or contribute to additional aerosol liquid water (for initially wet AS). However, my main concern is that the authors only attributed the decrease in relative SOA yield (between dry and wet AS) with increasing OH exposures to the effects of aerosol liquid water, while the experiment design/data presented preclude the isolation of this effect. In particular, from the composition data presented, this trend could have also arisen due to enhanced contribution of later generation products from the gas-phase oxidation of toluene to the final SOA formed. These later generation products, which the authors mentioned, are generally of smaller molecular weights, which would certainly result in less SOA mass, for the same number of toluene molecules reacted. Additionally, the heterogeneous OH oxidation of the formed SOA is important at higher OH exposures, and could have led to enhanced loss of SOA mass due to fragmentation for wet AS due to the effects of liquid water on viscosity. A greater discussion is warranted; can other possible explanations for the observed trend in relative SOA yield be ruled out?

R1: We emphasize that at moderate and atmospheric relevant RH, aerosol liquid water will exist and play an important role and it cannot be avoided, even if the experiment started with dry AS. We would argue that the hygroscopic properties of AS and SOA naturally leads to the PRESENCE of water in particles under such conditions. It is not feasible to isolate the role of water from SOA formation under these moderate RHs. We attempted to estimate the amount of ALW at different OH exposures based on the sulfate and OA data obtained from the AMS.

Yes, the later generation products would result in less absolute SOA yields, which is confirmed by the observed decrease in the absolute SOA yields with the increase of OH exposure for both dry and wet experiments (Fig. 2).

In general, decrease in SOA yield can be attributed to fragmentation in gas phase and heterogeneous reactions. Previous oxidation flow reactor studies investigating the aging of ambient air in urban and forest areas suggest that gas-phase chemistry dominates over heterogeneous OH oxidation at OH levels below $1.0\times10^{12}$ molecules $cm^{-3}$ s (Ortega et al., 2016; Palm et al., 2016). In this study, the highest OH exposure was $5.28\times10^{11}$ molecules $cm^{-3}$ s and heterogeneous oxidation of SOA may not play an important role in reducing the mass of SOA. In addition, glyoxal is an important oxidation product of toluene (Kamens et al., 2011). The reactive uptake of glyoxal has been demonstrated to enhance rather than reduce the SOA mass (Liggio et al., 2005). The following sentences have been added to the revised manuscript.

“Previous oxidation flow reactor studies suggest that gas-phase chemistry dominates over heterogeneous OH oxidation at OH levels below $1.0\times10^{12}$ molecules $cm^{-3}$ s (Ortega et al., 2016; Palm et al., 2016). In this study, the highest OH exposure was $5.28\times10^{11}$ molecules $cm^{-3}$ s and heterogeneous oxidation of SOA may not play an important role in reducing the mass of SOA, although we cannot exclude that it plays a role. In addition, glyoxal is an important oxidation product of toluene (Kamens et al., 2011). The reactive uptake of glyoxal has been demonstrated to enhance rather than reduce the SOA mass (Liggio et al., 2005a).” (Line 264-271).

**Q2:** Also, the authors only noted that the photo-oxidation of toluene was conducted under low/no NOx conditions in Figure 1 - this is a critical point that needs to be highlighted (especially in the abstract) and warrant a discussion.

R2: In a PAM, OH dominated reactions even at high $NO_x$. NO at ambient high levels is rapidly oxidized by the high concentrations of OH, $HO_2$ and $O_3$ and hence the reaction would still be OH dominant. To study $NO_x$ chemistry, extreme unrealistically high concentration of $NO_x$ (e.g. a few ppm) is used, which would render the reactions atmospherically irrelevant. Hence, we only studied the photooxidation of toluene in the absence of $NO_x$ as it is still a challenge to study $NO_x$ reactions in oxidation flow reactors without using atmospherically irrelevant high concentrations of NOx (Peng and Jimenez, 2017). However, aerosol liquid water may also be important to SOA formation under high NOx conditions that preferentially form highly water-soluble products (Ervens et al., 2011). Further studies are needed to elucidate the interplay between SOA and ALW under high $NO_x$ conditions. The following text has been added for clarification.

"in the absence of $NO_x$" (Line 25-26; Line 137).

"We only studied the photooxidation of toluene in the absence of $NO_x$ as it is still a challenge to study high-NO chemistry in oxidation flow reactors without using atmospherically irrelevant high concentrations of $NO_x$ (Peng and Jimenez, 2017). However, the ALW may also be important to SOA formation under high $NO_x$ conditions that preferentially form highly water-soluble products (Ervens et al., 2011)." (Line 440-445).

"under various $NO_x$ conditions at moderate RH" (Line 447-448).

## Specific comments:

**Q3:** Line 94: The experiment approach is similar (if not identical) to that used in Wong et al. (2015) and Faust et al. (2017) and should be referenced, especially since the introduction of the paper highlights the limitations of these previous studies as motivation of the current work.

R3: The following sentence has been added to the revised manuscript.

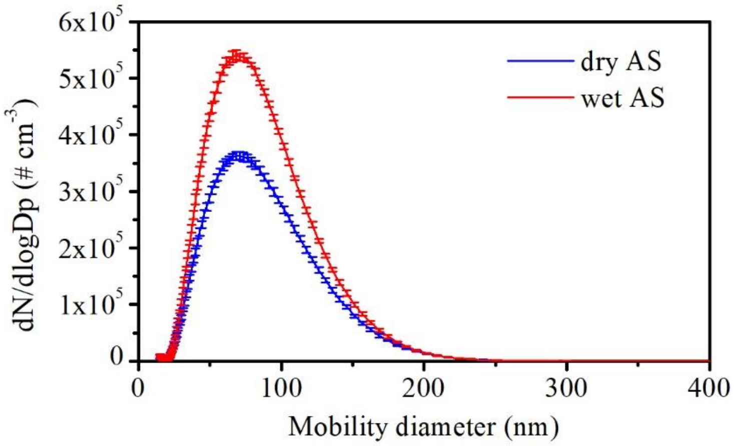
"similar to that used in Wong et al. (2015) and Faust et al. (2017)" (Line 109-110).

**Q4:** Line 114-118: Are the surface area distributions of the "initially" dry and wet AS seed particles? Also, are the total seed particle surface areas significantly high enough that homogeneous nucleation was suppressed?

R4: Yes. These are distributions of initially dry and wet AS seed particles. The term "initially" was added to the revised manuscript for clarification.

The total seed particle surface areas are high enough to suppress nucleation. As shown in the following figure (now Fig. S2), at the OH exposure of $4.66\times10^{10}$ molecules $cm^{-3}$ s, the particle number distributions for both cases are unimodal, indicating no nucleation. The following sentence was added to the revised manuscript.

"The unimodal size distributions of particle numbers show the SOA formation on AS seed particles without much nucleation mode particles (Fig. S2)." (Line 198-200)



**Q5:** Line 138: The extent to which the toluene + OH reaction perturbed the OH exposures may be estimated, given that the concentration of toluene added is known.

R5: The reduction in OH exposure due to the toluene + OH reaction was estimated to range from 15% at the highest OH exposure to 25% at the lowest OH exposure, using the method of Peng et al. (2016). We assume that this reduction is the same for dry and wet seeds and will not influence the relative SOA yields.

The sentence "*The addition of toluene may reduce the OH exposure.*" has been revised and now reads:

"The reduction in OH exposure due to the addition of toluene was estimated to range from 15% at the highest OH exposure to 25% at the lowest OH exposure, using the method of Peng et al. (2016)." (Line 157-160).

**Q6:** Line 152: What is the final mixing ratio of toluene in the oxidation flow reactor?

R6: The calculated final mixing ratio of toluene is now provided in Table 1. The following sentence has been added:

"The reacted and final concentrations of toluene were calculated from the OH exposure and the rate constant of the reaction between toluene and OH (Atkinson and Arey, 2003) (Table 1)." (Line 172-174).

**Table 1.** Summary of the results for the initially dry and wet AS seeds experiments.

| OH exposure (×10$^{11}$ molecules cm$^{-3}$ s) | [toluene]$_{reacted}$ (ppb) | [toluene]$_{final}$ (ppb) | $\varepsilon$ [a] | |
|---|---|---|---|---|
| | | | wet AS | dry AS |

| | | | | |
|---|---|---|---|---|
| 0.47 | 32.4 | 106.0 | 0.57 | 0.56 |
| 1.66 | 84.9 | 53.5 | 0.82 | 0.82 |
| 2.97 | 113.1 | 25.3 | 0.83 | 0.85 |
| 4.34 | 126.9 | 11.5 | 0.83 | 0.85 |
| 5.28 | 131.7 | 6.7 | 0.83 | 0.85 |

[a] The volume fraction of organics.

**Q7:** Line 154-155: Were the experiments at different OH exposures conducted separated or in a step-wise manner (e.g. increasing the OH exposures throughout an experiment)?

R7: The experiments were conducted with a step-wise increase in OH exposure. “*at each of*” now reads “with a step-wise increase in”. (Line 178).

**Q8:** Line 166-168: Given that fragmentation reactions can lead to the formation of $CO_2$ gas, the filter correction factor should change throughout the experiments.

R8: The concentration of formed $CO_2$ would be less than 1 ppm even all the toluene (~138 ppb) was oxidized to $CO_2$. An 1 ppm increase of $CO_2$ can only lead to 0.0006 ug/m$^3$ increase of SOA and has no detectable influence on O:C ratios. Therefore, the influence of the formation of this extremely low concentration of $CO_2$ on AMS data analysis is negligible.

**Q9:** Line 171-172: It is not clear how the results from Matthews et al. (2008) is comparable to that of the current study.

R9: Similar to Matthews et al. (2008), AS seed particles were also coated by liquid state of SOA.

“*A CE of 1 was used for processing all AMS data since the concentration of sulfate measured with the AMS varied by less than 5% of the average mass of sulfate after coated by SOA for both wet and dry AS seeds conditions.*” now reads:

“The toluene-derived SOA in these experiments was therefore liquid-like. The unimodal size distributions of particle numbers show the SOA formation on AS seed particles without much nucleation mode particles (Fig. S2). A CE of 1 was used for processing all AMS data since the AS seed particles were coated by liquid SOA. The adoption of this CE value was supported by that the concentration of sulfate measured with the AMS varied by less than 5% of the average mass of sulfate after coated by

SOA for both wet and dry AS seeds conditions." (Line 197-204).

**Q10:** Line 231-232: It is not clear what is driving the uncertainties in the calculated SOA yields.

R10: The reported uncertainties were solely due to the standard derivations when averaging the concentrations of SOA.

"*The uncertainty in the SOA yields fully reflected the uncertainty in the calculation of the SOA mass*" now reads: "The uncertainty in the SOA yields simply reflected the standard derivation when averaging the SOA mass" (Line 260).

**Q11:** Line 246-248: This statement assumes that the wall loss of dry and wet AS particles are identical - is this true?

R11: According to McMurry and Grosjean (1985), the wall loss coefficient was size dependent. We assumed the wall losses of wet and dry particles are similar considering their similar size distributions of particle number.

**Q12:** Lines 257-259: Given that the suppression in the DRH of AS is dependent on the fraction of organics, for the current study, what was the fraction(s) of organics as a function of OH exposure?

R12: The volume fractions of organics are now provided in Table 1.

"(Table 1)" was added to the revised manuscript. (Line 250).

**Q13:** Lines 321-322: Do the standard deviations reflect the variability from multiple experiments?

R13: They reflected the variability of the steady-state periods.

"determined for the steady-state periods" was added to the revised manuscript. (Line 382).

## Technical comments:

**Q14**: Line 81: It is not clear to whom "their" is referring to in this sentence.

R14: "their study" was changed to "Faust et al. (2017)". (Line 95).

References:

Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, Atmos. Chem. Phys., 11, 11069-11102, 10.5194/acp-11-11069-2011, 2011.

Kamens, R. M., Zhang, H. F., Chen, E. H., Zhou, Y., Parikh, H. M., Wilson, R. L., Galloway, K. E., and Rosen, E. P.: Secondary organic aerosol formation from toluene in an atmospheric hydrocarbon mixture: Water and particle seed effects, Atmos Environ, 45, 2324-2334, DOI 10.1016/j.atmosenv.2010.11.007, 2011.

Liggio, J., Li, S.-M., and McLaren, R.: Heterogeneous Reactions of Glyoxal on Particulate Matter: Identification of Acetals and Sulfate Esters, Environ Sci Technol, 39, 1532-1541, 10.1021/es048375y, 2005.

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Peng, Z., and Jimenez, J. L.: Modeling of the chemistry in oxidation flow reactors with high initial NO, Atmos. Chem. Phys., 17, 11991-12010, 10.5194/acp-17-11991-2017, 2017.