Response to Reviewer 2

We greatly appreciate the time and effort that reviewer 2 spent in reviewing our manuscript. The comments are really thoughtful and helpful to improve the quality of our paper. Reviewer 2 has provided both main comments and other specific comments. Below we make a point-by-point response to these comments. According to editor's requirement, the response to the reviewer 2 is structured in the following sequence: (1) comments from the reviewer in black color, (2) our response in blue color, and (3) our changes in the revised manuscript in red color.

Overview:

This study explore the role of relative humidity (RH) on the m-xylene SOA formation under OH initiated no NOx condition. The results showed that the SOA yield under high RH is significantly lower than that under low RH conditions. This study provides SOA yields and particle-phase SOA products under different RH levels. The LWC was measured by the particles mass deduction in the DAASS. The authors measured the SOA compositions by using a Fourier transform infrared (FTIR) spectra and ultrahigh performance liquid chromatograph electrospray ionization-high-resolution mass spectrometer (UPLC-ESI-HRMS). The authors reported that SOA yield found to be about 7 times high in dry condition (RH_13%) than that in wet condition (RH_75%). Overall, the experimental data to show the impact of RH on SOA yields and products and the conclusion originating from the chamber are doubtful. The small chamber used in this study will be significantly influenced by the gas-wall processes of organic species increasing the uncertainty in data and interpretation of results. This paper in its current form is not acceptable. Please find the comments below.

The chamber volume for our current experiments was around 1 m^3. All chambers have the wall losses of species. Though a larger volume reactor may minimize these effects, the fans are usually equipped inside this kind of reactor to make the heat generated by lights homogeneously mixed, which counteracts the decrease of wall effect by the larger volume (Carter et al., 2005; Cocker et al., 2001). In addition, relatively small reactors in the range of 0.2-3 m^3 are also ubiquitously used in smog chamber studies (Chen et al., 2017; Chu et al., 2016; Díaz-de-Mera et al., 2017; Huang et al., 2017; Peng et al., 2017; Schnitzler et al., 2014; Ye et al., 2018). After careful analysis of our experiments, we believe that our results are reliable and credible. Below are the specific replies to the comments.

Carter, W., Cockeriii, D., Fitz, D., Malkina, I., Bumiller, K., Sauer, C., Pisano, J., Bufalino, C., and Song, C.: A new environmental chamber for evaluation of gas-phase chemical mechanisms and secondary aerosol formation, Atmos. Environ., 39, 7768-7788, 10.1016/j.atmosenv.2005.08.040, 2005.

Chen, L., Bao, K., Li, K., Lv, B., Bao, Z., Lin, C., Wu, X., Zheng, C., Gao, X., and Cen, K.: Ozone and secondary organic aerosol formation of toluene/NO_x irradiations under complex pollution scenarios, Aerosol Air Qual. Res., 17, 1760-1771, 10.4209/aaqr.2017.05.0179, 2017.

Chu, B., Zhang, X., Liu, Y., He, H., Sun, Y., Jiang, J., Li, J., and Hao, J.: Synergetic formation of secondary inorganic and organic aerosol: effect of SO_2 and NH_3 on particle formation and growth, Atmos. Chem. Phys., 16, 14219-14230, 10.5194/acp-16-14219-2016, 2016.

Cocker, D. R., 3rd, Flagan, R. C., and Seinfeld, J. H.: State-of-the-art chamber facility for studying atmospheric aerosol chemistry, Environ. Sci. Technol., 35, 2594-2601, 10.1021/es0019169, 2001.

Díaz-de-Mera, Y., Aranda, A., Martínez, E., Rodríguez, A. A., Rodríguez, D., and Rodríguez, A.: Formation of secondary aerosols from the ozonolysis of styrene: Effect of SO_2 and H_2O, Atmos. Environ., 171, 25-31, 10.1016/j.atmosenv.2017.10.011, 2017.

Huang, M., Hao, L., Cai, S., Gu, X., Zhang, W., Hu, C., Wang, Z., Fang, L., and Zhang, W.: Effects of inorganic seed aerosols on the particulate products of aged 1,3,5-trimethylbenzene secondary organic aerosol, Atmos. Environ., 152, 490-502, 10.1016/j.atmosenv.2017.01.010, 2017.

Peng, J., Hu, M., Du, Z., Wang, Y., Zheng, J., Zhang, W., Yang, Y., Qin, Y., Zheng, R., Xiao, Y., Wu, Y., Lu, S., Wu, Z., Guo, S., Mao, H., and Shuai, S.: Gasoline aromatics: a critical determinant of urban secondary organic aerosol formation, Atmos. Chem. Phys., 17, 10743-10752, 10.5194/acp-17-10743-2017, 2017.

Schnitzler, E. G., Dutt, A., Charbonneau, A. M., Olfert, J. S., and Jaeger, W.: Soot aggregate restructuring due to coatings of secondary organic aerosol derived from aromatic precursors, Environ. Sci. Technol., 48, 14309-14316, 10.1021/es503699b, 2014.

Ye, J., Abbatt, J. P. D., and Chan, A. W. H.: Novel pathway of SO_2 oxidation in the atmosphere: reactions with monoterpene ozonolysis intermediates and secondary organic aerosol, Atmos. Chem. Phys., 18, 5549-5565, 10.5194/acp-18-5549-2018, 2018.

Major Comments:

1. The aromatics VOCs are gas pollutants that is found to be high in urban environments where the NOx is also abundant. It is unclear why the authors chose no NOx condition to study the humidity effects on the formation of xylene SOA. Clarify this.

It is true that aromatics are found to be high in urban environments where NO_x is also abundant. Real environment is relatively complicated. Nevertheless, the purpose of our study is to investigate the RH effect on the SOA formation from m-xylene only oxidized by the OH radicals and not interpreted by other factors. The NO_x can complicate the aromatics oxidation system, since NO_x conditions can provide OH and NO_3 radicals, and NO_x themselves can also participate in the oxidation reactions.

2. What is the effect of the wall on the loss gaseous H2O2? H2O2 is very hydrophilic and sticky to the wall. When RH is high, the water on the chamber wall becomes high forming a water film. This wet film can absorb a large amount of H2O2 and modulate the concentration of OH radicals. Please clarify how the authors measured OH radical concentrations under varying RH conditions. Why did the author use 20 ppm of H2O2 which was 40 times higher than the m-xylene concentration? What is the photolysis rate constant of H2O2 in the chamber?

We agree with the reviewer that H_2O_2 is very hydrophilic. According to the reviewer's comment, we estimated the wall loss of H_2O_2 at low and high RH at 299 K for 4 h in our study using the O_3 analyzer (49C, Thermo Environmental Instruments Inc.), since H_2O_2 can also absorb the light at 254 nm. Thus, the output by O_3 analyzer can basically represent the relative change in H_2O_2 concentration though it is not the real H_2O_2 concentration. The results for H_2O_2 wall loss experiments show that the numbers outputted by O_3 analyzer were in the range of 22.2-23.2 at low RH (8%) and in the range of 22.1-23.3 at high RH (75%) throughout each H_2O_2 wall loss experiment, respectively. Results indicate that there is no significant H_2O_2 wall loss throughout the experiments and no obvious difference between both RHs. In other words, H_2O_2 concentrations in the chamber were roughly constant during the experiment.

In this study there was no equipment for the measurement of OH radical concentrations, so we cannot directly obtain the OH radical concentration during the experiments. But it can be convinced that the OH concentrations were consistent at varying RHs, which can be realized from the similar change in concentrations of the reacted m-xylene (Fig. S1) (see below) that is added in the supplementary information according to the Comment 6 of the Reviewer 1. In addition, the MCM simulation was conducted to obtain the OH concentration of 1.6×10^{-4} ppb, for which a photolysis rate constant of 7.56×10^{-6} min^{-1} for H_2O_2 was used in the chamber.

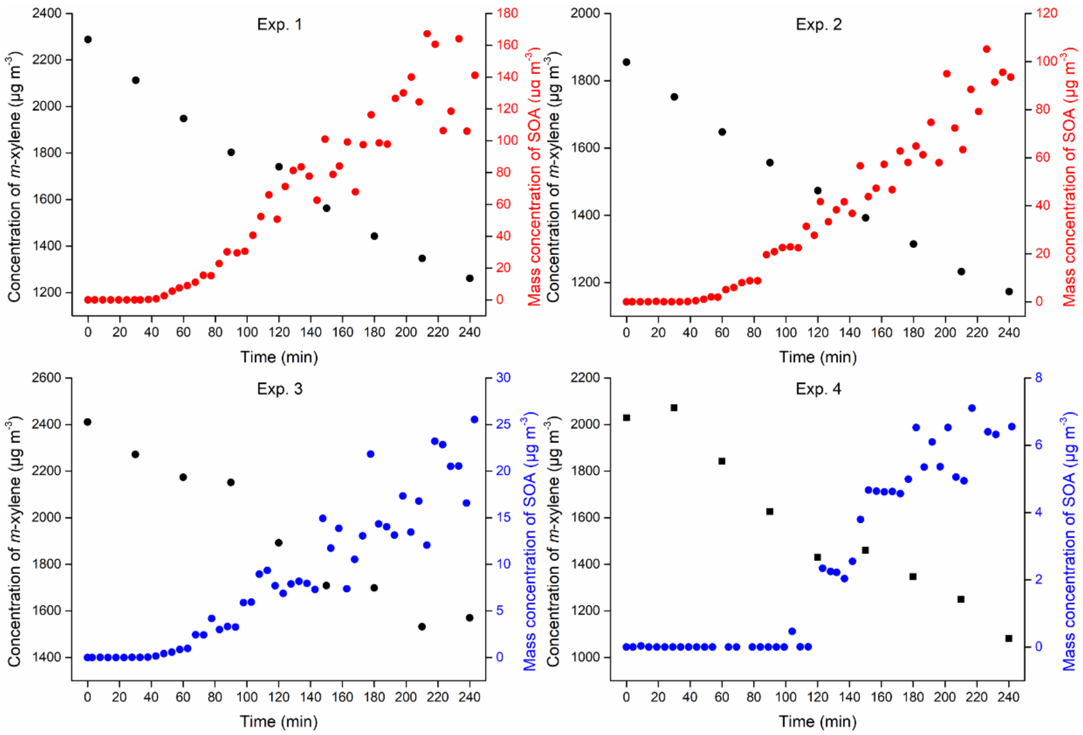


Fig. S1. Reaction time profiles of *m*-xylene measured by the GC-MS that accompanied the observed SOA growth for the four experiments

3. The size of chamber used in this study was one cubic meter and relatively very small. Thus, the wall of chemical species is very high. Additionally, the loss of chemical species to the chamber is very sensitive to humidity. The impact of RH on SOA yields can be very uncertain and doubtful. The reduction of SOA yields at the high humidity is more likely due to the chemical loss to the wet chamber wall. Thus, the conclusion

made by the authors could be incorrect. Hydrophilic products and reactive chemical species can more deposit to the wall at high humidity.

We agree with the reviewer that the reactor volume in this study is relatively small. As we mentioned in the beginning of reply to Reviewer 2, in recent years small reactors in the range of (0.2-3) m^3 are ubiquitously used in smog chamber studies. Indeed, small chambers have the wall losses of species, but wall effects also exist in big reactors, since big reactor is needed to be equipped with fans inside the reactor to make the heat generated by lights homogeneously mixed. For small reactors, the particle wall loss of 5.87×10^{-5} s^{-1} was measured in a 3 m^3 reactor (Chen et al., 2017) and $(3.21\text{-}5.57) \times 10^{-5}$ s^{-1} was measured in a 2 m^3 reactor (Chu et al., 2016). For big reactors, the particle wall loss of 8×10^{-5} s^{-1} was measured in a 90 m^3 reactor (Carter et al., 2005) and $(2.5\text{-}5.0) \times 10^{-5}$ s^{-1} was measured in the dual 28 m^3 (Cocker et al., 2001). It is obvious that the particle wall loss from different researchers is different, but there is no clear relation between particle wall loss and reactor volume for the reactor volume of over 1 m^3. It can be speculated that wall effects for other chemical species are probably similar between small and big reactors.

In addition, we agree with the reviewer that the loss of chemical species to the wall is sensitive to humidity. To clarify this, we have added a paragraph at the end of Sec. 3.1 following the newly added paragraph according to the Comment 2 of Review 1 in the revised manuscript to clarify the possible underestimation of SOA mass and the reliability of our study.

The wall loss of chemical species that is sensitive to humidity may affect the RH effect on SOA yields, as the reduction of SOA yields at the high humidity may be due to the chemical loss to the wet chamber wall. To estimate the extent of how much the wall loss of chemical species affects the SOA formation at different RHs, we take glyoxal and acetone as reference compounds. Glyoxal, a typical compound that can form SOA, can easily dissolve in the aqueous phase due to the large Henry's law constant of 4.19×10^5 M atm^{-1} (Ip et al., 2009), very sensitive to humidity. Loza et al. (2010) found that the wall loss of glyoxal was minimal at 5% RH, with $k_W = 9.6 \times 10^{-7}$ s^{-1}, whereas k_W was 4.7×10^{-5} s^{-1} at 61% RH. We assume that k_W linearly increases with RH, and the k_W value is estimated to be 6.1×10^{-5} s^{-1} at 80% and 7.4×10^{-6} at 13% RH, with the difference being 8.2 times. According to the wall loss of glyoxal, glyoxal only decreased by 10% at the end of our experiment at low RH, while glyoxal decreased by 59% at high RH. Acetone can hardly dissolve in the aqueous phase due to the small Henry's law constant of 29 M atm^{-1} (Poulain et al., 2010), which is 4 orders of magnitude less than that of glyoxal. Ge et al. (2017) obtained that the wall loss of acetone was 5.0×10^{-6} s^{-1} at 87% RH and 3.3×10^{-6} s^{-1} at 5% RH, with a factor of 1.5. The difference of wall loss between glyoxal and acetone at low RH is about 2 times, while it becomes about 12 times at high RH. Thus, it can be considered that the wall loss among different species at low RH is less affected by the Henry's law constant, but it is greatly affected at high RH. In our study glycolaldehyde (See the Sec. 3.3) is found to be an important SOA precursor that can form a large fraction of oligomers in our experiments, but the wall loss of glycolaldehyde is not available. The Henry's law constant of glycolaldehyde was obtained to be 4.14×10^4 M atm^{-1} (Betterton and Hoffmann, 1988), an order of magnitude lower than glyoxal, indicating that glycolaldehyde is less sensitive to humidity than glyoxal but much more sensitive to humidity than acetone. Based on the data of these two reference species, the wall loss of glycolaldehyde at low RH is taken to be 5×10^{-6} s^{-1}, and the difference in wall loss between high and low RHs is about 6 times. Then, the wall loss of glycolaldehyde at high RH can be 3×10^{-5} s^{-1}. Then, it is estimated that glycolaldehyde would decrease by 7% at low RH and by 35% at high RH at the end of our experiment, respectively. This means that SOA yield would be underestimated by 35% at high RH and by 7% at low RH if glycolaldehyde lost to the wall was completely transformed to SOA. If this wall effect of SOA precursors was taken into consideration, the SOA yields at high (Exp. 3) and low (Exp. 2) RHs would be 3.4% and 15.1%, respectively. Alternatively, the SOA yield at high RH was underestimated to be 42% relative to that at low RH. Even the sensitivity of the wall loss to RH was taken to be 8 times, the SOA yield at high RH would be underestimated to be 62% compared to that at low RH. In fact, there were many different SOA precursors from the m-xylene oxidation system that probably have much smaller Henry's law constant relative to that of glycolaldehyde. Thus, it is concluded that the RH effect on SOA formation from m-xylene oxidation by H_2O_2 without NO_x is negative.

Betterton, E. A. and Hoffmann, M. R.: Henry's law constants of some environmentally important aldehydes, Environ. Sci. Technol., 12, 1415-1418, 10.1021/es00177a004, 1988.

Carter, W., Cockeriii, D., Fitz, D., Malkina, I., Bumiller, K., Sauer, C., Pisano, J., Bufalino, C., and Song, C.: A new environmental chamber for evaluation of gas-phase chemical mechanisms and secondary aerosol formation, Atmos. Environ., 39, 7768-7788, 10.1016/j.atmosenv.2005.08.040, 2005.

Chen, L., Bao, K., Li, K., Lv, B., Bao, Z., Lin, C., Wu, X., Zheng, C., Gao, X., and Cen, K.: Ozone and secondary organic aerosol formation of toluene/NO_x irradiations under complex pollution scenarios, Aerosol Air Qual. Res., 17, 1760-1771, 10.4209/aaqr.2017.05.0179, 2017.

Chu, B., Zhang, X., Liu, Y., He, H., Sun, Y., Jiang, J., Li, J., and Hao, J.: Synergetic formation of secondary inorganic and organic aerosol: effect of SO_2 and NH_3 on particle formation and growth, Atmos. Chem. Phys., 16, 14219-14230, 10.5194/acp-16-14219-2016, 2016.

Cocker, D. R., 3rd, Flagan, R. C., and Seinfeld, J. H.: State-of-the-art chamber facility for studying atmospheric aerosol chemistry, Environ. Sci. Technol., 35, 2594-2601, 10.1021/es0019169, 2001.

Ge, S., Xu, Y., and Jia, L.: Effects of inorganic seeds on secondary organic aerosol formation from photochemical oxidation of acetone in a chamber, Atmos. Environ., 170, 205-215, 10.1016/j.atmosenv.2017.09.036, 2017.

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.

Loza, C. L., Chan, A. W., Galloway, M. M., Keutsch, F. N., Flagan, R. C., and Seinfeld, J. H.: Characterization of vapor wall loss in laboratory chambers, Environ. Sci. Technol., 13, 5074-5078, 10.1021/es100727v, 2010.

Poulain, L., Katrib, Y., Isikli, E., Liu, Y., Wortham, H., Mirabel, P., Le Calve, S., and Monod, A.: In-cloud multiphase behavior of acetone in the troposphere: gas uptake, Henry's law equilibrium and aqueous phase photooxidation, Chemosphere, 81, 312-320, 10.1016/j.chemosphere.2010.07.032, 2010.

4. In order to analyze the chemical compositions in gas and particles phase using a variety of aerosol, a large amount of air volume should be collected. The size of the chamber used in this study was only one cubic. It is hard to believe how the authors analyzed gas and aerosol with the air volume less than one cubic meter. Additionally, the chamber volume was getting small as the experiment progressed. The consumption

of the chamber air increased the wall effect. The authors should clarify this problem.

It is true that the chamber volume was getting small as the experiment progressed, but the change was not significant. The measurement of m-xylene concentration was conducted once every 30 min by a one-liter summa canister, so the total sampling volume for m-xylene measurement was only 9 L throughout each experiment. We also monitored the concentrations of ozone and NO_x once an hour by sampling 5 min, so the total sampling volume for ozone and NO_x measurement was only 30 L. The SMPS was on-line analysis, for which the flow rate was 0.3 L min^{-1}, and thus the total sampling volume was 72 L. Thus, before the SOA sampling, when the reaction stopped, the total volume for sampling was only around 110 L, approximately 10% of the size of reactor. Thus, the wall effect for gases and particles would not be significantly changed. After the reaction was finished, the DLPI and PILS simultaneously sampled for FTIR and HRMS analysis of chemical compositions of SOA, respectively. The DLPI sampled 150 L and the PILS needed 100 L. Thus, after the experiment was completely finished, the reactor still contained more than 700 L of air.

5. Page 5, line 4. The Master Chemical Mechanism can only provide the gas-phase reaction pathways. The yield of the products in particle phase may not directly connected to the yield of products in gas-phase. How does the author compare gas-phase oxygenated m-xylene products predicted using MCM to the measured particle-phase products from HRMS?

We agree with the reviewer that the MCM only provides the gas-phase reaction pathways. We went through the products in the MCM, and put the structure of these products in the Mass Frontier program, which can simulate the breakage of bonds made by the MS/MS analysis of HRMS. Meanwhile, we found 5 products in the gas phase by MCM those can match the HRMS analysis. These 5 products are considered to likely partition into the particle phase from the gas phase. Though we only find 5 products in the particle phase identified by HRMS that are also predicted in the gas phase by MCM, the MCM prediction can provide the formation pathway of RO2 radicals, which are helpful with the prediction of RO2 autoxidation.

6. Page 5, line 11. The value of the maximum SOA mass in Figure 1 is not consist with

the values reported in the text and the Table 1. The value of SOA mass under 73.6% and 79.1% in Figure 1 is about 40 and 10 ug/m3 but the value reported in the text is only 1.9 and 0.8 ug/m3 and the value reported in Table 1 is 15.8 and 7.9 ug/m3.

There are indeed some mistakes in the text and in Fig. 1. Together with the reply to the Comment 3 of Reviewer 1, the SOA mass was re-corrected by the particle wall loss rates. The values of the maximum SOA mass under 73.6% and 79.1% RH are 21.0 and 7.5 ug/m^3, respectively. We have modified in Page 5, line 11 in the text and in Fig 1. A sentence has been added in the revised manuscript: "The maximum mass concentrations fitted are 150.3 and 95.5 μg m^{-3} at low RHs, whereas they are 21.0 and 7.5 μg m^{-3} at high RHs, …"

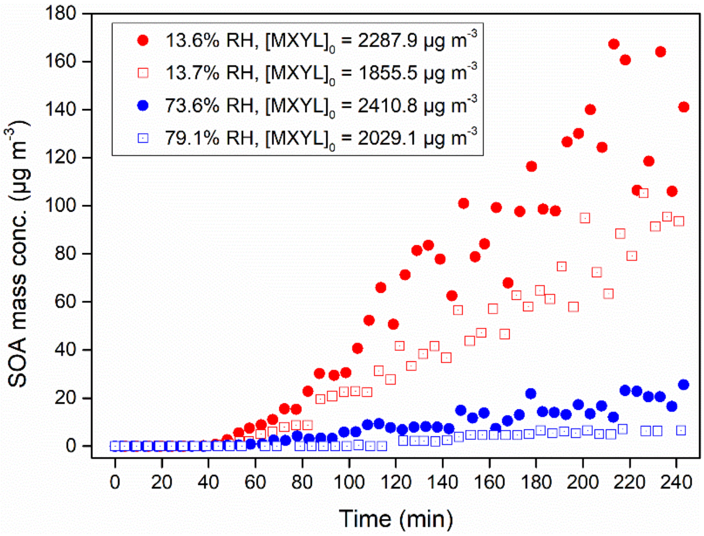


Figure 1. SOA mass concentrations as a function of irradiation time (corrected by particle wall loss and subtracted by LWC).

7 It is not clear how much LWC was present at the end of experiments and how much SOA mass was obtained after subtracting the LWC from total aerosol mass. What is the effects of LWC on the SOA formation in this study? The author mention that LWC can explain the positive effect of RH on SOA formation under high NOx condition. What is the difference in LWC between SOA with the high NOx condition and that with the low or no NOx condition?

At the end of experiments LWC volume concentration accounts for 34% and 45% in the Exps. 3-4 of the volume concentrations of wet particles, which are 5.1 and 2.4 μg m^{-3}, respectively. SOA mass obtained after subtracting the LWC from total aerosol mass were 21.0 and 7.5 $\mu g/m^3$ under 73.6% and 79.1% RH, respectively. The LWC has a negative effect on SOA formation in our study. LWC can generally promote SOA formation under high NO$_x$ condition, which was reported in many previous studies (Healy et al., 2009; Kamens et al., 2011; Zhou et al., 2011; Jia and Xu, 2014, 2018; Wang et al., 2016), but the recent study by Hinks et al. (2018) indicates the negative effect of RH on SOA. Although we did not conduct any experiments of m-xylene under high NO$_x$ condition, in previous studies, the LWC volume concentration was found to be 22% (78% RH, Jia and Xu, 2018) and 17% (85% RH, Prenni et al., 2007) of wet SOA volume concentration from toluene photoxidation under NO$_x$ concentrations of 300 ppb. This indicates that LWC is larger under the high NO$_x$ condition than under the low or no NO$_x$ condition.

Healy, R. M., Temime, B., Kuprovskyte, K., and Wenger, J. C.: Effect of relative humidity on gas/particle partitioning and aerosol mass yield in the photooxidation of *p*-xylene, Environ. Sci. Technol., 43, 1884-1889, 10.1021/es802404z, 2009.

Hinks, M. L., Montoya-Aguilera, J., Ellison, L., Lin, P., Laskin, A., Laskin, J., Shiraiwa, M., Dabdub, D., and Nizkorodov, S. A.: Effect of relative humidity on the composition of secondary organic aerosol from the oxidation of toluene, Atmos. Chem. Phys., 18, 1643-1652, 10.5194/acp-18-1643-2018, 2018.

Jia, L., and Xu, Y.: Effects of relative humidity on ozone and secondary organic aerosol formation from the photooxidation of benzene and ethylbenzene, Aerosol Sci. Technol., 48, 1-12, 10.1080/02786826.2013.847269, 2014.

Jia, L., and Xu, Y.: Different roles of water in secondary organic aerosol formation from toluene and isoprene, Atmos. Chem. Phys., 18, 8137-8154, 10.5194/acp-18-8137-2018, 2018.

Kamens, R. M., Zhang, H., 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, 10.1016/j.atmosenv.2010.11.007, 2011.

Prenni, A. J., Petters, M. D., Kreidenweis, S. M., DeMott, P. J., and Ziemann, P. J.: Cloud droplet activation of secondary organic aerosol, J. Geophys. Res., 112, D10223, 10.1029/2006JD007963, 2007.

Wang, Y., Luo, H., Jia, L., and Ge, S.: Effect of particle water on ozone and secondary organic aerosol formation from benzene-NO_2-NaCl irradiations, Atmos. Environ., 140, 386-394, 10.1016/j.atmosenv.2016.06.022, 2016.

Zhou, Y., Zhang, H., Parikh, H. M., Chen, E. H., Rattanavaraha, W., Rosen, E. P., Wang, W., and Kamens, R. M.: Secondary organic aerosol formation from xylenes and mixtures of toluene and xylenes in an atmospheric urban hydrocarbon mixture: Water and particle seed effects (II), Atmos. Environ., 45, 3882-3890, 10.1016/j.atmosenv.2010.12.048, 2011.

8. What is the particle size distribution of m-xylene SOA? Does all of the particle size smaller than 1000 nm and within the SMPS measurement range?

According to the reviewer's comment, we have added the particle size distribution of m-xylene SOA for the four experiments in the supplementary information (see Fig. S2). As shown in Fig. S2, all of the particle size is smaller than 1000 nm and within the SMPS measurement range.

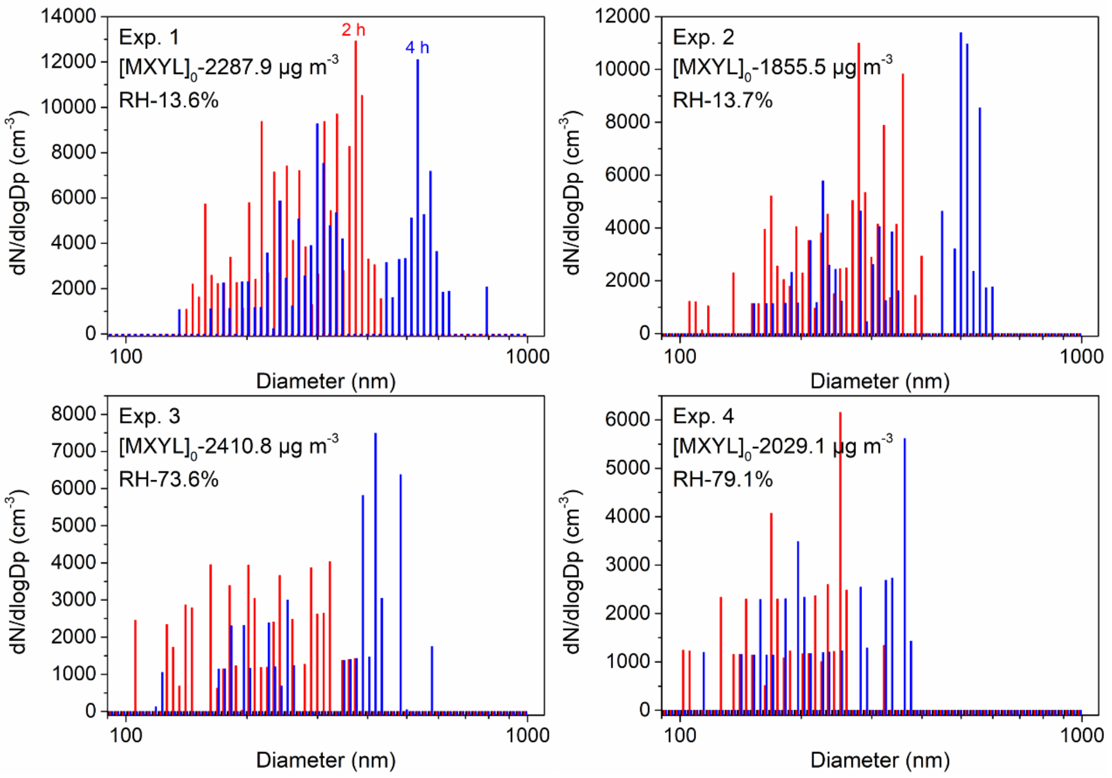


Fig. S2 Variations of particle size distribution of number and mass concentrations at the 2-h time point and at the end of the experiment for the four experiments.

9. Section 3.2. The intensity of the functional groups in FTIR spectrum was correlated to the sample mass. What was the SOA mass that collected on the disk and that measured using FTIR? Or does the author use same sampling duration for both RH conditions? What was the collection efficiency of the impactor on a sampling disk as a function of the particle size? Without knowing the mass of measured SOA, it is unreasonable to compare the peak intensity of the functional group between SOA from different samples.

We did not measure the mass of SOA collected on the disk, as the weight of ZnSe window is several grams, much larger than the SOA mass that is only several micrograms. We used the same sampling duration for both RH conditions and the FTIR spectra under different RH conditions can be comparable. The DLPI sampling flow rate was 10 L min^{-1}, and the sampling duration was 15 min. The total collection efficiency of the DLPI was 87%, and the efficiency varies for different impaction stages (Durand et al., 2014). DLPI has 13 stages. When we sampled using DLPI, the four plates for stages 4-7 were removed, so that particles in the range of 108-650 nm were collected on the third plate. As shown in Fig. S2 that is newly added in the reply to Comment 8, the particles in the range of 108-650 nm can represent the total SOA from m-xylene oxidation in this study. The mean collection efficiency of the DLPI for stages 4-7 is around 83% (Durand et al., 2014). SOA mass was obtained by the calculation based on the SMPS measurement and the DLPI collection efficiency, 10.3 and 3.0 μg at low RH (Exp. 2) and high RH (Exp. 3). The ratio of the SOA mass collected on disk at high RH to that at low RH is 0.29. The relative intensities of most functional groups in Table 2 match this SOA mass ratio. According to the reviewer's comment, we have added some sentences about the SOA mass collected on the ZnSe window after the first sentence of Sec. 3.2.

The DLPI sample flow rate was 10 L min^{-1}, and the sampling duration was 15 min. We used same sampling flow rate and duration for both RH conditions. DLPI has 13 stages, and it can collect particles in the size range of 30 nm - 10 mm. When we sampled using DLPI, the four plates for stages 4-7 were removed, so that particles in the range of 108-650 nm were collected on the third plate. As shown in Fig. S2 in the supplementary information, the particles in the range of 108-650 nm can represent the total SOA from m-xylene oxidation in this study. The mean collection efficiency of the DLPI was 83%

for stages 4-7 (Durand et al., 2014). Thus, the SOA mass collected on the ZnSe window was 10.3 and 3.0 μg at low RH (Exp. 2) and high RH (Exp. 3), based on the SMPS measurement and the DLPI collection efficiency.

Durand, T., Bau, S., Morele, Y., Matera, V., Bémer, D., and Rousset, D.: Quantification of low pressure impactor wall deposits during zinc nanoparticle sampling, Aerosol Air Qual. Res., 14, 1812-1821, 10.4209/aaqr.2013.10.0304, 2014.

10. Figure 2 and Table 2. There is also peak at 3000 cm-1 which is missing in Table 2.

Taking the reviewer's suggestion, we have added the peak at 3000 cm^{-1} in Table 2.

Table 2. Absorbance positions of functional groups and the intensities at low and high RHs.

Absorption frequencies	Functionality	Intensity (× 10^{-3})		Ratio [a]
		low RH	high RH	
3235	O-H	5.9	1.9	0.32
3000	C-H	4.5	1.4	0.31
1720	C=O	5.1	1.5	0.29
1415	CO-H	4.8	2.4	0.50
1180	C-O-C, C-O and OH of COOH	2.9	1.4	0.48
1080	C-C-OH	5.3	1.8	0.34

[a] Ratio of the intensity at high RH to that at low RH.

11. What is the measured glyoxal fraction in m-xylene SOA? Was oligomerization impacted by the RH in this study? Even though the concentration of highly oxygenated molecule (HOM) is much lower at high RH, the overall trend of the SOA mass, which is much less at high RH compare to low RH, cannot be explained by solely through HOMs. As mentioned in the previous comment above, the effect of the wet wall on SOA formation can be very significant particularly in small reaction. The time scale of the gas-wall partitioning of organic species can be significantly fast and results in the less SOA yields at higher humidity.

Glyoxal in SOA was not observed in our study. Instead, we obtained the glycolaldehyde (C2H4O2) fraction in SOA from MS/MS analysis which has been observed previously in the oxidation of m-xylene (Cocker et al., 2001). The RH suppresses oligomerization in this study as can be obviously observed in Fig. 4. In oligomerization reaction of glycolaldehyde with carbonyls by aldol condensation reactions, water is involved as a by-product, leading to the suppression of the oligomerization by high RH.

Indeed, we agree with the reviewer that it cannot be solely explained through HOMs that SOA mass at high RH is much less than that at low RH. To further explain the large discrepancy of SOA mass at low and high RHs, we have added a paragraph at the end of the Sec. 3.4.

The wall process of the reactor enlarges the difference of SOA mass between low and high RH. The wall loss of some chemical species is faster at high RH, which leads to the reduction of SOA yield. In addition, the difference of SOA mass can be also enhanced based on the gas to particle partitioning rule (Li et al, 2018).

Li, K., Li, J., Wang, W., Li, J., Peng, C., Wang, D., and Ge, M.: Effects of gas-particle partitioning on refractive index and chemical composition of *m*-xylene secondary organic aerosol, J. Phys. Chem. A, 122, 3250-3260, 10.1021/acs.jpca.7b12792, 2018.

12 The author claimed that the increase of the C-O-C stretching was resulted from the oligomerization of carbonyls under the high RH condition. However, the IR absorption at 1080 cm-1 can be also due to the existence of C-OH group. Clarify this.

The statement in the text was incorrect. The relative intensity of the C-O-C group is higher than that of the C=O group, indicating that C-O-C group is more than other functional groups at high RH, which does not mean that the oligomerization is higher at high RH. We have deleted the corresponding sentence in the last second sentence of the Sec. 3.2.

13. Fig. 2. Authors assigned the peak at 1600 cm-1 as carboxylate. The reviewer doubt this assignment. In general, dry organic aerosol cannot produce carboxylic acid ions. Even if the organic aerosol is produce in the wet condition, the aerosol water content is not enough to product the dissociation of carboxylic acid. In general, the pKa of

carboxylic acid ranges from 2 to 6. Even in the dilution in water, less than 1% of carboxylic acid is dissociable. In SOA, most carboxylic acids will be in the un-dissociated form.

We agree with the reviewer's comment that the peak in 1605 cm-1 cannot be assigned to dissociation of carboxylic acid. Thus, we have deleted the peak assignment in Table 2 and deleted the corresponding sentence in the second and third paragraph of the Sec. 3.2.

Table 2. Absorbance positions of functional groups and the intensities at low and high RHs.

Absorption frequencies	Functionality	Intensity (× 10^{-3})		Ratio [a]
		low RH	high RH	
3235	O-H	5.9	1.9	0.32
3000	C-H	4.5	1.4	0.31
1720	C=O	5.1	1.5	0.29
1415	CO-H	4.8	2.4	0.50
1180	C-O-C, C-O and OH of COOH	2.9	1.4	0.48
1080	C-C-OH	5.3	1.8	0.34

[a] Ratio of the intensity at high RH to that at low RH.

14. Fig. 4. Based on Fig. 4, a large mass appeared in negative ion mode suggesting that the aerosol has a large fraction of carboxylic acid. It is contradictable compared to either MCM simulation or the conclusion by the authors in the glyoxal was abundant. In general, a large fraction of gaseous products from MCM prediction are alcohols and carbonyls, and amount of carboxylic acids are small. Please clarify this.

Indeed, a large fraction of gaseous products from MCM prediction are alcohols and carbonyls and a few compounds are organic acids. Glyoxal is one of the relatively abundant gas-phase products in MCM simulation (about 20 ppb at the end of 4 h experiment). Carbonyls in SOA account for a large fraction of compounds that have been identified by HRMS in the positive mode (Fig. 4), some of which are in agreement with those in the gas phase simulated by MCM. In addition, we think that the large number of carboxylic acids observed in HRMS are also produced from the oxidation of organic species in the particle phase. In our original manuscript about FTIR analysis, we mentioned that the peak at 1080 cm-1 was assigned to be the C-C-OH, which could be considered as the glyoxal hydrate. This description may not be very accurate, since FTIR has limitation in identification of compounds. In further identification, the glyoxal fragment was not identified in HRMS analysis. For clarification of description of glyoxal in the text, some sentences started in Page 7 Line 7 have been modified.

The ratios of O-H, C-H, C=O and C-C-OH groups are 0.29 to 0.34, which is close to the ratio of SOA mass at high RH to that at low RH collected on the ZnSe disk, whereas the ratios of CO-H, C-O-C, C-O-H in COOH are above 0.48. The relative intensity of the C-O-C group is significantly higher than the C=O group, which can be explained by more oligomerization with the formation of C-O-C than other reactions at high RH. Nevertheless, the FTIR results cannot provide further information to well explain the differences of SOA yields between low and high RH, which will be further discussed in terms of mass spectra of SOA in the next section.

15. Fig. 4. Low carbon number products are generally more volatile than high carbon number products. Fig.4 showed that low carbon number products are high with the SOA with the low RH, possibly suggesting that volatile low carbon number products more likely deposited to the wall due to the gas-wall process.

Indeed, a fraction of low carbon number products at high RH are likely deposited to the wall. As we discussed in the reply to Comment 3, wall loss effects of organic vapors likely reduce formation of SOA, which is more obvious at high RH. However, it is considered that the decrease of low carbon number products in SOA are mainly due to the chemical reaction process at high RH.

16. What was the RH of the environment inside the FTIR spectrometer when FTIR spectra were obtained for Fig. 4?

The sample compartment of the FTIR spectrometer was purged by dry air desiccated from FTIR purge gas generator (Model 75-45-12VDC, Balston, Parker) ahead of the

FTIR measurement. The dew point temperature of the dry gas from this generator is as low as -65 °C. So the RH of the environment inside the FTIR spectrometer was extremely low, close to zero when FTIR spectra were obtained for Fig. 4.

17. What is the atmospheric implication of this study? What is the potential impact of RH on p-xylene and o-xylene as well as other aromatics? Will other aromatics also have the similar RH effects with m-xylene? What is the uncertainty of this study? Does the impaction or the PILS sampling has uncertainty? What is the duration of the experiments?

The atmospheric implication of this study is that the production of SOA from aromatics in low-NO_x environments can be strongly modulated by the ambient RH probably due to the influence of H_2O on the formation of HOMs and oligomers. We proposed that the clear pathway of the influence of H_2O on the formation of HOMs needs to be further studied in the future. Negative RH effect on the SOA yield is a common feature of the monocyclic aromatics oxidation under low NO_x conditions and using H_2O_2 as the OH radical source from the previous study on toluene SOA and this study on m-xylene SOA. The uncertainty of this study is mainly from the wall loss of chemical species at different RHs. In a previous study (Sorooshian et al., 2006), the PILS sampling uncertainty was reported to be 6%. The uncertainty of DLPI sampling was around 20% (Durand et al., 2014). The duration of the experiments was 4 h. Based on the reviewer's comment, we have added a sentence at the end of the Sec. 2.1 "The experiments were conducted for 4 h." and we have modified the Sec. 4 for clarification of the atmospheric implication.

Durand, T., Bau, S., Morele, Y., Matera, V., Bémer, D., and Rousset, D.: Quantification of low pressure impactor wall deposits during zinc nanoparticle sampling, Aerosol Air Qual. Res., 14, 1812-1821, 10.4209/aaqr.2013.10.0304, 2014.
Sorooshian, A., Brechtel, F. J., Ma, Y., Weber, R. J., Corless, A., Flagan, R. C., Seinfeld, J. H.: Modeling and characterization of a particle-into-liquid sampler (PILS), Aerosol Sci. Technol., 40, 396-409, 10.1080/02786820600632282, 2006.

The current study investigates the effect of RH on SOA formation from the oxidation of *m*-xylene under low NO_x conditions in the absence of seed particles. The elevated

RH can significantly obstruct the SOA formation from the *m*-xylene-OH system, so that the SOA yield decrease from 13.8% at low RH to 0.8% at high RH, with a significant discrepancy of higher than one order of magnitude. The FTIR results of functional groups show the relative increase of the C-O-C group at high RH as compared with low RH, indicating that the oligomers from carbonyl compounds cannot well explain the suppression of SOA yield. HOMs were observed to be suppressed in the HRMS spectra. The chemical mechanism for explaining the obvious difference of RH effects on SOA formation from *m*-xylene-OH system has been proposed based on the analysis of both FTIR and HRMS measurements as well as MCM simulations. The reduced SOA at high RH is mainly ascribed to the less formation of oligomers and the suppression of RO_2 autoxidation. Together with the previous study on toluene SOA, it is conceivable that the negative RH effect on the SOA yield is a common feature of the monocyclic aromatics oxidation under low NOx conditions and using H_2O_2 as the OH radical source. Our results obviously indicate that the production of SOA from aromatics in low-NO_x environments can be strongly modulated by the ambient RH probably due to the influence of H_2O on the formation of HOMs and oligomers. Our study highlights the role of water in the SOA formation, which is particularly related to chemical mechanisms used to explain observed air quality and to predict chemistry in air quality models and climate models. The clear pathway of the influence of H_2O on the formation of HOMs needs to be further studied in the future.

18. There are numerous grammatical problems. The manuscript needs to be approved by a native English speaker.

According to the advice of the reviewer, we have read the manuscript carefully and modified some sentences to correct grammatical errors.

19. Page 3 Line 13. The author may need to provide the reason why the author set the density of m-xylene SOA is set as 1.4 g/cm. According to the citation Ng et al. 2007 gives the density of m-xylene SOA as 1.33 _ 0.1 g/cm and Sato et al. 2007 provide the density of Toluene SOA as 1.42 _ 0.8 g/cm.

We agree with the reviewer’s comment that the density we cited is not consistent with this study. We made a mistake when we cited references. Thus, we have corrected this mistake in the text, "To obtain the particle mass concentrations and SOA yield, an SOA density of 1.4 g cm^{-3} was used (Song et al., 2007)."

Song, C., Na, K., Warren, B., Malloy, Q., and Cocker, D. R., III: Secondary organic aerosol formation from *m*-xylene in the absence of NO_x, Environ. Sci. Technol., 41, 7409-7416, 10.1021/es070429r, 2007.

20. Page 3 Line 17. The author mention about the uncertainty of SMPS. However, the uncertainty of SMPS measurement for the used data in the paper was not reported.

As we mentioned in the text, SMPS measurement uncertainty is mainly dominated by size-dependent aerosol charging efficiency uncertainties and CPC sampling flow rate variability. The size-dependent aerosol charging efficiency is typically characterized by an accuracy of ± 10% (Jiang et al., 2014), which was used in our study to calculate the uncertainties of SOA mass concentration on the premise that the uncertainty of organic vapor wall loss was not included. The standard error of linear regression of the m-xylene concentration and peak area obtained by GC-MS was 0.013, which was extremely low compared with the m-xylene concentration and can be negligible. Thus, the uncertainty of 10% was used in SOA yield. In the revised manuscript, we have modified the Table 1 with the addition of uncertainty of SOA mass concentration.

Table 1. Experimental conditions, SOA concentrations and yields at the end of the experiments in *m*-xylene-OH oxidation system.

Exp. No.	[*m*-xylene]$_0$ (μg m^{-3})	[*m*-xylene]$_{reacted}$ (μg m^{-3})	RH (%)	T (°C)	[SOA]$_e$ (μg m^{-3})	SOA yield (%)
1	2287.9	1026.3	13.6	25.9	150.3 ± 15.0	14.6 ± 1.5
2	1855.5	682.0	13.7	25.3	95.5 ± 9.5	14.0 ± 1.4
3	2410.8	941.4	73.6	27.5	21.0 ± 2.1	2.2 ± 0.2
4	2029.1	946.9	79.1	27.4	7.5 ± 0.7	0.8 ± 0.1

[SOA]$_e$ indicates the mass concentration of SOA at the end of each experiment with particle wall loss corrected.

21. Page 4 Line 6. For comparing the SOA yield between cited values and that of this study, it may need to provide the error range of the values. Additionally, numerous data of this paper need errors.

We used the uncertainty of 10% to calculate SOA mass concentration from SMPS measurement. As we explained in Comment 21, the uncertainty of 10% was used in SOA yield (see Table 1 above).

22. Pages 6 and 7 (section 3.2): The description to construct the functional group distribution using FTIR spectra is unclear. How to separate the FTIR peaks for each functional group? The intensity of each function group varies with vibration force constant and peak broadening changes with compositions.

We used the peak height to represent the functional group distribution. The separation of FTIR peaks for each functional group was conducted by the peak valleys between two peaks.

Minor comments:

Page 2, line 21. The sentence is confused that it compares the RH effects between low NOx condition and with NOx condition.

Taking the reviewer’s suggestion, we have corrected the sentence.

However, under low NOx level, it has been found that, in the study on toluene SOA formation, moderate RH level (48%) leads to a lower SOA yield than low RH level (17-18%).

Figure 3. The y-axis scale is negative for high RH and positive for Low RH. It is better to make them as a same positive scale.

Taking the reviewer’s advice, we have modified the y-axis scale for high RH in Fig 3.

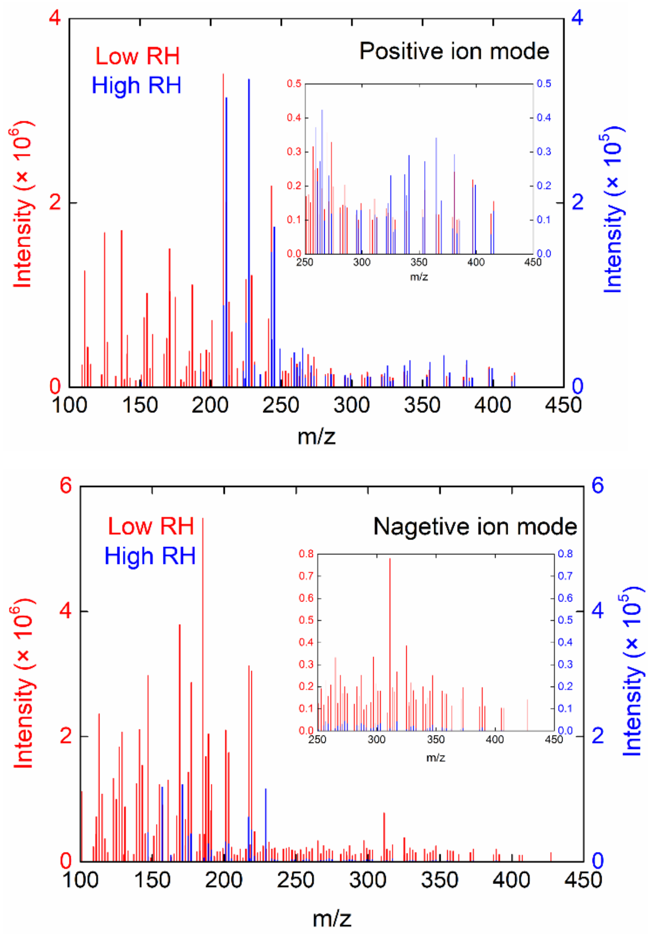


Figure 3. Selected background-subtraction HESI-Q Exactive-Orbitrap MS results of SOA in both positive and negative ion modes from the photooxidation of *m*-xylene-OH under both low and high RH conditions (Note that the Y-axis scales for low and high RH are largely different, 10^6 at low RH and 10^5 at high RH).

Figure 5: RH scale should range from 0 to 100 (negative is incorrect).

Taking the reviewer's advice, we have modified the RH scale and corrected the negative scale in Fig 5.

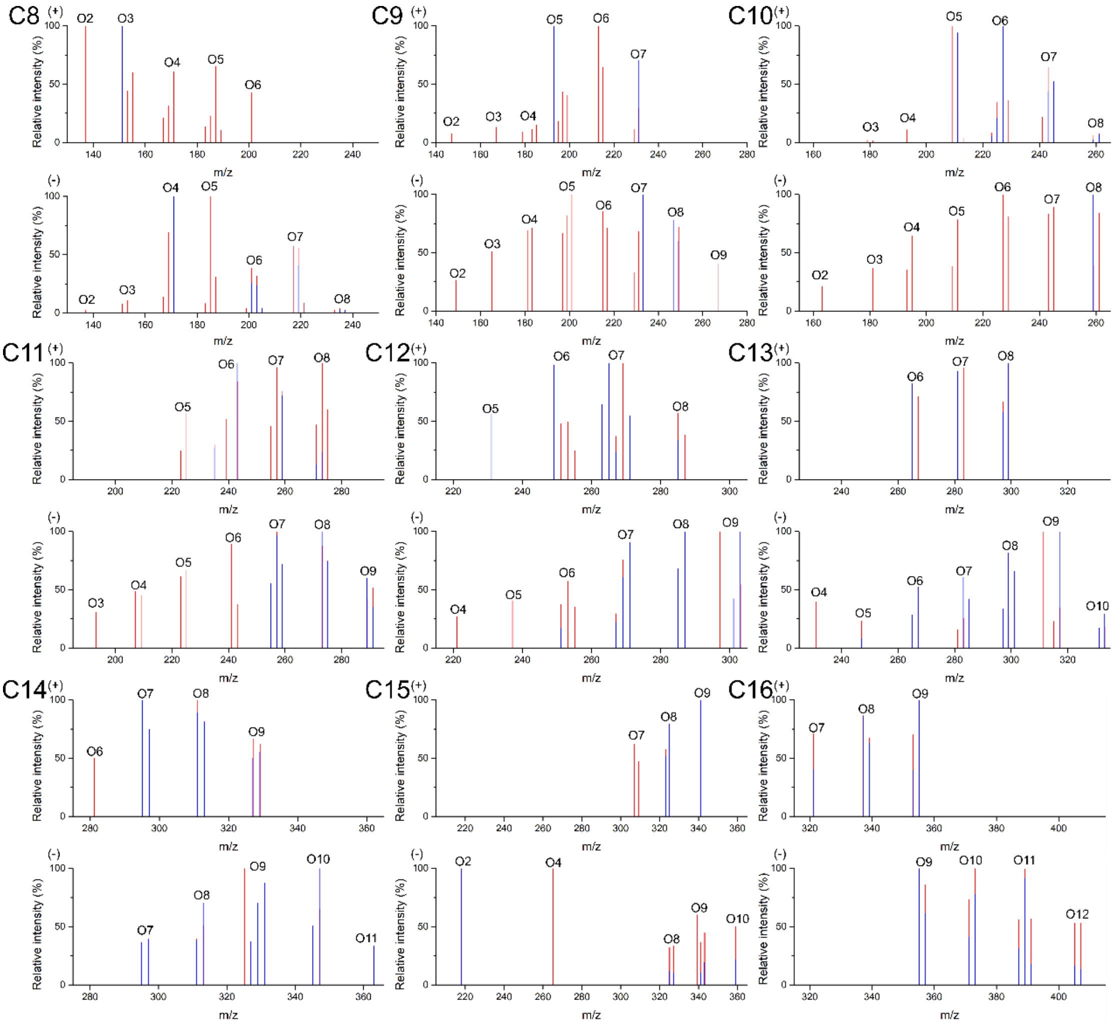


Figure 5. Mass spectra of SOA from *m*-xylene at both low (red) and high (blue) RH in the positive (+) and negative (-) ion modes, grouped with the same number of carbon atoms (from nC =8 to 16). On (n = 2, 3, ……, 12) means the number of oxygen atoms in the formula of the peak.

Page 2 line 15: it is better to use “have been conducted”.

Taking the reviewer’s advice, we have corrected this mistake, “Investigations of RH effects on aromatics SOA have been conducted in many previous works.”

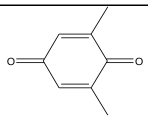
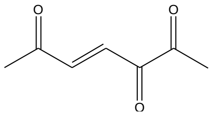
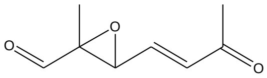
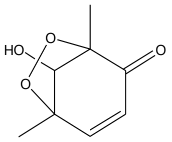
Page 2 line 19: after “as an OH radical source,” there supposed to use period instead of comma.

In this sentence, “no NOx were introduced artificially and photolysis of H2O2 was as an OH radical source” is an appositive clause to explain the “condition”, so the part before the comma is an adverbial modifier and thus we use a comma.

Table 3. The form of the table is better to unify with other tables.

Taking the reviewer's advice, we have unified the Table 3 with other tables.

Table 3. Plausibility of different types of compounds with elemental formulae measured by HRMS in the positive ion mode.

Low RH			High RH			Ion formula	Proposed structure
Measured (m/z)	Intensity	Error (mDa)	Measured (m/z)	Intensity	Error (mDa)		
137.0596	1.7×10^6	0.6	137.0593	1.4×10^5	1	$[C_8H_9O_2]^+$	
141.0545	5.6×10^6	1.3	141.0542	-	1.5	$[C_7H_9O_3]^+$	
155.0701	1.0×10^6	1.2	155.0699	-	1.5	$[C_8H_{11}O_3]^+$	
171.0651	1.0×10^6	1.2	171.0649	-	1.4	$[C_8H_{11}O_4]^+$	
187.06	1.1×10^6	1.2	187.0568	-	4.4	$[C_8H_{11}O_5]^+$