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 1.0×10^{12} molecules cm^{-3} s (Ortega et al., 2016; Palm et al., 2016). In this study, the highest OH exposure was 5.28×10^{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 1.0×10^{12} molecules cm^{-3} s (Ortega et al., 2016; Palm et al., 2016). In this study, the highest OH exposure was 5.28×10^{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.

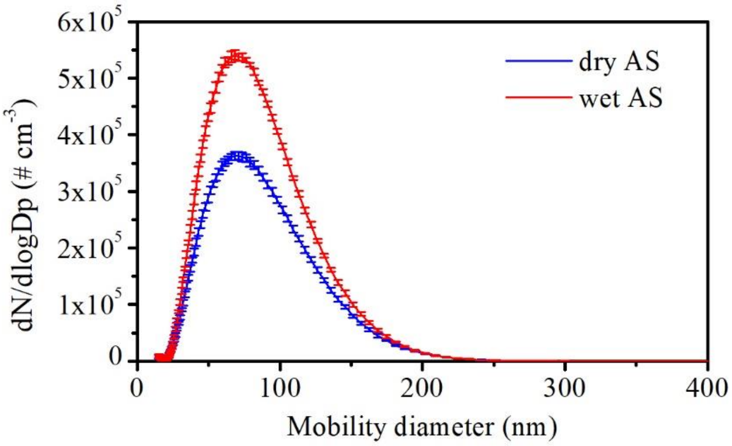
"similar to that used in Wong et al. (2015) and Faust et al. (2017)" (Line 109-110).

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 4.66×10^{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 ($\times 10^{11}$ molecules cm^{-3} s)	[toluene]$_{reacted}$ (ppb)	[toluene]$_{final}$ (ppb)	ε [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.

McMurry, P. H., and Grosjean, D.: Gas and aerosol wall losses in Teflon film smog chambers, Environ Sci Technol, 19, 1176-1182, 10.1021/es00142a006, 1985.

Ortega, A. M., Hayes, P. L., Peng, Z., Palm, B. B., Hu, W., Day, D. A., Li, R., Cubison, M. J., Brune, W. H., Graus, M., Warneke, C., Gilman, J. B., Kuster, W. C., de Gouw, J., Gutiérrez-Montes, C., and Jimenez, J. L.: Real-time measurements of secondary organic aerosol formation and aging from ambient air in an oxidation flow reactor in the Los Angeles area, Atmos. Chem. Phys., 16, 7411-7433, 10.5194/acp-16-7411-2016, 2016.

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., 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., 16, 4283-4305, 10.5194/acp-16-4283-2016, 2016.

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.

Response to Reviewer #2

General comments:

In this manuscript, the authors conducted flow reactor photooxidation experiments of toluene, and examined the SOA formation in the presence of initially wet or dry ammonium sulfate seeds. The approach followed that of Faust et al. (2017) to eliminate the effect of water on the gas-phase oxidation mechanisms, and allows experimenters to focus on the effect of aqueous vs dry seeds on gas-particle partitioning of organics. High resolution aerosol mass spectrometry was used to probe bulk composition, and various mechanisms were proposed to explain the changes in oxidation state, m/z fragment signal fractions and overall mass yields.

The results from this work are qualititatively consistent with those from Faust et al. There are some questions regarding the oxidation mechanisms that lead to observed changes. My main criticism is that this work report mostly observational results, and lack any detailed mechanistic insights. The results are interesting, and can be explored more in order to provide useful information for both understanding the system and modeling the oxidation. I therefore suggest a few areas to look into, and the manuscript can be strengthened if the following questions are considered.

R: Many thanks for the suggestions. We emphasize that at moderate and atmospherically relevant RH, aerosol liquid water will exist and play an important role and it cannot be avoided, even for experiments started with dry AS seeds. The hygroscopic properties of AS and SOA naturally lead to the PRESENCE of water in particles in both dry and wet experiments. Our goal is not to provide mechanistic details of the reactions. Nevertheless, we appreciate the comments and suggestions of the reviewer to improve the manuscript.

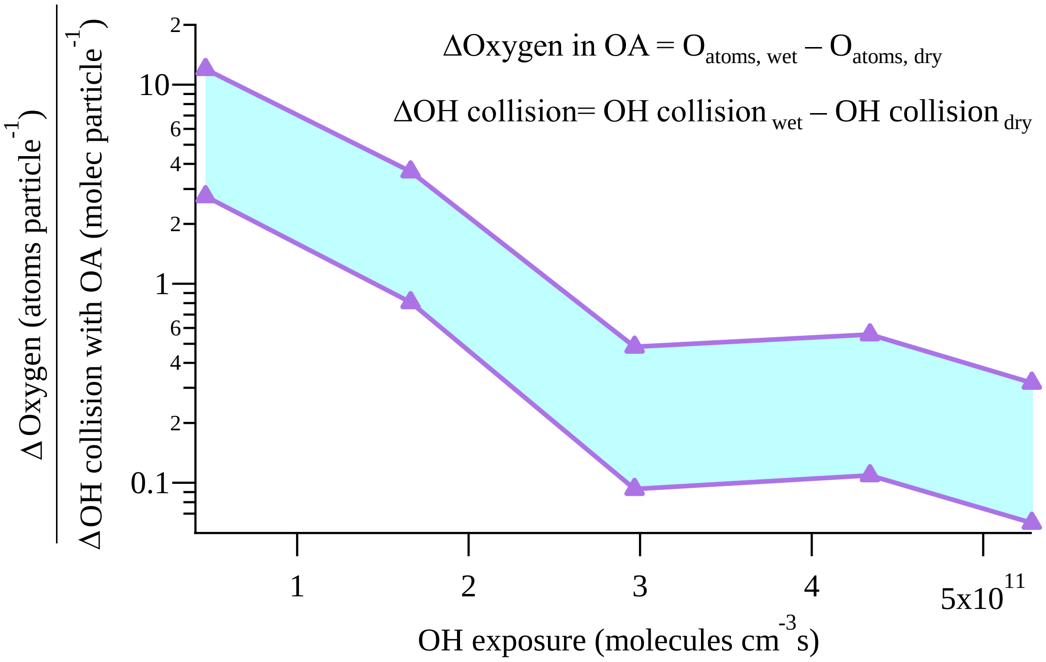
Major comments:

Q1: Oxidation mechanism: The major weakness in the paper is that it largely relies on bulk observation to probe mechanisms. While AMS is useful in obtaining bulk OA information and functional groups, the trends shown here are largely consistent with other aerosol aging observations in the lab or in the field. I am not sure if there are any novel insights in changes of m/z 43 and m/z 44, or the slope of the Van Krevelen diagram. It seems that the wet seed shows slightly different trends, but overall quite insignificant. The authors offer a few potential explanations (e.g. more OH aging, different gas-particle partitioning), but fail to go any deeper. If the explanation is more OH aging, then what is the equivalent change in OH exposure due to a wet seed (e.g. an OH exposure of 1 day at 65% RH is equivalent to an OH exposure of X days at 5%RH). Or, asking the question and framing the results in a different way: What is the increase in OH concentration in the aqueous phase that is required to explain the difference? Is this increase reasonable given the literature on aqueous OH production?

R1: AMS can provide insights to the overall evolution of OA and show the difference in bulk composition between initially dry and wet seeds without molecular level identification. The difference in SOA mass and composition between experiments with initially dry and wet seeds may be due to the enhanced gas-particle partitioning and/or enhanced OH aging in heterogeneous reactions. Since our experiments were conducted at 68%RH but not at 5%RH in both dry and wet cases, we cannot compare the results at different RH as proposed by the reviewer. Furthermore, though we cannot directly measure or calculate the OH concentration in the aqueous phase, we estimate the uptake of OH radicals to indirectly reflect the effects of enhanced OH aging on oxygen contents.

Specifically, we evaluate whether the enhanced uptake of OH radicals on initially wet AS seeds could explain the difference in oxygen contents, following the method of DeCarlo et al. (2008). We calculated R, the ratio of the difference in oxygen of OA between the initially wet and dry AS seed particles to the difference in the total number of OH collisions with OA at different OH exposures. To obtain R, the uptake coefficient (γ) of OH radicals was assumed to be 1 and 0.1/0.8 (lower/upper limit) for initially wet and dry AS seed particles, respectively (George and Abbatt, 2000). Note that as SOA formation takes place, the initially dry AS can become wet and the difference in γ between initially wet and dry seeds is reduced, especially at higher OH exposures. Without molecular level information on the organics, we assumed that each collision of OH with OA resulted in the addition of one oxygen atom to SOA. A value of R smaller than unity qualitatively indicates that the uptake of OH radicals can potentially explain the differences in oxygen contents in the dry and wet experiments.

The following figure (now Figure S6) shows that R is larger than unity at low OH exposures and smaller than unity at high OH exposures. This analysis suggests that the enhanced OH uptake may contribute to the difference in oxygen contents between dry and wet cases at higher OH exposures. At low OH exposures, the enhanced gas-particle partitioning may dominate the difference.



The following sentences have been added to the revised manuscript.

“We evaluate whether enhanced uptake of OH radicals on initially wet AS seeds could explain the difference in oxygen contents, following the method of DeCarlo et al. (2008). We calculated R, the ratio of the difference in oxygen of OA between the initially wet and dry AS seed particles to the difference in the total number of OH collisions with OA at different OH exposures. To obtain R, the uptake coefficient (γ) of OH radicals was assumed to be 1 and 0.1/0.8 (lower/upper limit) for initially wet and dry AS seed particles, respectively (George and Abbatt, 2000). Note that as SOA formation takes place, the initially dry AS can become wet and the difference in γ between initially wet and dry seeds is reduced, especially at higher OH exposures. We also assumed that each collision of OH with OA resulted in the addition of one oxygen atom to SOA. A value of R smaller than unity qualitatively indicates that the uptake of OH radicals can potentially explain the differences in oxygen contents in the dry and wet experiments. Fig. S6 shows that R is larger than unity at low OH exposures and smaller than unity at high OH exposures. This analysis suggests that the enhanced OH uptake may contribute to the difference in oxygen contents between dry and wet cases at higher OH exposures. At low OH exposures, the enhanced gas-particle partitioning may dominate the difference." (Line 398-414).

Q2: If the enhanced partitioning is due to availability of ALW, one can potentially explain the difference using Henry's law constants. What would the Henry's Law constants of the oxidation products need to be in order to show the difference in SOA yields between wet and dry seeds?

R2: The hydrophilic products should partition more readily into initially wet AS seeds than dry seeds and partially account for the difference in SOA yields. Both ALW and the Henry's law constant are relevant. Instead of focusing on the Henry's law constant alone, we focus on the uptake of glyoxal, a gas phase oxidation product of toluene oxidation, to illustrate the effects of enhanced partitioning of oxidation products on SOA yields. The following text has been added to the revised manuscript to estimate the effect of enhanced partitioning on SOA yields.

"The hydrophilic products should partition more readily into initially wet AS seeds than dry seeds and partially account for the difference in SOA yields. For example, as one of the important oxidation products, glyoxal was estimated to have an effective Henry's law constant of 4.52×10^{8} m atm^{-1} for our initially wet AS seeds due to the "salting-in" effect (Kampf et al., 2013), approximately 3 orders of magnitude higher than that in pure water (Ip et al., 2009). The uptake rate constant of glyoxal can be calculated as $(\gamma v A)/4$, where γ is the uptake coefficient, v is the gas-phase velocity of glyoxal, and A is the total surface area of AS seeds. The uptake rate constant is 4.5×10^{-4} s^{-1} for initially wet seeds with $\gamma = 2.4\times10^{-3}$ estimated from glyoxal uptake in AS seeds at 68% RH (Liggio et al., 2005b). The average gas-phase glyoxal concentration was modeled to be 4.3 ppb at OH exposure of 0.47×10^{11} molecules cm^{-3} s using the Master

Chemical Mechanism v 3.3.1 (Jenkin et al., 2003; Bloss et al., 2005), which would result in approximately 1.6 μg m^{-3} of glyoxal in particle phase for initially wet AS seeds. If the particle-phase concentration of glyoxal was assumed to be 0 for initially dry AS seeds, the enhanced partitioning of glyoxal alone would account for 24.5% of the mass difference of SOA. Note that other hydrophilic products were not included in this calculation. This analysis suggests that the enhanced partitioning of hydrophilic products may play an important role in the difference of SOA yields at low OH exposures. As discussed above, the initially dry AS seeds approached wet seeds and reduce the differences between wet and dry SOA yields at high OH exposures. " (Line 317-336).

Q3: The approach used to calculate ALW separately for AS and toluene assume that they are linearly additive. In a metastable solution of ammonium sulfate, the ionic strength would be very high, and can affect the water solubility of the organics. Would it be valid to assume then the water uptake that cannot be explained by literature kappa of toluene SOA is associated with AS?

R3: The approach used in this study has been found to be adequate to well estimate the hygroscopic growth of inorganic and organic mixtures in laboratory and ambient studies, even at relatively low RH (Choi and Chan, 2002; Cheung et al., 2015; Svenningsson et al., 2006; Nguyen et al., 2016).

Q4: Experimental uncertainties: I am not sure if the experimental uncertainty in yields include only that from quantification of aerosol. The quantification of toluene reacted would play an important role as well, especially since the reported yields (with only uncertainty of SOA) have almost negligible uncertainty. In this work, toluene is not quantified, but the amount reacted is based on estimation of OH exposure. Other work in the literature quantifying yields measure the hydrocarbon precursor directly (using either PTRMS or GC methods). Offline quantification of OH exposure using SO2 and assuming light conditions are constant can be problematic. There needs to be a systematic investigation of the uncertainties, particularly that associated with quantifying hydrocarbon decay.

R4: The experimental setup follows Wong et al. (2015) and Faust et al. (2017). The flow conditions were exactly the same for initially wet and dry seeds. The calibration and toluene photooxidation experiments were conducted over three days. The light condition was not expected to change in such a short period. Furthermore, we focus on the relative SOA yields, which are not expected to be much affected by the uncertainties in toluene quantification since the initial concentrations of toluene and OH exposures were the same for both cases. In offline calibration of OH exposures, the addition of toluene would perturb the calculated OH exposures. 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). Nevertheless, we assume that this reduction is the same for dry and wet seeds and will not influence the relative SOA yields.

For clarification, 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).

The following text was also added for clarification.

"The flow and light conditions were the same for initially wet and dry seeds. Therefore, the quantification of toluene would not introduce uncertainties to the relative SOA yields described in Section 3.1 as the initial concentrations of toluene and OH exposures were the same for both cases." (Line 174-177).

Minor comments:

Q5: Abstract: Should be less focused on specific details of the experiments. I suggest taking some of the numbers out (unless it is a really important number that, for example, a modeler can use or another experimentalist can directly compare). Rather, there may be broader implications other than these results warrant further study. What are the detailed mechanistic insights? What further developments are needed to better understand water uptake? Just a few sentences would suffice.

R5: Some parts of the abstract have been rewritten as suggested.

"*At an OH exposure of 4.66×10^{10} molecules cm^{-3} s, the ratio of the SOA yield on wet AS seeds to that on dry AS seeds was 1.31±0.02. However, this ratio decreased to 1.01±0.01 at an OH exposure of 5.28×10^{11} molecules cm^{-3} s. The decrease in the ratio of SOA yields as the increase of OH exposure may be due to the early deliquescence of initially dry AS seeds after coated by highly oxidized toluene-derived SOA.*" now reads "The ratio of the SOA yield on wet AS seeds to that on dry AS seeds, the relative SOA yield, decreased from 1.31±0.02 at an OH exposure of 4.66×10^{10} molecules cm^{-3} s to 1.01±0.01 at an OH exposure of 5.28×10^{11} molecules cm^{-3} s. This decrease may be due to the early deliquescence of initially dry AS seeds after coated by highly oxidized toluene-derived SOA." (Line 27-33).

"*Our results suggest that AS dry seeds soon turn to at least partially deliquesced particles during SOA formation and more studies on the interplay of SOA formation and ALW are warranted.*" now reads:

"Our results suggest that inorganic dry seeds become at least partially deliquesced particles during SOA formation and hence ALW is inevitably involved in the SOA formation at moderate RH. More laboratory experiments conducted with a wide variety of SOA precursors and inorganic seeds under different NO_x and RH conditions are warranted." (Line 44-48).

Q6: Line 36: m/z 29, 43, 44 are specific to the aerosol mass spectrometer (AMS).

R6: "obtained using an aerosol mass spectrometer (AMS)" was added. (Line 40-41).

Q7: Line 47-48: these references might not quite reflect the current state of knowledge. For example, Tsigaridis et al. (ACP, 2014) did a model intercomparison and found that the secondary nature of OA can be reproduced, but not the overall amount. Shrivastava et al (ACP, 2011) shows that the total SOA amount can be reproduced, but require some model tuning. Overall, there may be too many studies to cite for a simple argument here, but the de Gouw et al. and Volkamer et al. studies are quite out of date at this point.

R7: SOA models usually include update of the volatility basis set (VBS) formalism to treat gas-particle partitioning and multi-generation oxidation (Shrivastava et al., 2011; Tsigaridis et al., 2014), increased SOA yields that account for vapor wall loss in smog chambers (Zhang et al., 2014; Hayes et al., 2015) and additional SOA precursors such as S/IVOCs (Robinson et al., 2007). These updated models can better reduce the gap between the modeled and observed SOA, but have resulted in over-prediction of SOA at long aging times. It remains unclear whether these updated models improve the simulation of SOA for the right reasons. Here, we pointed out that the presence of ALW may influence the SOA yields, which is not well treated even in the updated models. To reflect the current state of knowledge, we added the following sentence to the revised manuscript.

"The updated models incorporating the volatility basis set (VBS) formalism (Donahue et al., 2006) can better predict the observed SOA, but SOA formation still remains under-constrained (Shrivastava et al., 2011; Tsigaridis et al., 2014; Hayes et al., 2015; Ma et al., 2017)." (Line 57-60).

Q8: Line 60: I would also add that understanding water uptake of SOA is important for estimating its loss by wet deposition, which is highly unknown at this point.

R8: The following sentence has been added as suggested.

"In addition, understanding water uptake of SOA is important for estimating its loss by wet deposition, which is not well constrained." (Line 72-74).

Q9: Line 97: is the silica gel diffusion dryer manufactured by TSI? If so, consider including the model number. Is the 30% outlet RH experimentally verified? I would imagine the outlet RH would be a function of the inlet RH.

R9: It is a homemade one. The outlet RH was verified to be lower than 30%. The inlet RH should be stable during the experiment as the flow rate was stable.

Q10: Line 103: Is it correct that the ALW is estimated using the method described later? If so, please mention.

R10: Yes. "see Section 2.4" was added for clarification. (Line 119).

Q11: Lines 140-146: Based on the OH exposure calculated, what is the amount of toluene consumed?

R11: The reacted amount 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).

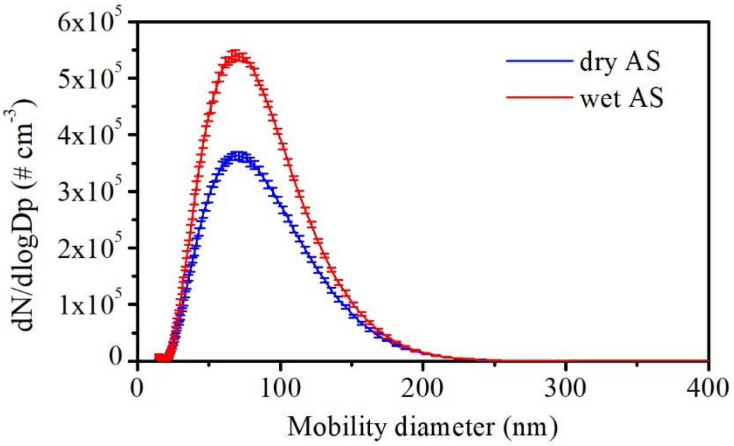
Q12: Line 166-167: is this filtered air flow with or without toluene and/or oxidation products?

R12: The filtered air flow was without oxidation products. These oxidation products were expected to have a negligible influence on the concentrations of major gases, e.g. N_2, O_2, and CO_2.

Q13: Line 177: Just to make sure that sulfate is indeed coated with SOA, it would be great to show size distributions: Either a unimodal SMPS number size distribution showing no nucleation, or the PTOF on the AMS showing that organics and sulfate are in the same mode.

R13: As shown in the following figure (now Fig. S2), at the OH exposure of 0.47×10^{11} 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)



Q14: Line 187: Is it really evaporation of the organics? Would 8% mass loss due to evaporation be enough to show up in shifts in particle mode or median diameter (it would be around a ~2% change in diameter)?

R14: We cannot rule out other possibilities based on the dataset. Hence we said that it is possibly due to reversible partitioning of the SVOCs in the original text. The ~2% shift in particle mode diameter was not enough to be captured by AMS or SMPS.

Q15: Line 252: I suggest keeping all OH exposure numbers to 10ˆ11 molec cm-3 s. For example, I recommend changing 4.66 x 10ˆ10 to 0.47 x 10ˆ11.

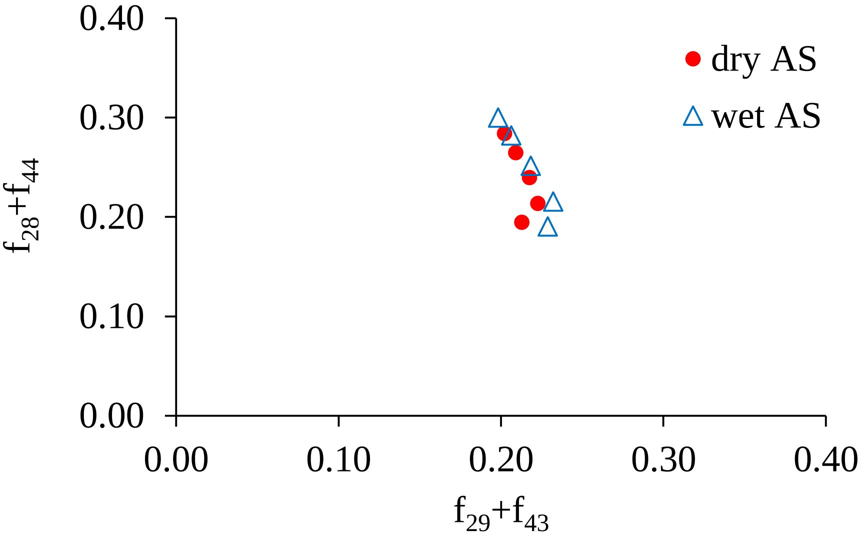
R15: Revised as suggested.

Q16: Line 290 – 292: The authors should be cautious about observations of oligomers on the AMS. The relatively low signal above m/z 80 does not mean there is little to no oligomerization. The AMS vaporizer at 600 C causes extensive thermal decomposition.

R16: Although the AMS can cause extensive thermal decomposition, previous studies suggest that m/z > 80 can be easily observed when the oligomers are abundant (Price et al., 2014; Gilardoni et al., 2016; Faust et al., 2017). We deleted this statement due to the lack of solid evidences.

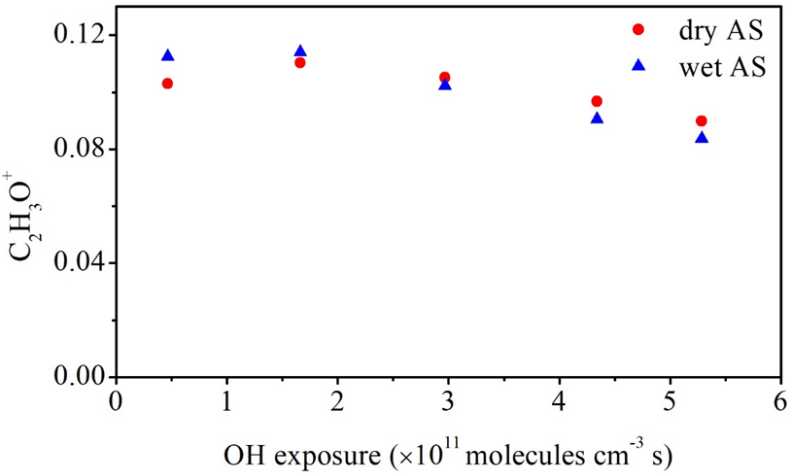
Q17: Line 298-303: Would a plot f(28+44) vs f(29+43) look different from f44 vs f43? The conversion of alcohols and aldehydes to acids described in the previous paragraph is fundamentally driving the trend of f44 and f43. So these two paragraphs are both conveying a similar observation, which is expected given the extensive literature on AMS description of aerosol aging. So I suggest condensing the discussion.

R17: As shown in the following figure, the f(28+44) vs f(29+43) plot looks similar as f44 vs f43 plot. The previous paragraph is focused on the comparison of the mass spectra between the lowest and highest OH exposure while this paragraph shows the overall evolution of f44 vs f43 from the lowest to the highest OH exposure, so we would like to keep the original discussions.



Q18: Line 314-315, and Fig. S4: The differences seem very minute to me and may not be statistically significant. The y-scale is misleading, and should start at zero.

R18: Fig. S4 has been revised accordingly as follows. The difference in the abundance of $C_2H_3O^+$ between dry and wet AS seeds is small but there is quite an obvious trend as OH exposure increases.



Q19: Line 314-315: If the trend is due to enhanced partitioning of water soluble organics to ALW, wouldn't the

R19: This issue of solubility of WSOC is likely addressed in response to Q1 and Q2.

Q20: Line 327: It looks like the subscript "C" in OSC is not capitalized, where it has been capitalized in other instances in the manuscript.

R20: Revised.

References:

Bloss, C., Wagner, V., Jenkin, M. E., Volkamer, R., Bloss, W. J., Lee, J. D., Heard, D. E., Wirtz, K., Martin-Reviejo, M., Rea, G., Wenger, J. C., and Pilling, M. J.: Development of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons, Atmos. Chem. Phys., 5, 641-664, 10.5194/acp-5-641-2005, 2005.

Cheung, H. H. Y., Yeung, M. C., Li, Y. J., Lee, B. P., and Chan, C. K.: Relative Humidity-Dependent HTDMA Measurements of Ambient Aerosols at the HKUST

Supersite in Hong Kong, China, Aerosol Sci Tech, 49, 643-654, 10.1080/02786826.2015.1058482, 2015.

Choi, M. Y., and Chan, C. K.: The Effects of Organic Species on the Hygroscopic Behaviors of Inorganic Aerosols, Environ Sci Technol, 36, 2422-2428, 10.1021/es0113293, 2002.

DeCarlo, P. F., Dunlea, E. J., Kimmel, J. R., Aiken, A. C., Sueper, D., Crounse, J., Wennberg, P. O., Emmons, L., Shinozuka, Y., Clarke, A., Zhou, J., Tomlinson, J., Collins, D. R., Knapp, D., Weinheimer, A. J., Montzka, D. D., Campos, T., and Jimenez, J. L.: Fast airborne aerosol size and chemistry measurements above Mexico City and Central Mexico during the MILAGRO campaign, Atmos. Chem. Phys., 8, 4027-4048, 10.5194/acp-8-4027-2008, 2008.

Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled Partitioning, Dilution, and Chemical Aging of Semivolatile Organics, Environ Sci Technol, 40, 2635-2643, 10.1021/es052297c, 2006.

Faust, J. A., Wong, J. P. S., Lee, A. K. Y., and Abbatt, J. P. D.: Role of Aerosol Liquid Water in Secondary Organic Aerosol Formation from Volatile Organic Compounds, Environ Sci Technol, 51, 1405-1413, 10.1021/acs.est.6b04700, 2017.

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

Gilardoni, S., Massoli, P., Paglione, M., Giulianelli, L., Carbone, C., Rinaldi, M., Decesari, S., Sandrini, S., Costabile, F., Gobbi, G. P., Pietrogrande, M. C., Visentin, M., Scotto, F., Fuzzi, S., and Facchini, M. C.: Direct observation of aqueous secondary organic aerosol from biomass-burning emissions, Proceedings of the National Academy of Sciences, 113, 10013-10018, 10.1073/pnas.1602212113, 2016.

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.

Ip, H. S. S., Huang, X. H. H., and Yu, J. Z.: Effective Henry's law constants of glyoxal, glyoxylic acid, and glycolic acid, Geophys Res Lett, 36, L01802, 10.1029/2008GL036212, 2009.

Jenkin, M. E., Saunders, S. M., Wagner, V., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 181-193, 10.5194/acp-3-181-2003, 2003.

Kampf, C. J., Waxman, E. M., Slowik, J. G., Dommen, J., Pfaffenberger, L., Praplan, A. P., Prévôt, A. S. H., Baltensperger, U., Hoffmann, T., and Volkamer, R.: Effective Henry's Law Partitioning and the Salting Constant of Glyoxal in Aerosols Containing Sulfate, Environ Sci Technol, 47, 4236-4244, 10.1021/es400083d, 2013.

Liggio, J., Li, S.-M., and McLaren, R.: Reactive uptake of glyoxal by particulate matter, Journal of Geophysical Research: Atmospheres, 110, D10304, 10.1029/2004JD005113, 2005.

Ma, P. K., Zhao, Y., Robinson, A. L., Worton, D. R., Goldstein, A. H., Ortega, A. M., Jimenez, J. L., Zotter, P., Prévôt, A. S. H., Szidat, S., and Hayes, P. L.: Evaluating the impact of new observational constraints on P-S/IVOC emissions, multi-generation oxidation, and chamber wall losses on SOA modeling for Los Angeles, CA, Atmos. Chem. Phys., 17, 9237-9259, 10.5194/acp-17-9237-2017, 2017.

Nguyen, T. K. V., Zhang, Q., Jimenez, J. L., Pike, M., and Carlton, A. G.: Liquid Water: Ubiquitous Contributor to Aerosol Mass, Environmental Science & Technology Letters, 3, 257-263, 10.1021/acs.estlett.6b00167, 2016.

Peng, Z., Day, D. A., Ortega, A. M., Palm, B. B., Hu, 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., 16, 4283-4305, 10.5194/acp-16-4283-2016, 2016.

Price, D. J., Clark, C. H., Tang, X., Cocker, D. R., Purvis-Roberts, K. L., and Silva, P. J.: Proposed chemical mechanisms leading to secondary organic aerosol in the reactions of aliphatic amines with hydroxyl and nitrate radicals, Atmos Environ, 96, 135-144, https://doi.org/10.1016/j.atmosenv.2014.07.035, 2014.

Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking Organic Aerosols: Semivolatile Emissions and Photochemical Aging, Science, 315, 1259-1262, 10.1126/science.1133061, 2007.

Shrivastava, M., Fast, J., Easter, R., Gustafson Jr, W. I., Zaveri, R. A., Jimenez, J. L., Saide, P., and Hodzic, A.: Modeling organic aerosols in a megacity: comparison of simple and complex representations of the volatility basis set approach, Atmos. Chem. Phys., 11, 6639-6662, 10.5194/acp-11-6639-2011, 2011.

Svenningsson, B., Rissler, J., Swietlicki, E., Mircea, M., Bilde, M., Facchini, M. C., Decesari, S., Fuzzi, S., Zhou, J., Mønster, J., and Rosenørn, T.: Hygroscopic growth and critical supersaturations for mixed aerosol particles of inorganic and organic compounds of atmospheric relevance, Atmos. Chem. Phys., 6, 1937-1952, 10.5194/acp-6-1937-2006, 2006.

Tsigaridis, K., Daskalakis, N., Kanakidou, M., Adams, P. J., Artaxo, P., Bahadur, R., Balkanski, Y., Bauer, S. E., Bellouin, N., Benedetti, A., Bergman, T., Berntsen, T. K., Beukes, J. P., Bian, H., Carslaw, K. S., Chin, M., Curci, G., Diehl, T., Easter, R. C., Ghan, S. J., Gong, S. L., Hodzic, A., Hoyle, C. R., Iversen, T., Jathar, S., Jimenez, J. L., Kaiser, J. W., Kirkevåg, A., Koch, D., Kokkola, H., Lee, Y. H., Lin, G., Liu, X., Luo, G., Ma, X., Mann, G. W., Mihalopoulos, N., Morcrette, J. J., Müller, J. F., Myhre, G., Myriokefalitakis, S., Ng, N. L., O'Donnell, D., Penner, J. E., Pozzoli, L., Pringle, K. J., Russell, L. M., Schulz, M., Sciare, J., Seland, Ø., Shindell, D. T., Sillman, S., Skeie, R. B., Spracklen, D., Stavrakou, T., Steenrod, S. D., Takemura, T., Tiitta, P., Tilmes, S., Tost, H., van Noije, T., van Zyl, P. G., von Salzen, K., Yu, F., Wang, Z., Wang, Z., Zaveri, R. A., Zhang, H., Zhang, K., Zhang, Q., and Zhang, X.: The AeroCom evaluation and intercomparison of organic aerosol in global models, Atmos. Chem. Phys., 14, 10845-10895, 10.5194/acp-14-10845-2014, 2014.

Wong, J. P. S., Lee, A. K. Y., and Abbatt, J. P. D.: Impacts of Sulfate Seed Acidity and Water Content on Isoprene Secondary Organic Aerosol Formation, Environ Sci Technol, 49, 13215-13221, 10.1021/acs.est.5b02686, 2015.

Zhang, X., Cappa, C. D., Jathar, S. H., McVay, R. C., Ensberg, J. J., Kleeman, M. J., and Seinfeld, J. H.: Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, P. Natl. Acad. Sci., 111, 5802-5807, 10.1073/pnas.1404727111, 2014.

A list of relevant changes

Line 3–add "at moderate relative humidity"

Line 22-24–Change "seed particles can exist as dry or wet particles" to "initially dry seed particles can exist as wet particles due to water uptake by the seeds as well as the SOA"

Line 3–add "in the absence of NO_x"

Line 27-33–Change "At an OH exposure of 4.66×10^{10} molecules cm^{-3} s, the ratio of the SOA yield on wet AS seeds to that on dry AS seeds was 1.31±0.02. However, this ratio decreased to 1.01±0.01 at an OH exposure of 5.28×10^{11} molecules cm^{-3} s. The decrease in the ratios of SOA yields as the increase of OH exposure may be due to the early deliquescence of initially dry AS seeds after coated by highly oxidized toluene-derived SOA." to "The ratio of the SOA yield on wet AS seeds to that on dry AS seeds, the relative SOA yield, decreased from 1.31±0.02 at an OH exposure of 4.66×10^{10} molecules cm^{-3} s to 1.01±0.01 at an OH exposure of 5.28×10^{11} molecules cm^{-3} s. This decrease may be due to the early deliquescence of initially dry AS seeds after coated by highly oxidized toluene-derived SOA."

Line 35-36–Delete "a large fraction of"

Line 37-38–Add "especially at high OH exposure" after "…ALW increased,"

Line 40-41–Add "obtained using an aerosol mass spectrometer (AMS)" after "…SOA mass spectra,"

Line 44-49–Change "Our results suggest that AS dry seeds soon turn to at least partially deliquesced particles during SOA formation and more studies on the interplay of SOA formation and ALW are warranted." to "Our results suggest that inorganic dry seeds become at least partially deliquesced particles during SOA formation and hence ALW is inevitably involved in the SOA formation at moderate RH. More laboratory experiments conducted with a wide variety of SOA precursors and inorganic seeds under different NO_x and RH conditions are warranted. "

Line 57-60–Add "The updated models incorporating the volatility basis set (VBS) formalism (Donahue et al., 2006) can better predict the observed SOA, but SOA formation still remains under-constrained (Shrivastava et al., 2011; Tsigaridis et al., 2014; Hayes et al., 2015; Ma et al., 2017)."

Line 60–Delete "traditional"

Line 63-65–Change "atmospheric relative humidity is often sufficiently high that aerosols often exist as wet aerosols, containing a large amount of aerosol liquid water (ALW)" to "atmospheric relative humidity is often sufficiently high that aerosols often contain aerosol liquid water (ALW) due to their hygroscopic properties"

Line 66–Delete "wet"

Line 72-74–Add "by incorporating ALW. In addition, understanding water uptake of SOA is important for estimating its loss by wet deposition, which is not well constrained." after "…transport models"

Line 95–Change "their study" to "Faust et al. (2017)"

Line 109-110–Add "similar to that used in Wong et al. (2015) and Faust et al. (2017)" after "…experimental setup"

Line 119–Add "(see Section 2.4)" after "…ALW"

Line 130–Add "initially" after "…distribution of"

Line 131–Add "initially" after "…that of"

Line 137–Add "in the absence of NO_x" after "…of toluene"

Line 152–Change "4.66×10^{10} " to "0.47×10^{11}"

Line 154-155–Delete "The addition of toluene may reduce the OH exposure."

Line 157-160–Add "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)." after "…Lambe et al., 2011a)."

Line 172-177–Add "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). The flow and light conditions were the same for initially wet and dry seeds. Therefore, the quantification of toluene would not introduce uncertainties to the relative SOA yields described in Section 3.1 as the initial concentrations of toluene and OH exposures were the same for both cases." after "…approximately 138 ppb."

Line 178–Change "at each of " to "with a step-wise increase in"

Line 197-204–Change "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." to "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 213–Change "Fig. S2" to "Fig. S3"

Line 220–Change "4.66×10^{10} " to "0.47×10^{11}"

Line 250–Add "(Table) 1" after "…the volume fraction of SOA."

Line 257-259–Delete "The mass of reacted toluene was calculated from the OH exposure and the rate constant of the reaction between toluene and OH (Atkinson and Arey, 2003)."

Line 259-261–Change "The uncertainty in the SOA yields fully reflected the uncertainty in the calculation of the SOA mass." to "The uncertainty in the SOA yields simply reflected the standard derivation when averaging the SOA mass."

Line 264-271–Add "Previous oxidation flow reactor studies suggest that gas-phase chemistry dominates over heterogeneous OH oxidation at OH levels below 1.0×10^{12} molecules cm^{-3} s (Ortega et al., 2016; Palm et al., 2016). In this study, the highest OH exposure was 5.28×10^{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 278–Add "the values of" after "…lower than"

Line 288–Add "the relative SOA yield" after "…AS seeds,"

Line 288–Change "4.66×10^{10} " to "0.47×10^{11}"

Line 305–Change "4.66×10^{10} " to "0.47×10^{11}"

Line 317-336–Add the following paragraph "The hydrophilic products can partition more readily into initially wet AS seeds than dry seeds and partially account for the difference in SOA yields. For example, as one of the important oxidation products, glyoxal was estimated to have an effective Henry's law constant of 4.52×10^{8} m atm^{-1}

for our initially wet AS seeds due to the "salting-in" effect (Kampf et al., 2013), approximately 3 orders of magnitude higher than that in pure water (Ip et al., 2009). The uptake rate constant of glyoxal can be calculated as (γvA)/4, where γ is the uptake coefficient, v is the gas-phase velocity of glyoxal, and A is the total surface area of AS seeds. The uptake rate constant is 4.5×10^{-4} s^{-1} for initially wet seeds with $\gamma = 2.4\times10^{-3}$ estimated from glyoxal uptake in AS seeds at 68% RH (Liggio et al., 2005b). The average gas-phase glyoxal concentration was modeled to be 4.3 ppb at OH exposure of 0.47×10^{11} molecules cm^{-3} s using the Master Chemical Mechanism v 3.3.1 (Jenkin et al., 2003; Bloss et al., 2005), which would result in approximately 1.6 μg m^{-3} of glyoxal in particle phase for initially wet AS seeds. If the particle-phase concentration of glyoxal was assumed to be 0 for initially dry AS seeds, the enhanced partitioning of glyoxal alone would account for 24.5% of the mass difference of SOA. Note that other hydrophilic products were not included in this calculation. This analysis suggests that the enhanced partitioning of hydrophilic products may play an important role in the difference of SOA yields at low OH exposures. As discussed above, the initially dry AS seeds approached wet seeds and reduce the differences between wet and dry SOA yields at high OH exposures."

Line 339–Change "4.66×10^{10} " to "0.47×10^{11}"

Line 340–Change "4.66×10^{10} " to "0.47×10^{11}"

Line 348-349–Delete "Furthermore, ions with $m/z > 80$ accounted for a negligible fraction of total SOA, suggesting that oligomerization might not be important in these experiments."

Line 350–Change "Fig. S3" to "Fig. S4"

Line 363–Change "Fig. S4" to "Fig. S5"

Line 364-367–Add "The f_{43}-f_{44} plot supports our earlier assertion that as OH exposure increased, the reaction products changed from earlier-generation products containing carbonyl functional groups dominated to later-generation products containing acidic functional groups dominated."

Line 372-375–Delete "The f_{43}-f_{44} plot supports our earlier assertion that as OH exposure increased, the reaction products changed from earlier-generation products containing carbonyl functional groups to later-generation products containing acidic functional groups."

Line 381-382–Change "The standard deviations for H:C and O:C values were both less than 0.01." to "The standard deviations for H:C and O:C values, determined for the steady-state periods, were all less than 0.01."

Line 388–Change “OS_c” to “OS_C”

Line 398-414–Add the following paragraph “We evaluate whether enhanced uptake of OH radicals on initially wet AS seeds could explain the difference in oxygen contents, following the method of DeCarlo et al. (2008). We calculated R, the ratio of the difference in oxygen of OA between the initially wet and dry AS seed particles to the difference in the total number of OH collisions with OA at different OH exposures. To obtain R, the uptake coefficient (γ) of OH radicals was assumed to be 1 and 0.1/0.8 (lower/upper limit) for initially wet and dry AS seed particles, respectively (George and Abbatt, 2000). Note that as SOA formation takes place, the initially dry AS can become wet and the difference in γ between initially wet and dry seeds is reduced, especially at higher OH exposures. We also assumed that each collision of OH with OA resulted in the addition of one oxygen atom to SOA. A value of R smaller than unity qualitatively indicates that the uptake of OH radicals can potentially explain the differences in oxygen contents in the dry and wet experiments. Fig. S6 shows that R is larger than unity at low OH exposures and smaller than unity at high OH exposures. This analysis suggests that the enhanced OH uptake may contribute to the difference in oxygen contents between dry and wet cases at higher OH exposures. At low OH exposures, the enhanced gas-particle partitioning may dominate the difference.”

Line 425–Change “4.66×10^{10} ” to “0.47×10^{11}”

Line 428-430–Add “Hence, the SOA yield and ALW of the initially dry AS seeds approached those of the initially wet AS seeds as OH exposure and ALW increased.”

Line 440-445–Add “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 448–Change “ in wet aerosols” to “under various NO_x conditions at moderate RH”

Line 503–Add the reference “DeCarlo, P. F., Dunlea, E. J., Kimmel, J. R., Aiken, A. C., Sueper, D., Crounse, J., Wennberg, P. O., Emmons, L., Shinozuka, Y., Clarke, A., Zhou, J., Tomlinson, J., Collins, D. R., Knapp, D., Weinheimer, A. J., Montzka, D. D., Campos, T., and Jimenez, J. L.: Fast airborne aerosol size and chemistry measurements above Mexico City and Central Mexico during the MILAGRO campaign, Atmos. Chem. Phys., 8, 4027-4048, https://doi.org/10.5194/acp-8-4027-2008, 2008.”

Line 513–Add the reference “Donahue, N. M., Robinson, A. L., Stanier, C. O., and

Pandis, S. N.: Coupled Partitioning, Dilution, and Chemical Aging of Semivolatile Organics, Environ. Sci. Technol., 40, 2635-2643, https://doi.org/10.1021/es052297c, 2006."

Line 531–Add the reference "George, I. J., and Abbatt, J. P. D.: Heterogeneous oxidation of atmospheric aerosol particles by gas-phase radicals, Nat. Chem., 2, 713-722, 2010."

Line 549–Add the reference "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, https://doi.org/10.5194/acp-15-5773-2015, 2015."

Line 575–Add references "Ip, H. S. S., Huang, X. H. H., and Yu, J. Z.: Effective Henry's law constants of glyoxal, glyoxylic acid, and glycolic acid, Geophys. Res. Lett., 36, L01802, https://doi.org/10.1029/2008GL036212, 2009.
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Line 586–Add the reference "Kampf, C. J., Waxman, E. M., Slowik, J. G., Dommen, J., Pfaffenberger, L., Praplan, A. P., Prévôt, A. S. H., Baltensperger, U., Hoffmann, T., and Volkamer, R.: Effective Henry's Law Partitioning and the Salting Constant of Glyoxal in Aerosols Containing Sulfate, Environ. Sci. Technol., 47, 4236-4244, https://doi.org/10.1021/es400083d, 2013."

Line 640–Add references "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, https://doi.org/10.1021/es048375y, 2005a.
Liggio, J., Li, S.-M., and McLaren, R.: Reactive uptake of glyoxal by particulate matter, J. Geophys. Res.-Atmos., 110, D10304, https://doi.org/10.1029/2004JD005113, 2005b."

Line 651–Add the reference "Ma, P. K., Zhao, Y., Robinson, A. L., Worton, D. R., Goldstein, A. H., Ortega, A. M., Jimenez, J. L., Zotter, P., Prévôt, A. S. H., Szidat, S., and Hayes, P. L.: Evaluating the impact of new observational constraints on P-S/IVOC emissions, multi-generation oxidation, and chamber wall losses on SOA modeling for Los Angeles, CA, Atmos. Chem. Phys., 17, 9237-9259, https://doi.org/10.5194/acp-17-9237-2017, 2017."

Line 691–Add references “Ortega, A. M., Hayes, P. L., Peng, Z., Palm, B. B., Hu, W., Day, D. A., Li, R., Cubison, M. J., Brune, W. H., Graus, M., Warneke, C., Gilman, J. B., Kuster, W. C., de Gouw, J., Gutiérrez-Montes, C., and Jimenez, J. L.: Real-time measurements of secondary organic aerosol formation and aging from ambient air in an oxidation flow reactor in the Los Angeles area, Atmos. Chem. Phys., 16, 7411-7433, https://doi.org/10.5194/acp-16-7411-2016, 2016.
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, https://doi.org/10.5194/acp-16-2943-2016, 2016.”

Line 710–Add the reference “Peng, Z., and Jimenez, J. L.: Modeling of the chemistry in oxidation flow reactors with high initial NO, Atmos. Chem. Phys., 17, 11991-12010, https://doi.org/10.5194/acp-17-11991-2017, 2017.”

Line 733–Add the reference “Shrivastava, M., Fast, J., Easter, R., Gustafson Jr, W. I., Zaveri, R. A., Jimenez, J. L., Saide, P., and Hodzic, A.: Modeling organic aerosols in a megacity: comparison of simple and complex representations of the volatility basis set approach, Atmos. Chem. Phys., 11, 6639-6662, https://doi.org/10.5194/acp-11-6639-2011, 2011.”

Line 757–Add the reference “Tsigaridis, K., Daskalakis, N., Kanakidou, M., Adams, P. J., Artaxo, P., Bahadur, R., Balkanski, Y., Bauer, S. E., Bellouin, N., Benedetti, A., Bergman, T., Berntsen, T. K., Beukes, J. P., Bian, H., Carslaw, K. S., Chin, M., Curci, G., Diehl, T., Easter, R. C., Ghan, S. J., Gong, S. L., Hodzic, A., Hoyle, C. R., Iversen, T., Jathar, S., Jimenez, J. L., Kaiser, J. W., Kirkevåg, A., Koch, D., Kokkola, H., Lee, Y. H., Lin, G., Liu, X., Luo, G., Ma, X., Mann, G. W., Mihalopoulos, N., Morcrette, J. J., Müller, J. F., Myhre, G., Myriokefalitakis, S., Ng, N. L., O'Donnell, D., Penner, J. E., Pozzoli, L., Pringle, K. J., Russell, L. M., Schulz, M., Sciare, J., Seland, Ø., Shindell, D. T., Sillman, S., Skeie, R. B., Spracklen, D., Stavrakou, T., Steenrod, S. D., Takemura, T., Tiitta, P., Tilmes, S., Tost, H., van Noije, T., van Zyl, P. G., von Salzen, K., Yu, F., Wang, Z., Wang, Z., Zaveri, R. A., Zhang, H., Zhang, K., Zhang, Q., and Zhang, X.: The AeroCom evaluation and intercomparison of organic aerosol in global models, Atmos. Chem. Phys., 14, 10845-10895, https://doi.org/10.5194/acp-14-10845-2014, 2014.”

The following table was added as **Table 1.**

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

OH exposure ($\times 10^{11}$ molecules cm^{-3} s)	[toluene]$_{\text{reacted}}$ (ppb)	[toluene]$_{\text{final}}$ (ppb)	ε [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.

Line 814–Change “4.66×10^{10} ” to “0.47×10^{11}”

Comparison of secondary organic aerosol formation from toluene on initially wet and dry ammonium sulfate particles at moderate relative humidity

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Abstract

The formation of secondary organic aerosol (SOA) has been widely studied in the presence of dry seed particles at low relative humidity (RH). At higher RH, initially dry seed particles can exist as wet particles due to water uptake by the seeds as well as the SOA~~seed particles can exist as dry or wet particles~~. Here, we investigated the formation of SOA from the photooxidation of toluene using an oxidation flow reactor in the absence of NO_x under a range of OH exposures on initially wet or dry ammonium sulfate (AS) seed particles at an RH of 68%. ~~At an OH exposure of 4.66×10^{10} molecules cm^{-3} s, t~~The ratio of the SOA yield on wet AS seeds to that on dry AS seeds, the relative SOA yield, ~~was~~ decreased from 1.31±0.02 at an OH exposure of 4.66×10^{10} molecules cm^{-3} s to ~~. However, this ratio decreased to~~ 1.01±0.01 at an OH exposure of 5.28×10^{11} molecules cm^{-3} s. ~~The~~ This decrease ~~in the ratios of SOA yields as the increase of OH exposure~~ may be due to the early deliquescence of initially dry AS seeds after coated by highly oxidized toluene-derived SOA. SOA formation lowered the deliquescence RH of AS and resulted in the uptake of water by both AS and SOA. Hence the initially dry AS seeds contained aerosol liquid water (ALW) soon after ~~a large fraction of~~ SOA formed and the SOA yield and ALW approached those of the initially wet AS seeds as OH exposure and ALW increased, especially at high OH exposure. However, a higher oxidation state of the SOA on initially wet AS seeds than that on dry AS seeds was observed at all levels of OH exposure. The difference in mass fractions of *m/z* 29, 43 and 44 of SOA mass spectra, obtained using an aerosol mass spectrometer (AMS), indicated that SOA formed on initially wet seeds may be enriched

in earlier-generation products containing carbonyl functional groups at low OH exposures and later-generation products containing acidic functional groups at high exposures. Our results suggest that ~~AS~~ inorganic dry seeds ~~soon~~ become ~~turn to~~ at least partially deliquesced particles during SOA formation and hence ALW is inevitably involved in the SOA formation at moderate RH. More laboratory experiments conducted with a wide variety of SOA precursors and inorganic seeds under different NO_x and RH conditions are warranted. ~~more studies on the interplay of SOA formation and ALW are warranted.~~

1. Introduction

Secondary organic aerosol (SOA) is an important component of atmospheric particulate matter, which influences air quality, climate and human health (Hallquist et al., 2009). SOA is mainly formed via the oxidation of volatile organic compounds (VOCs), followed by partitioning to the condensed phase. Traditional atmospheric chemical transport models largely underestimate the levels of SOA (de Gouw et al., 2005; Volkamer et al., 2006; Hodzic et al., 2010) and the degree of oxidation (Rudich et al., 2007; Ng et al., 2010). The updated models incorporating the volatility basis set (VBS) formalism (Donahue et al., 2006) can better predict the observed SOA, but SOA formation still remains under-constrained (Shrivastava et al., 2011; Tsigaridis et al., 2014; Hayes et al., 2015; Ma et al., 2017). SOA yields in ~~traditional~~ atmospheric chemical transport models are obtained from smog chamber experiments using dry seed particles (Barsanti et al., 2013; Mahmud and Barsanti, 2013) under dry conditions. Yet, atmospheric relative humidity is often sufficiently high that aerosols often ~~exist as wet aerosols, containing a large amount of~~contain aerosol liquid water (ALW) due to their hygroscopic properties (Liao and Seinfeld, 2005; Lee and Adams, 2010; Guo et al., 2015; Nguyen et al., 2016). The presence of ALW in ~~wet~~ aerosols may enhance SOA formation by facilitating the partitioning of semivolatile organic compounds and the uptake of water-soluble gases through aqueous-phase reactions (Hennigan et al., 2008; Lim et al., 2010; Ervens et al., 2011; Lee et al., 2011; Sareen et al., 2017). ALW may also promote photodegradation of dissolved SOA (Romonosky et al., 2014). Therefore, SOA formation under atmospherically relevant relative humidity needs to be better constrained in atmospheric chemical transport models by incorporating ALW. In addition, understanding water uptake of SOA is important for estimating its loss by wet deposition, which is not well constrained.

Aromatic hydrocarbons constitute a large fraction of the total non-methane hydrocarbons in the urban atmosphere (Calvert et al., 2002) and account for a significant fraction of SOA in urban areas (Ding et al., 2012; Zhao et al., 2017). Toluene is the most abundant aromatic hydrocarbon (Calvert et al., 2002; Zhang et al., 2016) and SOA yields from the photooxidation of toluene on dry or wet ammonium sulfate (AS) seeds has been studied by varying the RH in smog chambers. Kamens et al. (2011) observed higher yields of SOA from toluene at higher RHs. They attributed this increase to the initially wet seed particles. On the other hand, Edney et al. (2000) reported that wet seeds had no effect on the SOA yields of toluene compared with dry seeds. In these studies, different RHs used for dry and wet seeds experiments may influence the gas-phase chemistry and complicate the comparison of SOA formation.

SOA formation on initially dry and wet AS seeds has been compared using oxidation flow reactors at same RHs (Wong et al., 2015; Faust et al., 2017). Faust et al. (2017) found a 19% enhancement in the SOA yield of toluene on wet AS seeds over that on dry AS seeds at 70% RH. However, at such high RH, the initially dry and water-free AS seed particles can uptake water upon SOA formation because SOA themselves can be hygroscopic and they can also lower the deliquescence RH of the AS seeds (Takahama et al., 2007; Smith et al., 2011, 2012, 2013). The potential influence of SOA formation on the physical state of the initially dry seeds as well as and the overall water uptake by the aged particles was not explicitly discussed. In addition, the hydroxyl radicals (OH) exposure in ~~their study~~Faust et al. (2017) was approximately 2×10^{11} molecules cm^{-3} s, equivalent to about 1.5 days of oxidation in the atmosphere assuming an ambient OH concentration of 1.5×10^{6} molecules cm^{-3} (Mao et al., 2009). Atmospheric particles can undergo oxidation for as long as 1-2 weeks (Balkanski et al., 1993).

In this study, SOA formation from the photooxidation of toluene was investigated in an oxidation flow reactor at an RH of 68% under a wide range of OH exposures using initially wet or dry AS seed particles. The yields and composition of SOA as well as the estimated ALW contents for the initially wet and dry seeds are compared. We found that as OH exposure increased, the SOA yield and ALW of the initially dry seeds approached those of the initially wet seeds while the wet seeds yielded SOA of a higher degree of oxidation than the dry seeds did at all exposure levels.

2. Materials and methods

2.1 Generation of seed particles

A schematic of the experimental setup, similar to that used in Wong et al. (2015) and Faust et al. (2017), is shown in Fig. 1. AS seed particles were generated from an aqueous AS solution (Sigma-Aldrich) using an atomizer (TSI 3076, TSI Inc., USA). In experiments using dry seeds, the atomized aqueous AS droplets passed through a silica gel diffusion dryer so that the RH was reduced to less than 30% at which AS effloresced, while in experiments using wet seeds, they bypassed the diffusion dryer. The dry or wet seed particles then entered and mixed with a humidified $N_2/O_2/O_3$ flow in an oxidation flow reactor. The RH in the flow reactor was at 68%, which lies between the efflorescence and deliquescence RH of AS (Seinfeld and Pandis, 2006), so that the seed particles remained in their original phase with the wet particles containing ~18.6 μg m^{-3} ALW (see Section 2.4) and the dry particles anhydrous before reaction started. Hereafter, the experiments using initially wet and dry AS seed particles are simplified as wet and dry AS seeds, respectively. "Wet" and "dry" refer to the initial state of the seed particles before SOA formation.

When atomizing a given AS solution, the diameter of wet AS droplets is much larger than that of dry AS particles due to the water uptake of AS (Chan et al., 1992), resulting in a larger surface area of seed particles. Previous studies have demonstrated that a large surface area of seed particles may increase the SOA yields by reducing the wall loss of organic vapors (Matsunaga and Ziemman, 2010, Zhang et al., 2014, 2015; Huang et al., 2016; Krechmer et al., 2016). To obtain seed particles of comparable surface areas, we atomized 0.013 mM and 0.015 mM of the AS solution for wet and dry AS seeds, respectively. As shown in Fig. S1, the surface area distribution of initially wet AS seeds was similar to that of initially dry AS seeds. Because of the difference in AS concentration between the stock solutions used, wet AS seeds had a mean diameter of 88 nm and were slightly smaller than dry AS seeds which had a mean diameter of 102 nm. The total surface area of wet AS seeds was 21% larger than that of dry AS seeds. The mass loading of wet and dry AS seeds was 31.0 and 24.2 μg m^{-3}, respectively.

2.2 Oxidation flow reactor

SOA formation from the photooxidation of toluene in the absence of NO_x on initially dry or wet seeds was investigated in a potential aerosol mass (PAM) oxidation flow reactor, which has been described in detail elsewhere (Kang et al., 2007, 2011; Lambe et al., 2011a, 2015; Liu et al., 2017). Briefly, a PAM chamber is a continuous oxidation flow reactor using high and controlled levels of oxidants to oxidize gaseous precursors to produce SOA. The chamber used in this study had a volume of approximately 19 L (length 60 cm, diameter 20 cm). The total flow rate in the PAM chamber was set at 3 L min^{-1} using mass flow controllers, resulting in a residence time of approximately 380 s. The RH and temperature of the PAM outflow were measured continuously (HMP 110, Vaisala Inc, Finland) and stabilized at approximately 68% and 20 ºC, respectively. High OH exposures were realized through the photolysis of ozone irradiated by a UV lamp ($\lambda = 254$ nm) in the presence of water vapor. Ozone was produced by an ozone generator (1000BT-12, ENALY, Japan) via the irradiation of pure O_2. The OH concentration was adjusted by varying the concentration of ozone in the PAM chamber from 0.4 ppm to 4.3 ppm. The corresponding upper limit of OH exposure at these operating conditions ranged from ~~4.66~~0.47× ~~10^{10}~~–10^{11} molecules cm^{-3} s to 5.28×10^{11} molecules cm^{-3} s, equivalent to 0.36 to 4.08 days of atmospheric oxidation assuming an ambient OH concentration of 1.5×10^{6} molecules cm^{-3} (Mao et al., 2009). ~~The addition of toluene may reduce the OH exposure.~~ The upper limit of OH exposure was determined by measuring the decay of SO_2 (Model T100, TAPI Inc., USA) in the absence of toluene, following procedures described elsewhere (Kang et al., 2007; Lambe et al., 2011a). 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). Peng et al. (2016) found that non-OH chemistry, including photolysis at λ = 254 nm and reactions with O(^{1}D), O(^{3}P) and O_3, may play an important role in oxidation flow reactors. In this study, the PAM reactor was operated at water vapor mixing ratios above 0.5% and external OH reactivity below 20 s^{-1}. Non-OH chemistry is expected to play a negligible role under these conditions (Peng et al., 2016).

Before and after each experiment, the PAM reactor was cleaned under an OH exposure of ~1×10^{12} molecules cm^{-3} s until the mass concentration of background particles dropped below 3 μg m^{-3}. After characterizing dry or wet AS seed particles for half an hour, the UV lamp was turned on to oxidize the background gases at five different OH levels to measure the concentrations of background organics. A toluene mixture (29.6 ppm in nitrogen) with a flow rate of 0.013 L min^{-1} was then introduced to initiate SOA formation. The initial concentration of toluene in the PAM reactor was approximately 138 ppb. 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). The flow and light conditions were the same for initially wet and dry seeds. Therefore, the quantification of toluene would not introduce uncertainties to the relative SOA yields described in Section 3.1 as the initial concentrations of toluene and OH exposures were the same for both cases. SOA was measured for at least an hour ~~at each of~~ with a step-wise increase in the five OH levels.

2.3 Characterization of non-refractory components

The AS/SOA mixed particles were characterized for the chemical composition of non-refractory components including organics, sulfate and ammonium as well as the elemental ratios of organics using a high-resolution time-of-flight aerosol mass spectrometer (hereafter AMS, Aerodyne Research Incorporated, USA) (DeCarlo et al., 2006). The instrument was operated in the high sensitivity V-mode and the high resolution W-mode alternating every one minute. The toolkit Squirrel 1.57I and Pika 1.16I were used to analyze the AMS data. The molar ratios of hydrogen to carbon (H:C) and oxygen to carbon (O:C) were determined using the Aiken method (Aiken et al., 2007, 2008). The ionization efficiency of the AMS was calibrated using 300 nm ammonium nitrate particles. The particle-free matrix air, obtained by passing the air flow from the PAM reactor through a HEPA filter, was measured for at least 20 min before each experiment to determine the signals from major gases.

The collection efficiency (CE) of an AMS is dependent on the chemical composition and acidity as well as the phase state of particles (Matthew et al., 2008; Middlebrook et al., 2012). Matthew et al. (2008) found that the CE for solid particles thickly coated with liquid organics was 100%. In this study, experiments were conducted at an RH of 68%, exceeding the RH threshold for the semisolid-to-liquid phase transition for toluene-derived SOA (Bateman et al., 2015; Song et al., 2016). 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. For the quantification of SOA, the contribution from background organic aerosols was subtracted from the total organic aerosols. The ratio of SOA mass to background organic mass ranged from 7 to 59, indicating that the contribution from background organics was negligible. Aerosol particles typically pass through a silica gel diffusion dryer to remove ALW before they are measured by AMS. However, this may lead to some losses of semivolatile organics through reversible partitioning (Wong et al., 2015; Faust et al., 2016). In this study, the AS/SOA mixed particles stream passed through and bypassed a diffusion dryer alternately before they were measured by AMS. Overall less than 8% of SOA were lost for wet and dry AS seeds after passing the diffusion dryer (Fig. ~~S2~~S3), possibly due to reversible partitioning of the SVOCs. In this paper, the data reported are those bypassing the diffusion dryer.

A scanning mobility particle sizer (SMPS, TSI Incorporated, USA, classifier model 3082, CPC model 3775) was used to measure particle number concentrations and size distributions. Particle size ranged from 15 nm to 661 nm.

To evaluate the influence of seed surface area on SOA formation, we conducted another experiment at OH exposure of ~~4.66~~0.47×~~10^{10}~~-10^{11} molecules cm^{-3} s with 50% of the seed surface area used in the wet AS experiment. The difference in SOA concentration was approximately 1% between these two experiments. Hence the 20% difference in seed surface area as well as the difference in mass loadings between wet and dry AS particles cannot account for the difference in SOA yield to be discussed below.

2.4 Estimation of aerosol liquid water (ALW) content

The ALW content of the initially dry AS was zero. However, as reactions proceed, SOA themselves can uptake water and also lower the deliquescence RH of AS, leading to water uptake by AS and some fractions of AS in aqueous phase. The ALW contents of AS (ALW_{AS}) and toluene-derived SOA (ALW_{SOA}) were estimated from the following equations (Kreidenweis et al., 2008):

$$ALW_{AS} = V_{AS}\kappa_{AS} f \frac{\alpha_w}{1-\alpha_w}\rho_w \tag{1}$$

$$ALW_{SOA} = V_{SOA}\kappa_{SOA} \frac{\alpha_w}{1-\alpha_w}\rho_w \tag{2}$$

where V_{AS} and V_{SOA} represent the volume concentrations of dry AS and SOA particles, κ_{AS} is the hygroscopicity parameter of AS particles obtained from Kreidenweis et al. (2008), κ_{SOA} is the hygroscopicity parameter of toluene-derived SOA calculated using the linear correlation between κ_{SOA} and the O:C ratios of SOA proposed by Lambe et al. (2011b), the term f is the fraction of AS particles that dissolved, α_w is the water activity and ρ_w is the density of water (1.0 g cm^{-3}). Here, α_w was assumed to be equivalent to RH/100 for simplicity. The volume concentrations of dry AS and SOA particles were estimated from the measured mass concentration of AS and SOA assuming their respective particle densities to be 1.77 g cm^{-3} and 1.4 g cm^{-3} (Ng et al., 2007).

For the initially wet AS seeds, all AS particles were completely aqueous and therefore f = 1. For the initially dry AS seeds, before reactions, the AS particles were completely dry and $f = 0$. After reactions, the AS particles became partially or entirely deliquesced upon the formation of toluene-derived SOA. The dissolved fraction of AS particles was regulated by the liquidus curve of the deliquescence relative humidity (DRH(ε)) of AS particles coated with toluene-derived SOA (Smith et al., 2013):

$$f = \begin{cases} \dfrac{\varepsilon(1-\varepsilon_D)}{\varepsilon_D(1-\varepsilon)} & for\ \varepsilon < \varepsilon_D \\ 1 \quad for & \varepsilon \geq \varepsilon_D \end{cases} \tag{3}$$

The term ε is the volume fraction of SOA (Table 1). The term ε_D, representing the volume fraction of organics at which the mixture of SOA and AS particles deliquesced at an RH of 68%, was estimated to be 0.75 based on the liquidus curve.

3. Results and discussion

3.1 SOA yields

Figure 2a shows SOA yields from the photooxidation of toluene on initially wet and dry AS seed particles as a function of OH exposure. The SOA yield was calculated as the SOA mass divided by the mass of reacted toluene. ~~The mass of reacted toluene was calculated from the OH exposure and the rate constant of the reaction between toluene and OH (Atkinson and Arey, 2003).~~ The uncertainty in the SOA yields ~~fully~~ simply reflected the standard derivation when averaging~~uncertainty in the calculation of~~ the SOA mass. In both cases, SOA yields first exhibited an increase, followed by a decrease as the level of OH exposure increased. This trend may be due to the transition of functionalization reactions to fragmentation ones (Kroll et al., 2009; Lambe et al., 2011a). Previous oxidation flow reactor studies suggest that gas-phase chemistry dominates over heterogeneous OH oxidation at OH levels below 1.0×10^{12} molecules cm^{-3} s (Ortega et al., 2016; Palm et al., 2016). In this study, the highest OH exposure was 5.28×10^{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). The SOA yields for dry and wet AS seeds were 0.18–0.31 and 0.22–0.36, respectively, significantly higher than the value of 0.0059 observed in an oxidation flow reactor under comparable conditions (Faust et al., 2017) and the value of 0.09 obtained in another PAM chamber at 30% RH in the absence of seed particles (Kang et al., 2007). Faust et al. (2017) attributed their significantly lower yields than typical literature values of 0.09–0.30 (Lambe et al., 2011a; Ng et al., 2007) to the wall loss of particles and the fragmentation of organics in their flow reactor. On the other hand, the SOA yields we obtained are lower than the values of 0.30–0.37 from smog chamber experiments conducted at a similar temperature, SOA mass loading and OH exposure but a lower RH with dry AS seeds (Ng et al., 2007; Hildebrandt et al., 2009). Note that the wall loss of particles was not corrected in this study, so the SOA yields may be underestimated. As wet and dry AS seeds in this study had similar particle number size distributions, the wall loss of particles would not affect the comparison of SOA yield between wet and dry AS seeds.

As shown in Fig. 2a, a higher SOA yield was observed for wet AS seeds than for dry AS seeds at the same OH exposure and the difference in SOA yield decreased as the OH exposure increased. The ratio of SOA yields on wet AS seeds to those on dry

AS seeds, the relative SOA yield, was 1.31±0.02 at an OH exposure of ~~4.66~~0.47×~~10^{10}~~ 10^{11} molecules cm^{-3} s but decreased to 1.01±0.01 when the OH exposure was increased to 5.28×10^{11} molecules cm^{-3} s (Fig. 2b). These ratios are comparable to the 1.19±0.05 observed by Faust et al. (2017) at an OH exposure of approximately 2.0×10^{11} molecules cm^{-3} s.

The formation of SOA on initially dry AS particles may alter the deliquescence relative humidity (DRH) of AS particles. Smith et al. (2013) found that when coated with toluene-derived SOA, the DRH of AS particles decreased from 80% to 58% as the organic volume fraction increased from 0 to 0.8. Therefore, coating AS particles with toluene-derived SOA can change the physical state of initially dry AS seeds and increase the content of ALW$_{\text{AS, dry}}$. As shown in Fig. 3a, after reactions, the mass concentrations of ALW$_{\text{tot}}$ (= ALW$_{\text{SOA}}$ + ALW$_{\text{AS}}$) and ALW$_{\text{SOA}}$ increased for both wet and dry seeds as the OH exposure increased. The uncertainties for ALW$_{\text{SOA}}$ and ALW$_{\text{AS}}$ were 22% and less than 3%, respectively. They reflect the uncertainties in κ and volume concentrations of AS and SOA. The increase in ALW$_{\text{tot, wet}}$ was due to the increase in ALW$_{\text{SOA, wet}}$ while the increase in ALW$_{\text{tot, dry}}$ was driven by the increase in ALW$_{\text{AS, dry}}$ at lower OH exposure and by ALW$_{\text{SOA, dry}}$ at higher OH exposures. At OH exposure of ~~4.66~~0.47×~~10^{10}~~-10^{11} molecules cm^{-3} s, ALW$_{\text{AS, dry}}$ increased from 0 to 6.2 μg m^{-3} after reactions due to the partial deliquescence (*f*=0.43) of the originally dry AS particles after SOA formation. The difference in ALW$_{\text{AS, dry}}$ and ALW$_{\text{AS, wet}}$ narrowed and the ALW$_{\text{total}}$ of initially dry AS seeds partially resembled those of the wet ones. At OH exposure between 1.66×10^{11} and 5.28×10^{11} molecules cm^{-3} s, the total final organic volume fraction increased to approximately 0.8 and the initially dry AS particles entirely deliquesced after reactions. Based on the reported SOA yield, initial toluene concentration, OH exposure and assumed concentrations of AS seeds (~10-40 µg m^{-3}) in Faust et al. (2017), we estimated that an upper limit of 48% of the initially dry AS seeds has deliquesced in their study. Similar to this study, SOA coatings on seed particles may change the physical state of initially dry seeds and lower the difference of SOA yields between initially dry and wet seeds experiments.

The hydrophilic products can partition more readily into initially wet AS seeds than dry seeds and partially account for the difference in SOA yields. For example, as one of the important oxidation products, glyoxal was estimated to have an effective Henry's law constant of 4.52×10^{8} m atm^{-1} for our initially wet AS seeds due to the "salting-in" effect (Kampf et al., 2013), approximately 3 orders of magnitude higher than that in pure water (Ip et al., 2009). The uptake rate constant of glyoxal can be calculated as $(\gamma v A)/4$, where γ is the uptake coefficient, v is the gas-phase velocity of glyoxal, and A is the total surface area of AS seeds. The uptake rate constant is 4.5×10^{-4} s^{-1} for initially wet seeds with $\gamma = 2.4\times10^{-3}$ estimated from glyoxal uptake in AS seeds at 68% RH (Liggio et al., 2005b). The average gas-phase glyoxal concentration was modeled to be 4.3 ppb at OH exposure of 0.47×10^{11} molecules cm^{-3} s using the Master Chemical Mechanism v 3.3.1 (Jenkin et al., 2003; Bloss et al., 2005), which would result in approximately 1.6 µg m^{-3} of glyoxal in particle phase for initially wet AS seeds. If the particle-phase concentration of glyoxal was assumed to be 0 for initially dry AS seeds, the enhanced partitioning of glyoxal alone would account for 24.5% of the mass difference of SOA. Note that other hydrophilic products were not included in this calculation. This analysis suggests that the enhanced partitioning of hydrophilic products may play an important role in the difference of SOA yields at low OH exposures. As discussed above, the initially dry AS seeds approached wet seeds and reduce the differences between wet and dry SOA yields at high OH exposures.

3.2 Chemical composition of SOA

Figure 4 shows the high-resolution mass spectra of SOA for initially wet and dry AS seeds at OH exposures of ~~4.66~~0.47×~~10^{10}~~-10^{11} molecules cm^{-3} s and 5.28×10^{11} molecules cm^{-3} s. For both types of AS seeds, at an OH exposure of ~~4.66~~0.47×~~10^{10}~~-10^{11} molecules cm^{-3} s, the most prominent peaks were *m/z* 29 and 43, followed by *m/z* 28 and 44. *m/z* 29 was dominated by ion CHO^+, a tracer for alcohols and aldehydes (Lee et al., 2012). The *m/z* 28 and *m/z* 44 signals, respectively dominated by CO^+ and CO_2^+, are tracers for organic acids (Ng et al., 2010). At the OH exposure of 5.28×10^{11} molecules cm^{-3} s, the dominant peaks were *m/z* 28 and 44, followed by *m/z* 29 and 43. The increase of mass fractions of the oxygen-containing ions in the SOA mass spectra at a relatively high OH exposure suggests the formation of more oxidized organic aerosols. ~~Furthermore, ions with *m/z* > 80 accounted for a negligible fraction of total SOA, suggesting that oligomerization might not be important in these experiments.~~ On the basis of the mass fraction of ions, Fig. ~~S3~~ S4 shows that as OH exposure increased, the difference (wet minus dry) in the spectra of toluene-derived SOA changed from positive in *m/z* 29 (CHO^+) and *m/z* 43 ($C_2H_3O^+$) to *m/z* 28 (CO^+) and *m/z* 44 (CO_2^+). The increase in OH exposure resulted in a change from more alcohols or aldehydes to more organic acids in the wet seeded case when compared to the dry seeded case.

Fragments derived from the AMS data have been extensively used to infer the bulk compositions and evolution of organic aerosols (Zhang et al., 2005; Ng et al., 2010; Heald et al., 2010). Here we used the approach of Ng et al. (2010) and plotted the fractions of the total organic signal at *m/z* 43 (f_{43}) vs. *m/z* 44 (f_{44}) as well as the triangle based on the analysis of ambient AMS data (Fig. 5). Ng et al. (2010) proposed that aging would cause f_{43} and f_{44} to converge toward the triangle apex ($f_{43} = 0.02$, $f_{44} = 0.30$). For both wet and dry AS seeds, f_{43} first increased and then decreased with the increase of OH exposure, while f_{44} increased all the time. This reversing trend of f_{43} was the result of the increase and subsequent decrease in $C_2H_3O^+$ (Fig. ~~S4~~S5), an indicator of products containing carbonyl functional groups. The f_{43}-f_{44} plot supports our earlier assertion that as OH exposure increased, the reaction products changed from earlier-generation products containing carbonyl functional groups dominated to later-generation products containing acidic functional groups dominated. It was also observed for SOA formed from other precursors such as alkanes and naphthalene (Lambe et al., 2011b). Before the decrease in f_{43}, SOA formed on wet AS seeds had higher f_{43} and similar f_{44} to SOA formed on dry AS seeds at the same OH exposure. As OH exposure increased, SOA formed on wet AS seeds had higher f_{44} and lower f_{43} than SOA formed on dry AS seeds. ~~The f_{43}-f_{44} plot supports our earlier assertion that as OH exposure increased, the reaction products changed from earlier-generation products containing carbonyl functional groups to later-generation products containing acidic~~

~~functional groups.~~ In addition, as OH exposure increased, SOA formed on wet AS seeds initially had more earlier-generation products but later had more acidic later-generation products than SOA formed on dry AS seeds, likely due to the enhanced partitioning of these products on initially wet AS seeds and/or enhanced uptake of water-soluble gases through aqueous phase reactions.

Figure 6 shows the changes in H:C and O:C ratios as a function of OH exposure in a Van Krevelen diagram (Heald et al., 2010). The standard deviations for H:C and O:C values, determined for the steady-state periods, were ~~both~~ all less than 0.01. The O:C ratios for dry and wet AS seeds were in the ranges of 0.59–0.89 and 0.63–0.95, respectively. At the same OH exposure, SOA on wet AS seeds had both higher O:C ratios and estimated average carbon oxidation state (OS_C) ($OS_C \approx 2\times O{:}C - H{:}C$) (Kroll et al., 2011) than dry AS seeds had. Fig. 6 also shows some of the identified SOA products from the photooxidation of toluene (Bloss et al., 2005; Hamilton et al., 2005; Sato et al., 2007). The elevated OS_C~~OS_c~~ (exceeding 0.5) could only be due to the formation of highly oxgenerated small acids such as pyruvic acid (OS_C = 0.67), glycolic acid (OS_C = 1), formic acid (OS_C = 2), oxalic acid (OS_C = 3), malonic acid (OS_C = 1.33) and glyoxylic acid (OS_C = 2). Small acids may be important products of toluene-derived SOA at high OH exposures. Fisseha et al. (2004) found that small organic acids accounted for 20–45% of SOA from the photooxidation of 1,3,5-trimethylbenzene. The higher OS_C at high OH exposures for wet AS seeds might suggest that these small acids were more abundant, likely due to their enhanced retention in the presence of ALW and/or the more efficient uptake of OH radicals by wet AS seeds and further oxidation reactions in aqueous phase (Ruehl et al., 2013).

We evaluate whether enhanced uptake of OH radicals on initially wet AS seeds could explain the difference in oxygen contents, following the method of DeCarlo et al. (2008). We calculated R, the ratio of the difference in oxygen of OA between the initially wet and dry AS seed particles to the difference in the total number of OH collisions with OA at different OH exposures. To obtain R, the uptake coefficient (γ) of OH radicals was assumed to be 1 and 0.1/0.8 (lower/upper limit) for initially wet and dry AS seed particles, respectively (George and Abbatt, 2000). Note that as SOA formation takes place, the initially dry AS can become wet and the difference in γ between initially wet and dry seeds is reduced, especially at higher OH exposures. We also assumed that each collision of OH with OA resulted in the addition of one oxygen atom to SOA. A value of R smaller than unity qualitatively indicates that the uptake of OH radicals can potentially explain the differences in oxygen contents in the dry and wet experiments. Fig. S6 shows that R is larger than unity at low OH exposures and smaller than unity at high OH exposures. This analysis suggests that the enhanced OH uptake may contribute to the difference in oxygen contents between dry and wet cases at higher OH exposures. At low OH exposures, the enhanced gas-particle partitioning may dominate the difference.

The change in the slope of H:C vs O:C is consistent with the earlier analysis that the mechanism of SOA formation changed from functionalization dominated by the addition of alcohol/peroxide (Heald et al., 2010; Ng et al., 2011) at low exposures to the addition of both acid and alcohol/peroxide functional groups without fragmentation, and/or the addition of acid groups with fragmentation at high exposures.

3.3 Atmospheric implications

In this work, yields and composition of SOA formed from the photooxidation of toluene on initially wet and dry AS seeds were compared over a wide range of OH exposures, covering the transition from functionalization reactions to fragmentation reactions. We found that the ratio of SOA yield on wet AS seeds to that on dry AS seeds decreased from 1.31 to 1.01 as the OH exposure increased from ~~4.66~~0.47×~~10^{10}~~-10^{11} to 5.28×10^{11} molecules cm^{-3} s. This decrease coincides with the decrease of differences in ALW between the wet and dry cases, which may be due to water uptake by SOA as well as the early deliquescence of dry AS particles as a result of SOA formation. Hence, the SOA yield and ALW of the initially dry AS seeds approached those of the initially wet AS seeds as OH exposure and ALW increased.

In addition to relatively higher SOA yields, higher O:C and OS_C of SOA derived from the photooxidation of toluene were also observed on initially wet AS seeds. Particularly, the O:C in the presence of initially wet AS seeds could be as high as 0.95. Chen et al. (2015) observed large gaps between laboratory and ambient measured O:C of OA and suggested that OA having a high O:C (> 0.6) was required to bridge these gaps. The multiphase oxidation of toluene in the presence of wet aerosols may be a pathway to contribute to this gap. However, the relative importance of such chemistry to the evolution of ambient OA remains unclear.

Our results suggest that dry seeds would quickly turn to at least partially deliquesced particles upon SOA formation under moderate RH conditions. 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). Since ambient RH is rarely at such low values that inorganic particles remain dry even after SOA formation, more laboratory and field studies are needed to elucidate the formation and evolution of OA under various NO_x conditions ~~in wet aerosols~~at moderate RH.

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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, 8350-8358, https://doi.org/10.1021/ac071150w, 2007.

Aiken, A. C., DeCarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry, Environ. Sci. Technol., 42, 4478-4485, https://doi.org/10.1021/es703009q, 2008.

Atkinson, R., and Arey, J.: Atmospheric Degradation of Volatile Organic Compounds, Chem. Rev., 103, 4605-4638, https://doi.org/10.1021/cr0206420, 2003.

Balkanski, Y. J., Jacob, D. J., Gardner, G. M., Graustein, W. C., and Turekian, K. K.: Transport and residence times of tropospheric aerosols inferred from a global three-dimensional simulation of 210Pb, J. Geophys. Res.-Atmos., 98, 20573-20586, https://doi.org/10.1029/93JD02456, 1993.

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, https://doi.org/10.5194/acp-13-12073-2013, 2013.

Bateman, A. P., Bertram, A. K., and Martin, S. T.: Hygroscopic Influence on the Semisolid-to-Liquid Transition of Secondary Organic Materials, J. Phys. Chem. A, 119, 4386-4395, https://doi.org/10.1021/jp508521c, 2015.

Bloss, C., Wagner, V., Jenkin, M. E., Volkamer, R., Bloss, W. J., Lee, J. D., Heard, D. E., Wirtz, K., Martin-Reviejo, M., Rea, G., Wenger, J. C., and Pilling, M. J.: Development of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons, Atmos. Chem. Phys., 5, 641-664, https://doi.org/10.5194/acp-5-641-2005, 2005.

Calvert, J. G., Atkinson, R., Becker, K. H., Kamens, R. M., Seinfeld, J. H., Wallington, T. H., and Yarwood, G.: The Mechanisms of Atmospheric Oxidation of the Aromatic Hydrocarbons, Oxford University Press, New York, 556 pp., 2002.

Chen, Q., Heald, C. L., Jimenez, J. L., Canagaratna, M. R., Zhang, Q., He, L.-Y., Huang, X.-F., Campuzano-Jost, P., Palm, B. B., Poulain, L., Kuwata, M., Martin, S. T., Abbatt, J. P. D., Lee, A. K. Y., and Liggio, J.: Elemental composition of organic aerosol: The gap between ambient and laboratory measurements, Geophys. Res. Lett., 42, 2015GL063693, https://doi.org/10.1002/2015GL063693, 2015.

de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P. D., Kuster, W. C., Roberts, J. M., Fehsenfeld, F. C., Worsnop, D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W. C., Marchewka, M., Bertman, S. B., and Bates, T. S.: Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, J. Geophys. Res.-Atmos., 110, D16305, https://doi.org/10.1029/2004JD005623, 2005.

DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-Deployable, High-Resolution, Time-of-Flight Aerosol Mass Spectrometer, Anal. Chem., 78, 8281-8289, https://doi.org/10.1021/ac061249n, 2006.

DeCarlo, P. F., Dunlea, E. J., Kimmel, J. R., Aiken, A. C., Sueper, D., Crounse, J., Wennberg, P. O., Emmons, L., Shinozuka, Y., Clarke, A., Zhou, J., Tomlinson, J., Collins, D. R., Knapp, D., Weinheimer, A. J., Montzka, D. D., Campos, T., and Jimenez, J. L.: Fast airborne aerosol size and chemistry measurements above Mexico City and Central Mexico during the MILAGRO campaign, Atmos. Chem. Phys., 8, 4027-4048, https://doi.org/10.5194/acp-8-4027-2008, 2008.

Ding, X., Wang, X.-M., Gao, B., Fu, X.-X., He, Q.-F., Zhao, X.-Y., Yu, J.-Z., and Zheng, M.: Tracer-based estimation of secondary organic carbon in the Pearl River Delta, south China, J. Geophys. Res.-Atmos., 117, D05313, https://doi.org/10.1029/2011JD016596, 2012.

Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled Partitioning, Dilution, and Chemical Aging of Semivolatile Organics, Environ. Sci. Technol., 40, 2635-2643, https://doi.org/10.1021/es052297c, 2006.

Edney, E. O., Driscoll, D. J., Speer, R. E., Weathers, W. S., Kleindienst, T. E., Li, W., and Smith, D. F.: Impact of aerosol liquid water on secondary organic aerosol yields of irradiated toluene/propylene/NOx/(NH4)2SO4/air mixtures, Atmos. Environ., 34, 3907-3919, 2000.

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, https://doi.org/10.5194/acp-11-11069-2011, 2011.

Faust, J. A., Wong, J. P. S., Lee, A. K. Y., and Abbatt, J. P. D.: Role of Aerosol Liquid Water in Secondary Organic Aerosol Formation from Volatile Organic Compounds, Environ. Sci. Technol., 51, 1405-1413, https://doi.org/10.1021/acs.est.6b04700, 2017.

Fisseha, R., Dommen, J., Sax, M., Paulsen, D., Kalberer, M., Maurer, R., Höfler, F., Weingartner, E., and Baltensperger, U.: Identification of Organic Acids in Secondary Organic Aerosol and the Corresponding Gas Phase from Chamber Experiments, Anal. Chem., 76, 6535-6540, https://doi.org/10.1021/ac048975f, 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.

Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite Jr, J. R., Carlton, A. G., Lee, S. H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and pH in the southeastern United States, Atmos. Chem. Phys., 15, 5211-5228, https://doi.org/10.5194/acp-15-5211-2015, 2015.

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., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prévôt, 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, https://doi.org/10.5194/acp-9-5155-2009, 2009.

Hamilton, J. F., Webb, P. J., Lewis, A. C., and Reviejo, M. M.: Quantifying small molecules in secondary organic aerosol formed during the photo-oxidation of toluene with hydroxyl radicals, Atmos. Environ., 39, 7263-7275, http://dx.doi.org/10.1016/j.atmosenv.2005.09.006, 2005.

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, https://doi.org/10.5194/acp-15-5773-2015, 2015.

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., and Artaxo, P.: A simplified description of the evolution of organic aerosol composition in the atmosphere, Geophys. Res. Lett., 37, L08803, https://doi.org/10.1029/2010gl042737, 2010.

Hennigan, C. J., Bergin, M. H., Dibb, J. E., and Weber, R. J.: Enhanced secondary organic aerosol formation due to water uptake by fine particles, Geophys. Res. Lett., 35, L18801, https://doi.org/10.1029/2008GL035046, 2008.

Hildebrandt, L., Donahue, N. M., and Pandis, S. N.: High formation of secondary organic aerosol from the photo-oxidation of toluene, Atmos. Chem. Phys., 9, 2973-2986, https://doi.org/10.5194/acp-9-2973-2009, 2009.

Hodzic, A., Jimenez, J. L., Madronich, S., Canagaratna, M. R., DeCarlo, P. F., Kleinman, L., and Fast, J.: Modeling organic aerosols in a megacity: potential contribution of semi-volatile and intermediate volatility primary organic compounds to secondary organic aerosol formation, Atmos. Chem. Phys., 10, 5491-5514, https://doi.org/10.5194/acp-10-5491-2010, 2010.

Huang, D. D., Zhang, X., Dalleska, N. F., Lignell, H., Coggon, M. M., Chan, C.-M., Flagan, R. C., Seinfeld, J. H., and Chan, C. K.: A note on the effects of inorganic seed aerosol on the oxidation state of secondary organic aerosol—α-Pinene ozonolysis, J. Geophys. Res.-Atmos., 121, 2016JD025999, https://doi.org/10.1002/2016JD025999, 2016.

Ip, H. S. S., Huang, X. H. H., and Yu, J. Z.: Effective Henry's law constants of glyoxal, glyoxylic acid, and glycolic acid, Geophys. Res. Lett., 36, L01802, https://doi.org/10.1029/2008GL036212, 2009.

Jenkin, M. E., Saunders, S. M., Wagner, V., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 181-193, https://doi.org/10.5194/acp-3-181-2003, 2003.

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, https://doi.org/doi:10.1016/j.atmosenv.2010.11.007, 2011.

Kampf, C. J., Waxman, E. M., Slowik, J. G., Dommen, J., Pfaffenberger, L., Praplan, A. P., Prévôt, A. S. H., Baltensperger, U., Hoffmann, T., and Volkamer, R.: Effective Henry's Law Partitioning and the Salting Constant of Glyoxal in Aerosols Containing Sulfate, Environ. Sci. Technol., 47, 4236-4244, https://doi.org/10.1021/es400083d, 2013.

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, https://doi.org/10.5194/acp-7-5727-2007, 2007.

Kang, E., Toohey, D. W., and Brune, W. H.: Dependence of SOA oxidation on organic aerosol mass concentration and OH exposure: experimental PAM chamber studies, Atmos. Chem. Phys., 11, 1837-1852, https://doi.org/10.5194/acp-11-1837-2011, 2011.

Krechmer, J. E., Pagonis, D., Ziemann, P. J., and Jimenez, J. L.: Quantification of Gas-Wall Partitioning in Teflon Environmental Chambers Using Rapid Bursts of Low-Volatility Oxidized Species Generated in Situ, Environ. Sci. Technol., 50, 5757-5765, https://doi.org/10.1021/acs.est.6b00606, 2016.

Kreidenweis, S. M., Petters, M. D., and DeMott, P. J.: Single-parameter estimates of aerosol water content, Environ. Res. Lett., 3, 035002, 2008.

Kroll, J. H., Smith, J. D., Che, D. L., Kessler, S. H., Worsnop, D. R., and Wilson, K. R.: Measurement of fragmentation and functionalization pathways in the heterogeneous oxidation of oxidized organic aerosol, Phys. Chem. Chem. Phys., 11, 8005-8014, https://doi.org/10.1039/B905289E, 2009.

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., Ahern, A. T., Williams, L. R., Slowik, J. G., Wong, J. P. S., Abbatt, J. P. D., Brune, W. H., Ng, N. L., Wright, J. P., Croasdale, D. R., Worsnop, D. R., Davidovits, P., and Onasch, T. B.: Characterization of aerosol photooxidation flow reactors: heterogeneous oxidation, secondary organic aerosol formation and cloud condensation nuclei activity measurements, Atmos. Meas. Tech., 4, 445-461, https://doi.org/10.5194/amt-4-445-2011, 2011a.

Lambe, A. T., Onasch, T. B., Massoli, P., Croasdale, D. R., Wright, J. P., Ahern, A. T., Williams, L. R., Worsnop, D. R., Brune, W. H., and Davidovits, P.: Laboratory studies of the chemical composition and cloud condensation nuclei (CCN) activity of secondary organic aerosol (SOA) and oxidized primary organic aerosol (OPOA), Atmos. Chem. Phys., 11, 8913-8928, https://doi.org/10.5194/acp-11-8913-2011, 2011b.

Lambe, A. T., Chhabra, P. S., Onasch, T. B., Brune, W. H., Hunter, J. F., Kroll, J. H., Cummings, M. J., Brogan, J. F., Parmar, Y., Worsnop, D. R., Kolb, C. E., and Davidovits, P.: Effect of oxidant concentration, exposure time, and seed particles on secondary organic aerosol chemical composition and yield, Atmos. Chem. Phys., 15, 3063-3075, https://doi.org/10.5194/acp-15-3063-2015, 2015.

Lee, A. K. Y., Herckes, P., Leaitch, W. R., Macdonald, A. M., and Abbatt, J. P. D.: Aqueous OH oxidation of ambient organic aerosol and cloud water organics: Formation of highly oxidized products, Geophys. Res. Lett., 38, L11805, https://doi.org/10.1029/2011GL047439, 2011.

Lee, Y. H., and Adams, P. J.: Evaluation of aerosol distributions in the GISS-TOMAS global aerosol microphysics model with remote sensing observations, Atmos. Chem. Phys., 10, 2129-2144, https://doi.org/10.5194/acp-10-2129-2010, 2010.

Liao, H., and Seinfeld, J. H.: Global impacts of gas-phase chemistry-aerosol interactions on direct radiative forcing by anthropogenic aerosols and ozone, J. Geophys. Res.-Atmos., 110, D18208, https://doi.org/10.1029/2005JD005907, 2005.

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, https://doi.org/10.1021/es048375y, 2005a.

Liggio, J., Li, S.-M., and McLaren, R.: Reactive uptake of glyoxal by particulate matter, J. Geophys. Res.-Atmos., 110, D10304, https://doi.org/10.1029/2004JD005113, 2005b.

Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Aqueous chemistry and its role in secondary organic aerosol (SOA) formation, Atmos. Chem. Phys., 10, 10521-10539, https://doi.org/10.5194/acp-10-10521-2010, 2010.

Liu, T., Li, Z., Chan, M., and Chan, C. K.: Formation of secondary organic aerosols from gas-phase emissions of heated cooking oils, Atmos. Chem. Phys., 17, 7333-7344, https://doi.org/10.5194/acp-17-7333-2017, 2017.

Ma, P. K., Zhao, Y., Robinson, A. L., Worton, D. R., Goldstein, A. H., Ortega, A. M., Jimenez, J. L., Zotter, P., Prévôt, A. S. H., Szidat, S., and Hayes, P. L.: Evaluating the impact of new observational constraints on P-S/IVOC emissions, multi-generation oxidation, and chamber wall losses on SOA modeling for Los Angeles, CA, Atmos. Chem. Phys., 17, 9237-9259, https://doi.org/10.5194/acp-17-9237-2017, 2017.

Mahmud, A., and Barsanti, K.: Improving the representation of secondary organic aerosol (SOA) in the MOZART-4 global chemical transport model, Geosci. Model Dev., 6, 961-980, 10.5194/gmd-6-961-2013, 2013.

Mao, J., Ren, X., Brune, W. H., Olson, J. R., Crawford, J. H., Fried, A., Huey, L. G., Cohen, R. C., Heikes, B., Singh, H. B., Blake, D. R., Sachse, G. W., Diskin, G. S., Hall, S. R., and Shetter, R. E.: Airborne measurement of OH reactivity during INTEX-B, Atmos. Chem. Phys., 9, 163-173, https://doi.org/10.5194/acp-9-163-2009, 2009.

Matsunaga, A., and Ziemann ‡, P. J.: Gas-Wall Partitioning of Organic Compounds in a Teflon Film Chamber and Potential Effects on Reaction Product and Aerosol Yield Measurements, Aerosol Sci. Tech., 44, 881-892, https://doi.org/10.1080/02786826.2010.501044, 2010.

Matthew, B. M., Middlebrook, A. M., and Onasch, T. B.: Collection Efficiencies in an Aerodyne Aerosol Mass Spectrometer as a Function of Particle Phase for Laboratory Generated Aerosols, Aerosol Sci. Tech., 42, 884-898, https://doi.org/10.1080/02786820802356797, 2008.

Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass

Spectrometer using Field Data, Aerosol Sci. Tech., 46, 258-271, https://doi.org/10.1080/02786826.2011.620041, 2012.

Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from m-xylene, toluene, and benzene, Atmos. Chem. Phys., 7, 3909-3922, https://doi.org/10.5194/acp-7-3909-2007, 2007.

Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L., Donahue, N. M., DeCarlo, P. F., Lanz, V. A., Prévôt, A. S. H., Dinar, E., Rudich, Y., and Worsnop, D. R.: Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, Atmos. Chem. Phys., 10, 4625-4641, https://doi.org/10.5194/acp-10-4625-2010, 2010.

Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Chhabra, P. S., Seinfeld, J. H., and Worsnop, D. R.: Changes in organic aerosol composition with aging inferred from aerosol mass spectra, Atmos. Chem. Phys., 11, 6465-6474, https://doi.org/10.5194/acp-11-6465-2011, 2011.

Nguyen, T. K. V., Zhang, Q., Jimenez, J. L., Pike, M., and Carlton, A. G.: Liquid Water: Ubiquitous Contributor to Aerosol Mass, Environ. Sci. Technol. Lett., 3, 257-263, https://doi.org/10.1021/acs.estlett.6b00167, 2016.

Ortega, A. M., Hayes, P. L., Peng, Z., Palm, B. B., Hu, W., Day, D. A., Li, R., Cubison, M. J., Brune, W. H., Graus, M., Warneke, C., Gilman, J. B., Kuster, W. C., de Gouw, J., Gutiérrez-Montes, C., and Jimenez, J. L.: Real-time measurements of secondary organic aerosol formation and aging from ambient air in an oxidation flow reactor in the Los Angeles area, Atmos. Chem. Phys., 16, 7411-7433, https://doi.org/10.5194/acp-16-7411-2016, 2016.

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, https://doi.org/10.5194/acp-16-2943-2016, 2016.

Parikh, H. M., Carlton, A. G., Vizuete, W., and Kamens, R. M.: Modeling secondary organic aerosol using a dynamic partitioning approach incorporating particle aqueous-phase chemistry, Atmos. Environ., 45, 1126-1137, http://dx.doi.org/10.1016/j.atmosenv.2010.11.027, 2011.

Peng, Z., Day, D. A., Ortega, A. M., Palm, B. B., Hu, 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., 16, 4283-4305, https://doi.org/10.5194/acp-16-4283-2016, 2016.

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

Romonosky, D. E., Laskin, A., Laskin, J., and Nizkorodov, S. A.: High-Resolution Mass Spectrometry and Molecular Characterization of Aqueous Photochemistry Products of Common Types of Secondary Organic Aerosols, The Journal of Physical Chemistry A, 119, 2594-2606, https://doi.org/10.1021/jp509476r, 2015.

Rudich, Y., Donahue, N. M., and Mentel, T. F.: Aging of organic aerosol: Bridging the gap between laboratory and field studies, Annual Review of Physical Chemistry, 58, 321-352, https://doi.org/10.1146/annurev.physchem.58.032806.104432, 2007.

Ruehl, C. R., Nah, T., Isaacman, G., Worton, D. R., Chan, A. W. H., Kolesar, K. R., Cappa, C. D., Goldstein, A. H., and Wilson, K. R.: The Influence of Molecular Structure and Aerosol Phase on the Heterogeneous Oxidation of Normal and Branched Alkanes by OH, J. Phys. Chem. A, 117, 3990-4000, https://doi.org/10.1021/jp401888q, 2013.

Sareen, N., Waxman, E. M., Turpin, B. J., Volkamer, R., and Carlton, A. G.: Potential of Aerosol Liquid Water to Facilitate Organic Aerosol Formation: Assessing Knowledge Gaps about Precursors and Partitioning, Environ. Sci. Technol., 51, 3327-3335, https://doi.org/10.1021/acs.est.6b04540, 2017.

Sato, K., Hatakeyama, S., and Imamura, T.: Secondary organic aerosol formation during the photooxidation of toluene: NOx dependence of chemical composition, J. Phys. Chem. A, 111, 9796-9808, https://doi.org/10.1021/jp071419f, 2007.

Seinfeld, J. H.; Pandis, S. N. Atmospheric Chemistry and Physics:From Air Pollution to Climate Change, 2nd ed.; Wiley: Hoboken, NJ, 2006.

Shrivastava, M., Fast, J., Easter, R., Gustafson Jr, W. I., Zaveri, R. A., Jimenez, J. L., Saide, P., and Hodzic, A.: Modeling organic aerosols in a megacity: comparison of simple and complex representations of the volatility basis set approach, Atmos. Chem. Phys., 11, 6639-6662, https://doi.org/10.5194/acp-11-6639-2011, 2011.

Smith, M. L., Kuwata, M., and Martin, S. T.: Secondary Organic Material Produced by the Dark Ozonolysis of α-Pinene Minimally Affects the Deliquescence and Efflorescence of Ammonium Sulfate, Aerosol Sci. Tech., 45, 244-261, https://doi.org/10.1080/02786826.2010.532178, 2011.

Smith, M. L., Bertram, A. K., and Martin, S. T.: Deliquescence, efflorescence, and phase miscibility of mixed particles of ammonium sulfate and isoprene-derived secondary organic material, Atmos. Chem. Phys., 12, 9613-9628, https://doi.org/10.5194/acp-12-9613-2012, 2012.

Smith, M. L., You, Y., Kuwata, M., Bertram, A. K., and Martin, S. T.: Phase Transitions and Phase Miscibility of Mixed Particles of Ammonium Sulfate, Toluene-Derived Secondary Organic Material, and Water, J. Phys. Chem. A, 117, 8895-8906, https://doi.org/10.1021/jp405095e, 2013.

Song, M., Liu, P. F., Hanna, S. J., Zaveri, R. A., Potter, K., You, Y., Martin, S. T., and Bertram, A. K.: Relative humidity-dependent viscosity of secondary organic material from toluene photo-oxidation and possible implications for organic particulate matter over megacities, Atmos. Chem. Phys., 16, 8817-8830, https://doi.org/10.5194/acp-16-8817-2016, 2016.

Takahama, S., Pathak, R. K., and Pandis, S. N.: Efflorescence Transitions of Ammonium Sulfate Particles Coated with Secondary Organic Aerosol, Environ. Sci. Technol., 41, 2289-2295, https://doi.org/10.1021/es0619915, 2007.

Tsigaridis, K., Daskalakis, N., Kanakidou, M., Adams, P. J., Artaxo, P., Bahadur, R., Balkanski, Y., Bauer, S. E., Bellouin, N., Benedetti, A., Bergman, T., Berntsen, T. K., Beukes, J. P., Bian, H., Carslaw, K. S., Chin, M., Curci, G., Diehl, T., Easter, R. C., Ghan, S. J., Gong, S. L., Hodzic, A., Hoyle, C. R., Iversen, T., Jathar, S., Jimenez, J.

L., Kaiser, J. W., Kirkevåg, A., Koch, D., Kokkola, H., Lee, Y. H., Lin, G., Liu, X., Luo, G., Ma, X., Mann, G. W., Mihalopoulos, N., Morcrette, J. J., Müller, J. F., Myhre, G., Myriokefalitakis, S., Ng, N. L., O'Donnell, D., Penner, J. E., Pozzoli, L., Pringle, K. J., Russell, L. M., Schulz, M., Sciare, J., Seland, Ø., Shindell, D. T., Sillman, S., Skeie, R. B., Spracklen, D., Stavrakou, T., Steenrod, S. D., Takemura, T., Tiitta, P., Tilmes, S., Tost, H., van Noije, T., van Zyl, P. G., von Salzen, K., Yu, F., Wang, Z., Wang, Z., Zaveri, R. A., Zhang, H., Zhang, K., Zhang, Q., and Zhang, X.: The AeroCom evaluation and intercomparison of organic aerosol in global models, Atmos. Chem. Phys., 14, 10845-10895, https://doi.org/10.5194/acp-14-10845-2014, 2014.

Volkamer, R., Jimenez, J. L., San Martini, F., Dzepina, K., Zhang, Q., Salcedo, D., Molina, L. T., Worsnop, D. R., and Molina, M. J.: Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected, Geophys. Res. Lett., 33, L17811, https://doi.org/10.1029/2006gl026899, 2006.

Wong, J. P. S., Lee, A. K. Y., and Abbatt, J. P. D.: Impacts of Sulfate Seed Acidity and Water Content on Isoprene Secondary Organic Aerosol Formation, Environ. Sci. Technol., 49, 13215-13221, https://doi.org/10.1021/acs.est.5b02686, 2015.

Zhang, X., Cappa, C. D., Jathar, S. H., McVay, R. C., Ensberg, J. J., Kleeman, M. J., and Seinfeld, J. H.: Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, P. Natl. Acad. Sci., 111, 5802-5807, https://doi.org/10.1073/pnas.1404727111, 2014.

Zhang, X., Schwantes, R. H., McVay, R. C., Lignell, H., Coggon, M. M., Flagan, R. C., and Seinfeld, J. H.: Vapor wall deposition in Teflon chambers, Atmos. Chem. Phys., 15, 4197-4214, https://doi.org/10.5194/acp-15-4197-2015, 2015.

Zhang, Z., Zhang, Y., Wang, X., Lü, S., Huang, Z., Huang, X., Yang, W., Wang, Y., and Zhang, Q.: Spatiotemporal patterns and source implications of aromatic hydrocarbons at six rural sites across China's developed coastal regions, J. Geophys. Res.-Atmos., 121, 2016JD025115, https://doi.org/10.1002/2016JD025115, 2016.

Zhao, Y., Saleh, R., Saliba, G., Presto, A. A., Gordon, T. D., Drozd, G. T., Goldstein, A. H., Donahue, N. M., and Robinson, A. L.: Reducing secondary organic aerosol formation from gasoline vehicle exhaust, P. Natl. Acad. Sci., 114, 6984-6989, https://doi.org/10.1073/pnas.1620911114, 2017.

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

OH exposure ($\times 10^{11}$ molecules cm^{-3} s)	[toluene]$_{\text{reacted}}$ (ppb)	[toluene]$_{\text{final}}$ (ppb)	ε [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.

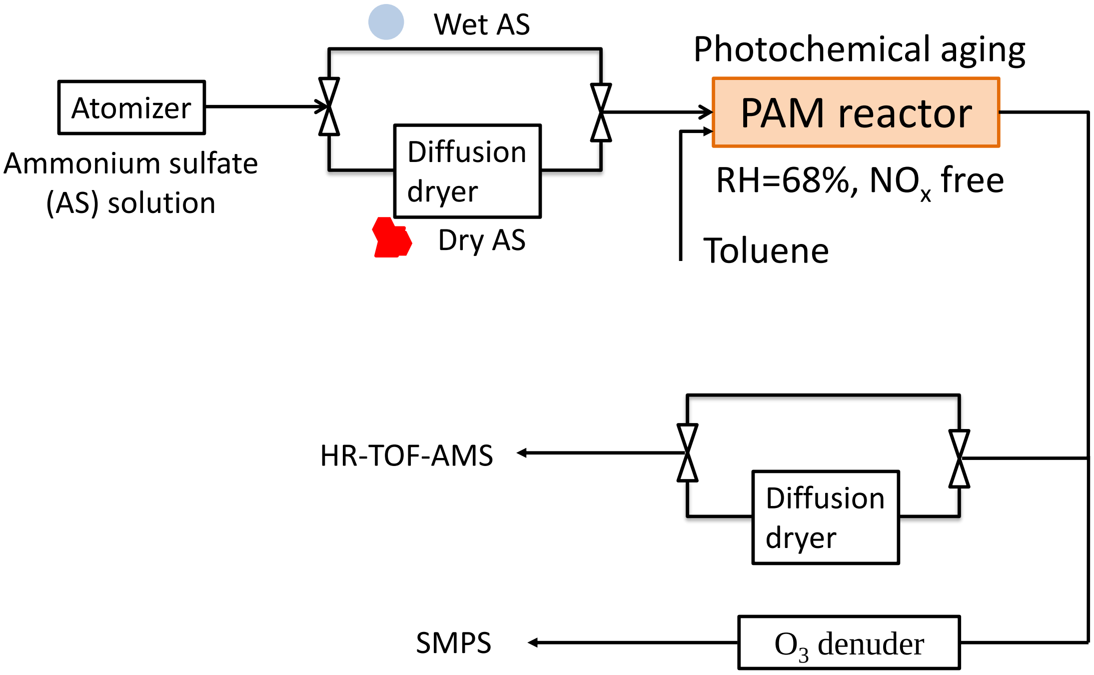

Fig. 1. Schematic of the experimental setup. The aqueous ammonium sulfate (AS) seed particles either passed through a diffusion dryer so that the phase of the seed particles could be altered or bypassed the diffusion dryer. Either wet or dry AS served as seed particles for the experiments.

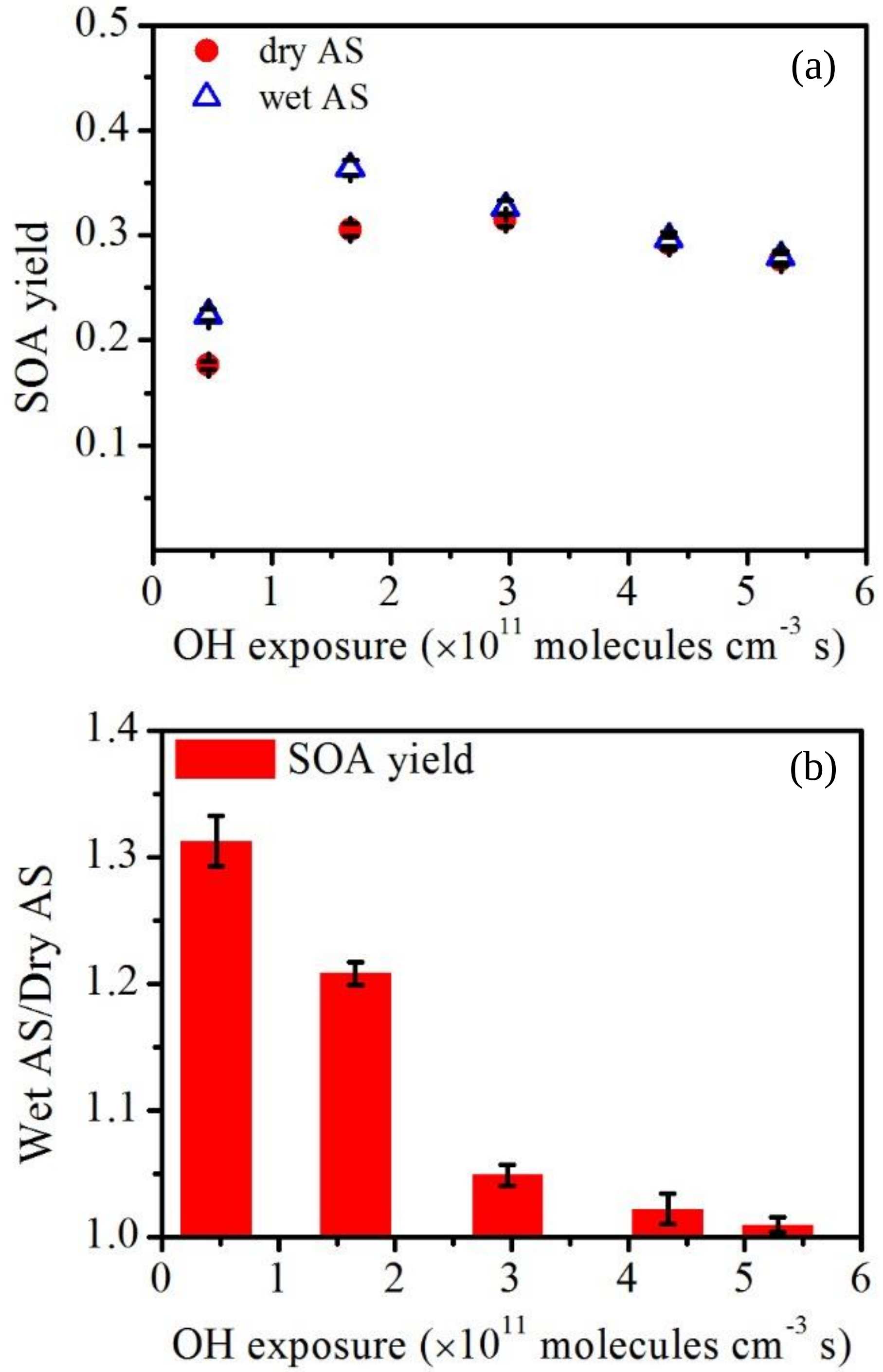

Fig. 2. (a) Yield of toluene-derived SOA formed on initially wet and dry AS as a function of OH exposure. (b) Ratio of SOA yields on initially wet AS to those on initially dry AS as a function of OH exposure.

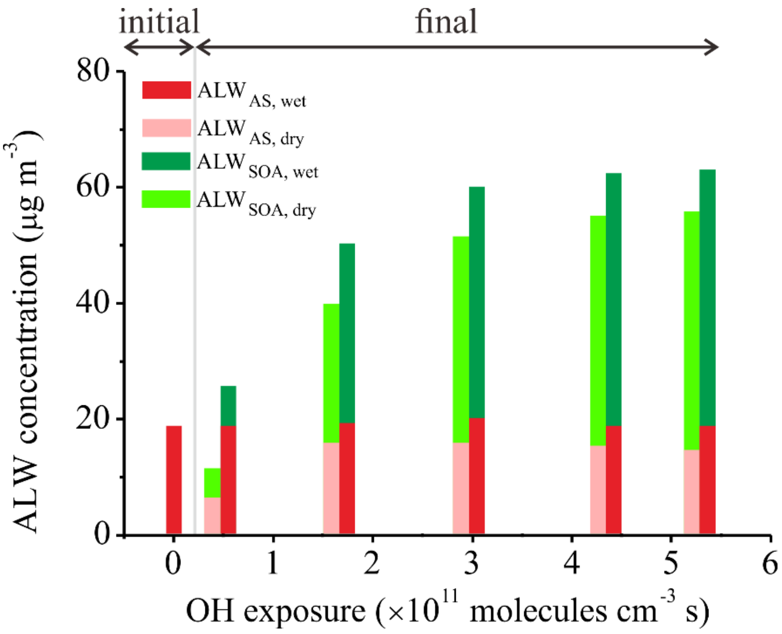

Fig. 3. Mass concentration of ALW uptake by AS and toluene-derived SOA before (initial) and after reactions (final) for both initially wet and dry AS seeds. Adjoining bars for initially wet and dry seeds have same OH exposures.

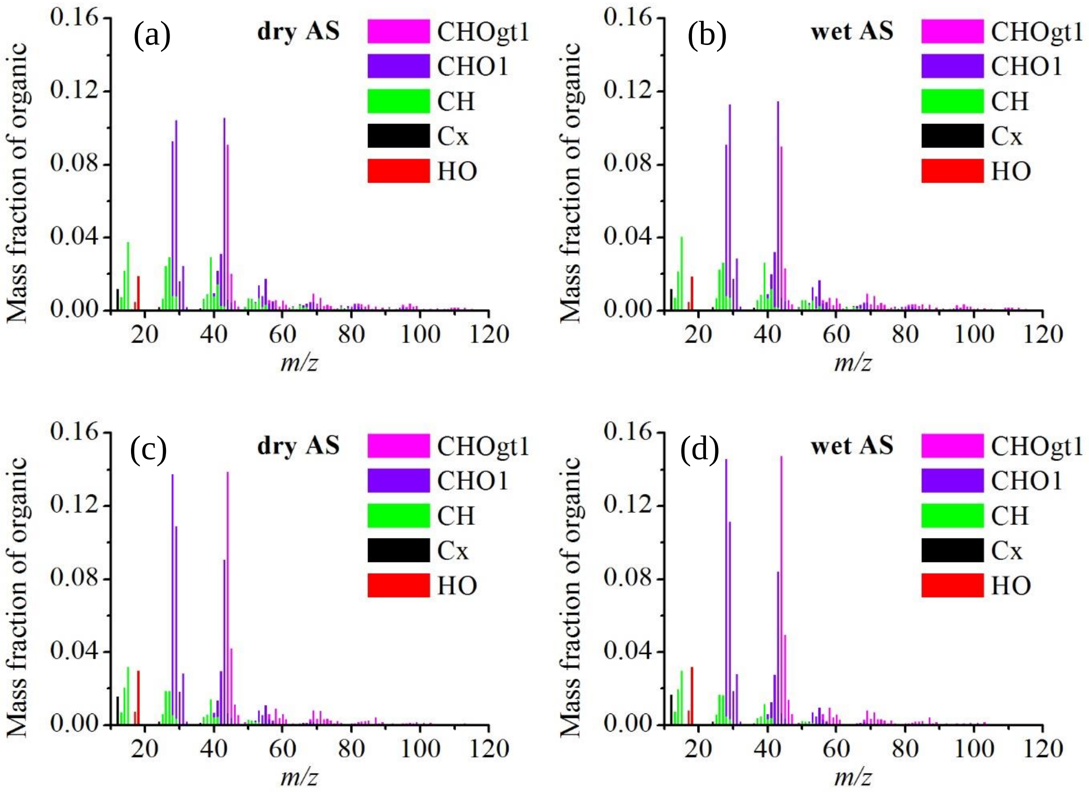

Fig. 4. High-resolution mass spectra of toluene-derived SOA on initially wet and dry AS at an OH exposure of (a, b) ~~4.66~~0.47×~~10^{10}~~10^{11} molecules cm^{-3} s and (c, d) 5.28×10^{11} molecules cm^{-3} s.

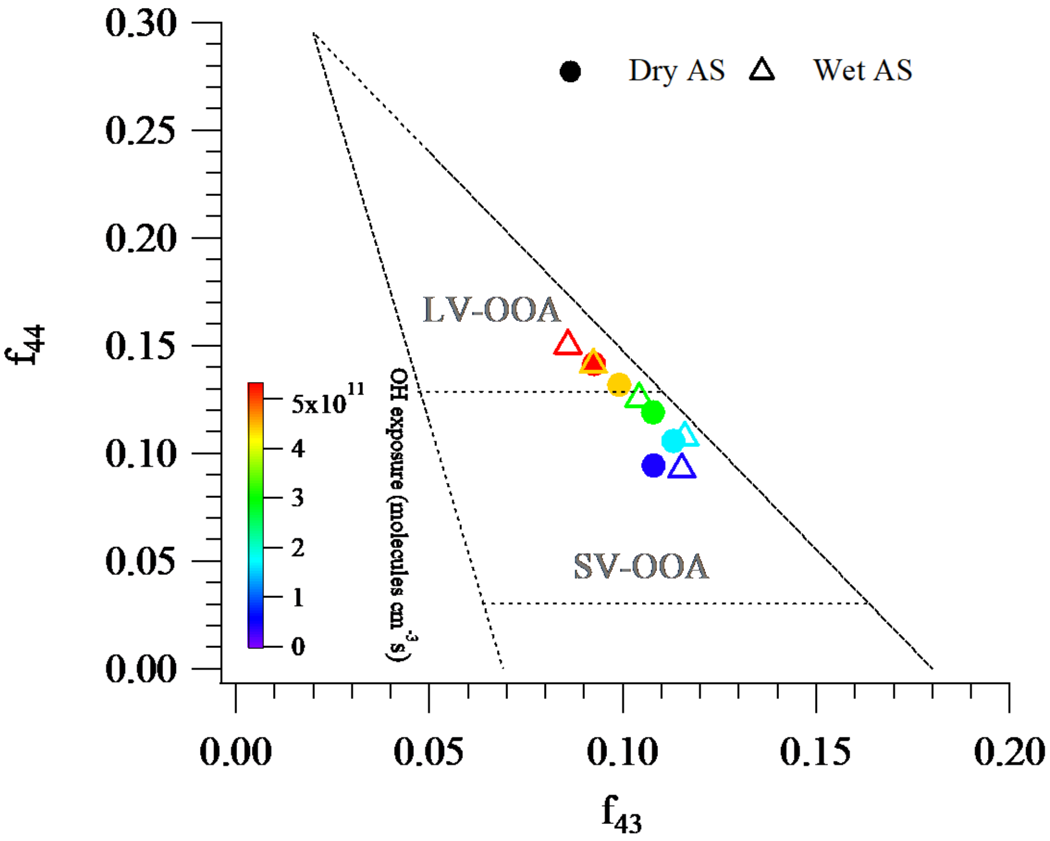

Fig. 5. Fractions of total organic signal at *m/z* 43 (f_{43}) vs. *m/z* 44 (f_{44}) from SOA data obtained in this study together with the triangle plot of Ng et al. (2010). Ambient SV–OOA and LV–OOA regions are adapted from Ng et al. (2010). Data are colored according to the OH exposure.

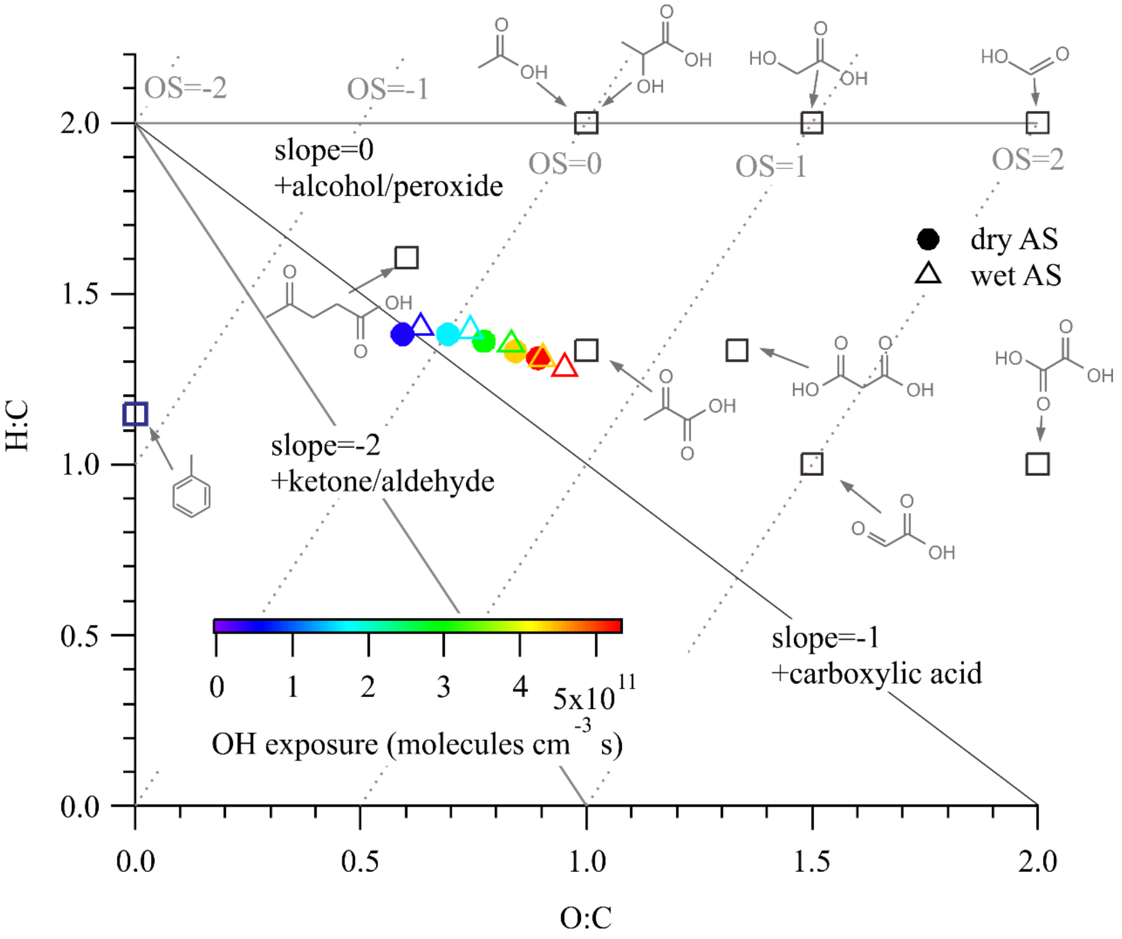

Fig. 6. Van Krevelen diagram of SOA derived from the photooxidation of toluene on initially wet and dry AS seed particles. SOA data are colored according to the OH exposure. Products identified in toluene-derived SOA are shown in boxes (Bloss et al., 2005; Hamilton et al., 2005; Sato et al., 2007). Average carbon oxidation states from Kroll et al. (2011) and functionalization slopes from Heald et al. (2010) are shown for reference.