We greatly value the careful reading and the detailed comments provided by the Referee. The responses to the Referee's comments in our direct reply and within the revised manuscript are provided below. The original comments from Referee are in black, our replies are in blue and the tracked changes in the main manuscript are in red color text.

This manuscript aimed to study SOA formation from furan under photooxidation conditions with varied NOx and RH. SOA mass, O3 concentration, and SOA composition were carefully measured. The authors concluded that furan photooxidation is dominated by RO2 + NO chemistry that leads to formation of carbonyl-rich products. SOA formation was found to enhance under higher relative humidity and higher VOC/NOx concentration. The results are clearly presented, but there are a few important issues that need to be addressed before becoming publishable. My major comment is that the manuscript did not provide sufficient chemistry insights given the suite of instruments used.

Author reply:

We greatly appreciate the thoughtful and helpful comments proposed by the Referee. To have a more sufficient chemistry insights into the furan SOA formation, we have added five more experiments under a series of NOx and RH conditions for the analysis of an improved chemical identification instrument. According to the latest results that sufficiently eliminate the interference of artifacts on the Exactive-Orbitrap MS, few parts of the discussion have been modified. Spectra results and reaction mechanism have been updated as well. Further discussion is given in later sections.

Major:

1. The authors claims that the O3 maximum concentration decreases with increasing RH likely due to that high RH favors the partitioning of the NOx reservoir, RNO2 and RONO2 into the particle phase. Thus the release of NOx is limited. However, it is

unclear how much more pronounced is the RNO2 and RONO2 uptake at higher RH and whether this enhancement is sufficient to affect O3 formation. These species need to be very soluble to show distinct partitioning behavior under different RH. What are their possible structures and could the Henry's law constants be estimated? Were any RNO2 or RONO2 species enhanced in the SOA samples under higher RH? From the ESI-MS results, the authors said that the SOA composition is similar between higher RH and low RH. Does this contradict what the authors concluded earlier? You have a max SOA yield of 5% and only a small fraction of that is RNO2 or RONO2. Thus are they important enough to affect gas-phase NOx concentration. Evidence is needed. Alternatively, could wall loss of the RNO2 and RONO2 under high RH better explain the observation?

Author reply:

According to the updated HESI-Q Exactive-Orbitrap MS results in the revised manuscript, the intensities of multifunctional hydroxyl nitrates and dihydroxyl dinitrate (m/z⁻ 146, 225) were indeed enhanced under high RH conditions (Fig. 8). As demonstrated by a previous study, these multifunctional hydroxyl nitrates and dihydroxyl dinitrate have low volatilities and can partition into the particle phase (Schwantes et al., 2019). It should also be noted that some products generated from the furan photooxidation have C=C bonds conjugated with the carbonyl and acid groups. These products can absorb strongly in the ~200-300 nm range and contribute to the signal of O₃ concentration detected by O₃ analyzer (Strollo and Ziemann, 2013). However, under high RH conditions, these carbonyl-rich products were favourable to condense on the moist surface of particles and thus lowered the O₃ concentration detected by O_3 analyzer. This assumption is reasonable since the intensities of m/z⁺ 85 and 101 carbonyl-rich products were observed to increase when RH increased from dry condition to 30%. However, the intensities of the assigned carbonyl-rich products exhibited a slight decrease under higher RH conditions. This decreasing trend resulted from the aqueous phase reactions of hydroxyfuranone $(m/z^+ 101)$ with 4-dialdehyde

 $(m/z^+ 85)$, leading to the appearance of the generated hemiacetal compound $(m/z^+ 185)$. In addition, there is a possibility that the wall losses of the organonitrates species would inhibit the O₃ formation under high RH as suggested by the Referee. To provide more information about the decreased O₃ concentration under high RH, the following changes have been made to the revised manuscript.

Page 7, line 28:

"However, it should be noted that the apparent high O_3 concentration monitored by the O_3 analyzer was due to species other than O_3 and that have absorption around 254 nm. The generated gas-phase reaction products that have carbonyl, carboxylic acid, and ester groups conjugated with C=C bonds can absorb strongly in the ~200-300 nm range and, accordingly, contribute to the apparent intense signal of O_3 detected by the O_3 monitor (Strollo and Ziemann, 2013)."

Page 8, line 16:

"Additionally, the slight change in O₃ maximum concentration under different RH conditions may also be caused by the consumption of gas-phase reaction products that contain functional groups conjugated with C=C bonds and respond to the O₃ analyzer. This assumption is reasonable because these carbonyl-rich products were favourable to condense on the moist surface of particles and thus lowered the O₃ concentration detected by the O₃ analyzer, which has been further confirmed by the MS results with enhanced intensities of corresponding organonitrates. The wall loss of the organonitrates species would also explain the decreasing trend of O₃ concentration as RH increases."



Figure 8: Selected background-subtraction HESI-Q Exactive-Orbitrap MS results of SOA in both negative (blue) and positive (pink) ion modes from the photooxidation of furan under different RH conditions.

Table 3. Ion peaks with the assigned compounds observed in the HESI-Q Exactive-Orbitrap MS. Proposed assignments are based on the formula from HESI-Q Exactive-Orbitrap MS.

Ion mode	No	Mass	Ion Mode	Ion	Delta	Proposed Structure	
		(m/z)		Formula	(amu)	Troposed Substance	
Positive ion mode	1	85.0018	[M+H] ⁺	$C_4H_5O_2{}^+$	-0.027	0	
	2	101.0894	$[M+H]^+$	$C_4H_5O_3^+$	0.066		
	3	185.0504	$[M+H]^+$	$\mathrm{C_8H_9O_5^+}$	0.006		
Negative ion mode	4	146.0161	[M-H] ⁻	C4H4O5N-	0.007	$HO \qquad O_2NO \ O_2NO \ O_2NO \$	
	5	225.0125	[M-H] ⁻	$C_4H_5O_9N_2^-$	0.012		
	6	262.0132	[M-H] ⁻	C ₈ H ₈ O ₉ N ⁻	-0.007		

2. The ESI-MS results presented grouped ions and observed m/z 200-299 as the most abundant group. What does this mean? What are the major chemical formulas observed in this range? I think a lot more discussion of the ESI-MS results could be included here. For example:

(1) Could the authors group all nitrogen-containing species and discuss their presence?

(2) What are the ranges of O:C ratio and oxidation state?

(3) Any variation as the furan/NOx and RH changed?

(4) For soluble species uptaking onto aqueous particles, they will likely oligomerize.Do the authors see oligomers in the ESI-MS?

(5) There is a substantial decrease of large molecules under lower furan/NOx ratio and higher RH in the negative ion mode (but not in the positive ion mode). What does that suggest?

(6) what is the ion in the negative ion mode around m/z 380?

In the current form, there is very little discussion (page 11, line 16-24, page 12, line 2-7, and page 13, line 8-11)

Author reply:

A simple discussion of the m/z 200-299 parts may be confusing for a better understanding of the SOA components. In our revised manuscript, this part has been deleted and a detailed introduction of the updated Exactive-Orbitrap MS results was presented. Specifically, the nitrogen-containing species have been grouped and discussed in the revised manuscript as suggested by the Referee. Generally, three kinds of nitrogen-containing organic species were observed by the HRMS with m/z^- of 146.0161, 225.0125 and 263.0132 being detected in negative ion mode. The assignments of these ion peaks, the molecular weights, and proposed structures are summarized in Table 3. However, owing to the limits of our techniques, the ranges of O:C and oxidation state cannot be provided here. For carbonyl-rich species, these products were favourable to condense on the moist surface of particles and took part in further reactions. According to the mass results, the observed hemiacetal compound $(m/z^+ 185)$ was generated from the oligomerizations of hydroxyfuranone $(m/z^+ 101)$ and 4-dialdehyde $(m/z^+ 85)$. After removing the interference both from the sampling filter and residues from the detection instruments, new experiments have been conducted. The collected particles have been re-detected and the detected products were re-assigned in the revised manuscript. Moreover, the ESI-MS results have been significantly expanded as following:

Page 11, line 21:

"The MS spectra of generated species from different NOx level and RH conditions, which show evidence for the OH-furan reaction, are presented in Fig. 7 and Fig. 8, respectively. The major peaks are m/z^+ 85.0018, 101.0894, and 185.0504 in positive ion mode, and m/z^- 146.0161, 225.0125 and 263.0132 in the negative ion mode. The prominent peaks in the HR-MS spectra detected on negative ion mode are comprised of various functionalized hydroxyl nitrates and dihydroxyl dinitrates. However, in the positive ion mode analysis, most carbonyl components were detected. The assignments of these ion peaks, the molecular weights of the products observed, and proposed structures are summarized in Table 3. These detected compounds provide additional evidence for the proposed radical reaction mechanism."

Page 12, line 3:

"Moreover, the formed alkylperoxy radicals (RO₂·) can either react with RO₂/HO₂ or NO to yield the corresponding alkoxy radical (RO·), which can (i) decompose and then react with O₂ to yield 1,4-aldoester (A), (ii) react with NO₂/NO/O₂ to form hydroxyl nitrate compound isomers with m/z^- 146, or (iii) react with O₂ to form unsaturated products, hydroxyfuranone (B) and 1,4-aldoacid (C). The ring-opened alkylperoxy radical generated from (d) can decompose to generate an unsaturated 1,4-dialdehyde (D). The formation of 1,4-dialdehyde with a m/z^+ 85 detected in the positive ion mode suggests that these unsaturated 1,4-dicarbonyls are formed after initial OH addition at 2- or 5-positions. We note that OH radical addition at 2, 3-positions would lead to carbonyl product isomers with same m/z^+ 101. In addition, some dihydroxyl dinitrates with m/z^{-} 225 were also detected in negative ion mode. However, the pathways favouring the generation of these dihydroxyl dinitrates could only take place under high NOx levels. Scheme 1 shows the formation of second-generation products hemiacetals (E) via the reactions of the hydroxyfuranone (B) with 1,4-dialdehyde (D). After uptake from the gas-phase, the combination of hydroxyfuranone with 4-dialdehyde appeared to occur by H-abstraction, followed by dehydration, thus forming m/z^{+} 185 compounds. This reaction pathway has also been identified in previous studies of OH-radical initiated reactions of furans (Strollo and Ziemann, 2013; Aschmann et al., 2014). According to the results of HR-MS, this aqueous phase reaction is more favoured in aqueous particles."

Page 13, line 6:

"These carbonyl-containing products have lower volatility and contribute to the SOA formation. The peak intensities in the MS of the products $(m/z^+ 85, 101)$ generated by the pathways involving HO_2 (as indicated by the scheme 1) decreased with the increase of NOx concentration. Additionally, more products of dihydroxyl dinitrates $(m/z^2 225)$ with multifunctional groups were detected under high NOx conditions. As shown in Scheme 1, the multifunctional organonitrates detected in negative ion mode are produced mostly from later-generation chemistry. Hydroxyl nitrates with m/z^{-} 149 can be formed through pathways 1-a, 2-a, and 3-a by the reaction of RO₂ with NOx. We note that the m/z^{-} 149 compound was detected both at low NOx levels and high NOx levels. However, the peak intensity of this product was decreased with increasing NOx concentration. This phenomenon might be caused by the later-reaction of the unsaturated hydroxyl nitrates going through a second OH-initiated reaction and leading to the formation of the dihydroxyl dinitrate with m/z^{-} 225. In addition, the peak intensities changes of SOA products detected in the positive mode, such as, the peaks at m/z^+ 85 and 101 were reduced under high NOx conditions, which resulted from the fact that the RO2 radical fate was dominated by the pathway of RO₂+NO or RO₂+NO₂. This result supports that the fate of RO₂ is not a single channel reaction. There exists a competition between RO₂ reacting with NOx and with HO₂ under high NOx conditions but the former pathway is more favourable. There are two pathways for hydroxyl nitrates formation from RO₂ radicals in the presence of NOx according to which RO₂ radicals may react with NO and NO₂ to form RONO₂ and ROONO₂, respectively (Kroll and Seinfeld, 2008). However, the formed peroxynitrates could easily thermally dissociate and convert to RONO₂.

Furthermore, by analyzing the OH concentration and products components, we conclude that there are two possible explanations for the increasing trend of SOA yield as the NOx level increases: (i) the SOA production is closely related to the oxidation capacity in the photooxidation experiments. Experiments conducted under different NOx levels indicate that the OH concentration is controlled by the NOx level if there is no additional OH precursor added before the start of the experiment. As shown in Fig. S3, an increase in NOx level results in more OH generation and a faster furan decay rate. This justifies the observed higher SOA mass concentration and higher SOA yield. (ii) HRMS fragments associated with multifunctional organonitrates are enhanced under high NOx conditions (Fig. 7). As presented in Scheme 1, the furan dihydroxyl dinitrates are generated from the first-generation hydroxyl nitrate reacting with OH to form a peroxy radical, which reacts thereafter reacts with NO. Together with multifunctional hydroxyl nitrates, these low-volatility species can easily partition into the particle phase and increase the SOA mass concentration. More importantly, the seed particle added initially plays an important role in the processes of gas-particle partitioning as indicated by a recent study, which showed that sufficient seed surface area at the start of the reaction largely suppressed the effects of vapour wall losses of low-volatility compounds (Schwantes et al., 2019). Therefore, the NaCl seed particle added in the present work promoted the partitioning of the formed low-volatility functional organonitrates."

Page 14, line 28:

"It is highly probable that the particle surface area increases with increasing amount of ALW as shown in Fig. S7, which likely promotes the dissolution of semi-volatile matters produced during the experiments. According to the HESI-Q Exactive-Orbitrap MS results shown in Fig. 8, the intensities of multifunctional hydroxyl nitrates and dihydroxyl dinitrate (m/z^- 146 and 225, respectively) exhibited positive correlations with RH. Slight peak intensities increases of m/z^+ 85 and 101 products were also observed under high RH conditions. This phenomenon indicates that the gas-particle phase partitioning of low-volatility compounds was enhanced under high RH conditions may also be attributed to the condensation of the produced multifunctional compounds."

Page 15, line 9:

"The appearance of m/z^+ 185 and m/z^- 262 detected by the HESI-Q Exactive-Orbitrap MS further demonstrated that aqueous phase reactions indeed took place under high RH conditions. As shown in Scheme 1, the peak of m/z^+ 185 could form by aqueous phase reaction of the hydroxyfuranone (B) and 1,4-dialdehyde (D). The formation of hemiacetal (E) has also been detected by a previous study of the OH-initiated reaction of 3-methylfuran in the presence of NOx (Strollo and Ziemann, 2013). The proposed hemiacetal compound (E) plays a substantial role in the obvious increase of m/z +185 product formation under high RH conditions. A pathway of organonitrate $(m/z^2 262)$ formation in the aqueous particles with the presence of NO₃⁻ was suggested in the present study based on a previous work, which indicated a radical-radical reaction pathway for organosulfate formation from aqueous OH oxidation of glycolaldehyde in the presence of sulfuric acid (Perri et al., 2010). Increasing the RH also resulted in an overall addition of peak intensities in the negative ion mode, due to the fact that the sample obtained at high RH during the SOA generation had a larger particle surface. Specifically, a relatively stronger intense band of $C_8H_8O_9N^-$ ($m/z^-=262$) was found under a high RH. Consequently, the heterogeneous products in wet seed particles will further contribute to the formation of SOA, because higher aerosol liquid water content enables more aqueous phase reactions.

In conclusion, the reasons for the increasing trend of SOA formation under high RH conditions may be summarized as following: firstly, higher concentration of OH radical will certainly promote the SOA formation as RH increases. A faster decay rate of furan will also contribute to the formation of products that can partition into the particle phase. In addition, it is possible that the aqueous surface of seed particles provides a new substrate for the photooxidation of furan. Previously, N₂O₅ and HNO₃ have been proven to be the key products in the VOC-NOx irradiation experiments (Wang et al., 2016). The moist surface under high RH conditions is more favorable for the condensation of products with low vapor pressure, leading to the increasing production of SOA formation. The high RH environment favors the formation of the hemiacetal compound. Moreover, the effect of RH on SOA formation in furan photooxidation can be also determined by the aqueous photochemistry under high RH conditions as discussed above. The aqueous phase reactions at the surface of particles promotes the formation of hemiacetal-like products, which likely plays an important role in the process of SOA formation. Previously, unsaturated first-generation reaction products of 3-methyl furan have also been suggested to undergo acid-catalyzed condensed-phase reactions, with SOA yields up to 15% (Strollo and Ziemann, 2013). In addition, the reinforced effect of RH on SOA yield was also ascribed from the photooxidation of other aromatic compounds, such as, benzene (Ng et al., 2007), toluene (Hildebrandt et al., 2009; Kamens et al., 2011), and xylene (Zhou et al., 2011)."



Figure 7: Selected background-subtraction HESI-Q Exactive-Orbitrap MS results of

SOA in both negative (blue) and positive (pink) ion modes from the photooxidation of furan under different RH conditions.



Figure 8: Selected background-subtraction HESI-Q Exactive-Orbitrap MS results of SOA in both negative (blue) and positive (pink) ion modes from the photooxidation of furan under different RH conditions.



Scheme 1: Proposed chemical mechanism of furan-NOx photooxidation under different experimental conditions. SOA constituents in blue and

pink boxes are proposed SOA constituents detected by HESI-Q Exactive-Orbitrap MS under negative and positive ion mode, respectively. The detected nitrates and dinitrates in red are low-volatility organic species, which can easily partition into the particle phase and enhance the SOA formation.

3. The observation of enhanced SOA formation with increased NO is interesting, because most previous work have shown that increase of NO tend to promote RO2+NO chemistry which lead to fragmentation. Why are SOA yields higher with higher NO in the case of furan photooxidation? The authors gave these possibilities in the text, but did not further conclude it based on the mechanism. Is this because furan is a cyclic compound and the fragmentation does not break the C4 backbone? Or were OH concentrations very different between different furan/NOx experiments (as in the cases for the two referred studies)? Or both?

Author reply:

In our experiments, the OH radical was indeed produced during the photooxidation of furan instead of being added before the experiments started. But the original intension of our study was not to determine the OH effect on furan SOA formation. As indicated previously, SOA yields increase with increasing NOx concentration at low NOx levels and then decrease at higher NOx concentration (Sarrafzadeh et al., 2016a; Loza et al., 2014; Hoyle et al., 2011; Chan et al., 2010). All these studies demonstrated that the increase of SOA yield at low NOx levels was attributed to an increase of OH concentration. After eliminating the effect of OH concentration on the SOA mass growth, the SOA yield only decreased with increasing NOx concentration. To control the effect of OH concentration on furan SOA formation in the present work, four more experiments have been added with additional injection of H₂O₂ as OH precursor before the experiments started. The results suggested that there remains a positive correlation between SOA formation and NOx concentration as shown in Table S1 and Fig. 3. To further understand the effect of NOx level on SOA formation, four more experiments were carried out for HESI-Q Exactive-Orbitrap MS detection. The MS results revealed the formation of a number of cyclical hydroxyl nitrates and dihydroxyl dinitrates with low-volatility, which can significantly contribute to the SOA formation (Schwantes et al., 2019). In addition, according to the proposed mechanism, the fragmentation can hardly break the C4 backbone for the cyclic compound furan. Many newly published studies suggested that increasing NOx concentration is beneficial to nitrates formation, which are regarded as low volatility species that can easily partition into the particle phase and enhance the SOA formation (Liu et al., 2019; Rissanen, 2018). To provide a better illustration of the NOx effect on SOA formation, the following changes have been made in the revised manuscript.

Page 7, line 2:

"To further assess the effect of OH produced during the furan-NOx photooxidation, four experiments (Table S1, Exp.13-16) were conducted by injecting H₂O₂ in the chamber before the experiments started. For Exp.6-12, different RH levels coupled with similar furan/NOx ratios were monitored to assess the RH impact on SOA formation. To analyze the SOA composition, five additional experiments (Table S2, Exp. 17-21) were carried out to analyze the HESI-Q Exactive-Orbitrap MS, which intended to compare the role of NOx and RH on the SOA formation."

Page 9, line 5:

"It is generally accepted that experiments with low NOx levels lead to higher SOA yields than those with higher NOx levels at the same VOC concentration (Song et al., 2005). However, as shown in Fig. 3, an increasing SOA mass concentration and SOA yield with increasing NOx was observed. There are two possible explanations to this phenomenon: (i) The concentration of OH radicals produced *in situ* in the present study before additional source of OH was insufficient to produce a considerable amount of SOA under low-NOx conditions. As shown in Fig. S3, the OH concentration exhibits a gradual increase with NOx concentration and there appears to be a correlation between NOx concentration, OH concentration and SOA yield. Therefore, at low-NOx conditions, the increase of SOA yield was attributed to an increase of OH concentration, which was affected by OH recycling following reaction (R6) (see Fig. 1) and contributed to the enhancement of SOA formation. This result is consistent with a previous study concerning the impact of NOx and OH on SOA

formation from β-pinene photooxidation, which has proved that the positive correlation between SOA yield and NOx levels ([VOC]₀/[NOx]₀ > 10 ppbC/ppb) was caused by the NOx-induced increase of OH concentration (Sarrafzadeh et al., 2016b). (ii) Differently, Sarrafzadeh et al. found that after eliminating the effect of OH concentration on SOA mass growth, SOA yield only decreased with increasing NOx levels (Sarrafzadeh et al., 2016b). To further investigate the NOx effect on furan generated SOA formation under adequate OH conditions, four more experiments (see Table S1) were carried out with additional injection of H₂O₂ as the OH radical source before the start of each experiment. The SOA yield trend at different C4H4O/NOx ratios is also shown in Fig. 3. The continuous growth trend of SOA yield with increasing NOx concentration at a relative high NOx level may result from the partitioning of generated semi/low-volatility compounds (multifunctional nitrates and dinitrates) to the particle phase, leading to significant furan SOA formation under high NOx conditions. Similarly, SOA from OH-initiated isoprene oxidation under high-NOx conditions was comprehensively investigated by Schwantes et al., who suggested that low volatility hydroxyl nitrates and dihydroxyl dinitrates generated conspicuously more aerosol than previously thought (Schwantes et al., 2019). Our results showing the increase of SOA mass formation at high-NOx conditions also agree with a previous study, which indicated that a high level of NO_2 can participate in the OH-induced reaction of guaiacol, consequently leading to the formation of organic nitrates and the enhancement of guaiacol SOA formation (Liu et al., 2019)."

Page 11, line 21:

"The MS spectra of generated species from different NOx level and RH conditions, which show evidence for the OH-furan reaction, are presented in Fig. 7 and Fig. 8, respectively. The major peaks are m/z^+ 85.0018, 101.0894, and 185.0504 in the positive ion mode, and m/z^- 146.0161, 225.0125 and 263.0132 in the negative ion mode. The prominent peaks in the HR-MS spectra detected on negative ion mode are comprised of various functionalized hydroxyl nitrates and dihydroxyl dinitrates. However, in the positive ion mode analysis, most carbonyl components were detected. The assignments of these ion peaks, the molecular weights of the products observed, and proposed structures are summarized in Table 3. These detected compounds provide additional evidence for the proposed radical reaction mechanism."

Page 12, line 4:

"(i) decompose and then react with O₂ to yield a 1,4-aldoester (A). (ii) react with NO₂/NO/O₂ to form hydroxyl nitrate compound isomers with m/z^{-146} , or (iii) react with O₂ to form unsaturated products and hydroxyfuranone (B) and 1,4-aldoacid (C). The ring-opened alkylperoxy radical generated from (d) can decompose to generate an unsaturated 1,4-dialdehyde (D). The formation of 1,4-dialdehyde with m/z^+ 85 detected in the positive ion mode suggests that these unsaturated 1,4-dicarbonyls are formed after initial OH addition at 2- or 5-positions. We note that OH radical addition at 2, 3-positions would lead to carbonyl product isomers with same m/z^+ 101. In addition, some dihydroxyl dinitrates with m/z^2 225 were also detected in negative ion mode. However, pathways favouring the generation of these dihydroxyl dinitrates could only take place under high NOx levels. Scheme 1 shows the formation of second-generation products hemiacetals (E) via the reactions of the hydroxyfuranone (B) with 1,4-dialdehyde (D). After uptake from the gas-phase, the combination of hydroxyfuranone with 4-dialdehyde appeared to occur by H-abstraction, followed by dehydration, thus forming m/z^+ 185 compounds. This reaction pathway has also been identified in previous studies of OH-initiated reactions of furans (Strollo and Ziemann, 2013; Aschmann et al., 2014). According to the results of HR-MS, this aqueous phase reaction is more favoured in aqueous particles."

Page 13, line 4:

"In the present study, an increasing trend of SOA formation was observed with the increase of NOx concentration. As shown in the HESI-Q Exactive Orbitrap-MS results, all the detected primary products are carbonyl-rich, and even the organonitrates have at least two carbonyl functional groups. These carbonyl-containing products have lower volatility and contribute to the SOA

formation. The peak intensities in the MS of the products $(m/z^+ 85, 101)$ generated by the pathways involving HO₂ (as indicated by the scheme 1) decreased with the increase of NOx concentration. Additionally, more products of dihydroxyl dinitrates $(m/z^{-} 225)$ with multifunctional groups were detected under high NOx conditions. As shown in Scheme 1, the multifunctional organonitrates detected in negative ion mode are produced mostly from later-generation chemistry. Hydroxyl nitrates with m/z^2 149 can be formed through pathways 1-a, 2-a, and 3-a by the reaction of RO₂ with NOx. We note that the m/z^{-} 149 compound was detected both at low NOx levels and high NOx levels. However, the peak intensity of this product was decreased with increasing NOx concentration. This phenomenon might be caused by the later-reaction of the unsaturated hydroxyl nitrates going through a second OH-initiated reaction and leading to the formation of the dihydroxyl dinitrate with m/z^2 225. In addition, the peak intensities changes of SOA products detected in the positive mode, such as, the peaks at m/z^+ 85 and 101 were reduced under high NOx conditions, which resulted from the fact that the RO₂ radical fate was dominated by the pathway of RO₂+NO or RO₂+NO₂. This result supports that the fate of RO₂ is not a single channel reaction. There exists a competition between RO₂ reacting with NOx and with HO₂ under high NOx conditions but the former pathway is more favourable. There are two pathways for hydroxyl nitrates formation from RO₂ radicals in the presence of NOx according to which RO₂ radicals may react with NO and NO₂ to form RONO₂ and ROONO₂, respectively (Kroll and Seinfeld, 2008). However, the formed peroxynitrates could easily thermally dissociate and convert to RONO₂.

Furthermore, by analyzing the OH concentration and products components, we conclude that there are two possible explanations for the increasing trend of SOA yield as the NOx level increases: (i) the SOA production is closely related to the oxidation capacity in the photooxidation experiments. Experiments conducted under different NOx levels indicate that the OH concentration is controlled by the NOx level if there is no additional OH precursor added before the start of the experiment. As shown in Fig. S3, an increase in NOx level results in more OH generation and a faster

furan decay rate. This justifies the observed higher SOA mass concentration and higher SOA yield. (ii) HRMS fragments associated with multifunctional organonitrates are enhanced under high NOx conditions (Fig. 7). As presented in Scheme 1, the furan dihydroxyl dinitrates are generated from the first-generation hydroxyl nitrate reacting with OH to form a peroxy radical, which reacts thereafter with NO. Together with multifunctional hydroxyl nitrates, these low-volatility species can easily partition into the particle phase and increase the SOA mass concentration. More importantly, the seed particle added initially plays an important role in the processes of gas-particle partitioning as indicated by a recent study, which showed that sufficient seed surface area at the start of the reaction largely suppressed the effects of vapour wall losses of low-volatility compounds (Schwantes et al., 2019). Therefore, the NaCl seed particle added in the present work promoted the partitioning of the formed low-volatility functional organonitrates."



Figure 3: Dependence of the SOA mass concentration and SOA yield on the C₄H₄O/NOx ratio. Since the particle wall loss has a weak RH dependence in our chamber, a mean value of 3.6×10^{-5} s⁻¹ was used for wall loss correction. A density of 1.4 g cm⁻³ was used in SMPS (Jia and Xu, 2018; Kostenidou et al., 2007).



Figure 7: Selected background-subtraction HESI-Q Exactive-Orbitrap MS results of SOA in both negative (blue) and positive (pink) ion modes from the photooxidation of furan under different RH conditions.

Table S1. Summary of experimental conditions with the additional injection of H_2O_2 in the study of the NOx effect on SOA formaiton.

No.	[furan] ₀ (ppb)	[H ₂ O ₂] ₀ (ppm)	[NOx]₀ (ppb)	RH (%)	C4H4O/NOx (ppbC/ppb)	SOA ^e (µg m ⁻³)	SOA yield (%)
13	802	1.7	15.3	< 10	52.4	30.1	3.7
14	811	1.6	40.2	< 10	20.2	76.3	9.4
15	807	1.7	87.5	< 10	9.2	169.2	20.9
16	797	1.7	200.1	< 10	4.0	216.9	27.2

No.	[furan] ₀ (ppb)	[H ₂ O ₂] ₀ (ppm)	[NOx] ₀ (ppb)	RH (%)	C4H4O/NOx (ppbC/ppb)	Aim
17	723.5	3.5	26.4	<5	36.3	
18	748.3	6.5	152.6	<5	5.8	for HESI-Q Exactive-Orbitrap
19	764.8	7.2	163.5	30	5.9	MS
20	755.1	7.3	149.8	62	5.9	

Table S2. Summary of experimental conditions for HESI-Q Exactive-Orbitrap MS detection.

4. The discussion of the RH effect on SOA using the mass spectral data was very vague. The authors only discussed two ions, m/z 187 and m/z 255. First, it seems the m/z 187 ion is C4H4O4Cl2 from high-resolution fitting. But how is it formed? The authors proposed Cl adduct for the major ions m/z 187, 255, and 281. It is probabaly the case for m/z 255 and 281, since they contain nitrogen and have only one Cl on the ion. But m/z 187 is probably not. The C4H4O4 compound does not exist in Scheme 1. The compound D is C4H4O3. How does it form C4H4O4 in the mechanism? Further, for the m/z 255 ion, the formulas provided in Figure 6 is incorrect. [C4H4O4]35Cl2-has an exact mass of 185.949; [C4HO9N2]35Cl- has an exact mass of 255.938; [C8H8O8N]35Cl- has an exact mass of 280.994. The authors need to make sure the chemical formula assignments are correct before discussing the mechanism.

Author reply:

We thank the Referee for the thoughtful comments. According to the revised MS results, the chemical formulae have been reassigned in the revised manuscript. The discussion part, supporting figures and chemical mechanism have been shown in our

reply to Comment 2.

Minor and technical comments:

1. Abstract: The abstract should deliver the most important scientific findings. It is unnecessary to describe how the measurements were performed in the abstract (e.g., how particle mass concentration and size distribution were determined). Additionally, "the SOA mass concentration and yield increase with increasing humidity, because higher aerosol liquid water content brings more aqueous phase reactions" does not make sense. More aqueous phase reactions do not mean higher product yield.

Author reply:

We thank the referee for this suggestion. The abstract has been rewritten in the revised manuscript:

"Atmospheric furan is a primary and secondary pollutant in the atmosphere, and its emission contributes to the formation of ultrafine particles. We investigate the effects of NOx level and humidity on the formation of secondary organic aerosol (SOA) generated from the photooxidation of furan in the presence of NaCl seed particles. SOA mass concentration and yield were determined under different NOx and humidity levels. A significant difference is observed both in the variation of SOA mass concentration and SOA yield with the initial experimental conditions. Varying VOC/NOx ratios over the range 48.1 to 8.2 contributes to the effective formation of SOA in the presence of NaCl seed particles, with the SOA mass concentration and SOA yield ranging from 0.96 μ g m⁻³ to 23.46 μ g m⁻³ and from 0.04 % to 1.01 %, respectively. We found that there was a favourable relationship between the SOA yield and NOx concentration. Especially, the increase of SOA yield with increasing NOx concentration was continuously observed at high NOx levels owing to a corresponding increase of the amount of low-volatility hydroxyl nitrates and dihydroxyl dinitrates that can partition into particle phase. In addition, varying RH from 5% to 88% increased the SOA yield from 1.01% to 5.03%. The enhanced SOA

formation from humid conditions may result from the high OH concentration, rapid furan decay rate, enhanced carbonyl-rich products condensation, and the aqueous-phase reactions. Using hybrid quadrupole-orbitrap mass spectrometer equipped with electrospray ionization (HESI-Q Exactive-Orbitrap MS), three carbonyl-rich products and three kinds of organonitrates were identified in the collected SOA. Based on the MS analysis and FTIR spectra, the reaction mechanism of furan photooxidation was proposed. This study demonstrates the effects of NOx and humidity on SOA formation during the furan-NOx-NaCl photooxidation, and provides new insights into the oxidation regime and SOA composition in furan photooxidation. The results also illustrate the importance of studying SOA formation over a comprehensive range of environmental conditions. Only such evaluations can induce meaningful SOA mechanisms to be implemented in air quality models."

2. Second sentence in the introduction puts different categories together. Remove black carbon and brown carbon.

Author reply:

We have now removed this part accordingly.

3. Page 2, line 1. Change volatile organic compound to VOC.

Author reply:

This has been changed.

4. In the introduction, some statements about cited studies are incorrect. For example, page 2, line 3-4, the Chan et al. (2010) study demonstrated that isoprene SOA formed under high NO2/NO is large, not under high-NOx conditions; the Zhang et al. (2012) as well as the Zhang et al. 2011 studies show different compositions under dry and wet conditions.

Author reply:

We have revised this part accordingly as:

Page 3, line 8

Another study of the SOA formation from the irradiation of propylene showed that the SOA yield decreased with increasing propylene/NOx ratio (Ge et al., 2017b)."

Page 3, line 12

"A study focusing on the photooxidation of toluene and m-xylene has demonstrated that aerosol yields decrease as NOx level increases (Xu et al., 2015), while another study showed that the SOA yield from photooxidation of isoprene under high NO_2/NO is 3 times more important than that measured under low NO_2/NO level (Chan et al., 2010)."

5. Page 10, line 10. What is C4H4O4Cl? Does the authors have a prediction of the possible structure? How does the NaCl interacts with the organic components in SOA to form this species? On page 11, line 24, some discussion was made, but it is still unclear how "Cl adduction of SOA product" happens.

Author reply:

According to the latest results that sufficiently eliminate the interference of artifacts, the Cl-containing products have not been detected, which indicates that there were no Cl adduction reactions happening.

6. Page 10, line 13. The carboxylic acids may not generate enough acidity to catalyze reactions as the authors mentioned, unless the authors could provide evidence.

Author reply:

We have removed this speculation from the revised manuscript.

7. Page 12, line 28. The authors said "it is highly probable that the particle surface area increases with the amount of ALW increasing". Could the SMPS measurements provide quantitative evidence?

Author reply:

We agree with the Referee's suggestions that the SMPS measurements could provide quantitative evidence. We have compared the surface particle sizes under different RH conditions and found that the particle surface area increases as the amount of ALW increases. To make the conclusion more persuasive, we have added the following figure in the revised version.



Figure S7: Variations of surface particle sizes and ALW under different experimental RH conditions.

8. Page 13, line 4. Under high RH, the acidity, if any, is likely lower due to water dilution.

Author reply:

The "acid catalyzed reactions" is now removed in the revised manuscript.

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