

## Response to the comments of Anonymous Referee #2

General comments:

In the study by Zhang et al., the authors explore the effect of humidity (RH) on the formation of secondary organic aerosol (SOA) from ozonolysis of two structurally different monoterpenes; limonene and  $\Delta^3$ -carene, and the sesquiterpene  $\beta$ -caryophyllene. Experiments are performed at constant temperature in an oxidation flow reactor at RHs ranging from 1-60 % whilst monitoring SOA particle number and mass concentrations followed by off-line analyses of the SOA chemical composition using ultra-high performance liquid chromatography quadrupole time-of-flight mass spectrometry (LC-MS). The study reports large differences in the effect of RH on the SOA formation from limonene and  $\Delta^3$ -carene, with the former showing increasing SOA mass and particle number concentration at elevated RH whilst little or no effects are observed in the case of  $\Delta^3$ -carene. From the chemical composition of the formed SOA the authors explain these discrepancies by water-influenced reactions on exocyclic double bonds yielding lower volatile organic compounds under higher RH.

The topic is relevant and fall within the scope of ACP, however, the manuscript is in need of major revision before any consideration for publication in ACP

Major concerns include the far from atmospheric relevant conditions applied in the study experiments, lack of validation of experimental approach, lack of discussion on contribution of other oxidizing agents, as well as scarce evidence of enhanced dimer formation at elevated RH from chemical analysis of formed the SOA. These are concerns that needs to be addressed if the manuscript is in any way to contribute to the work of the many previous studies reporting on the influence of RH on the formation of SOA from monoterpenes.

Response: We thank the Referee for providing the feedback on our manuscript. We have carefully considered all of the concerns raised by the Referee and made revisions accordingly. Below are the specific changes we have made:

1. We have conducted a low-concentration limonene ozonolysis experiment to better simulate atmospheric conditions and enhance the relevance of our findings.
2. In order to give an evidence of enhanced dimer formation at elevated RH from chemical analysis of formed the SOA, we have reanalyzed the distribution of the dimers formed by limonene and  $\Delta^3$ -carene ozonolysis. Additionally, we have added the distribution of the monomers, dimers, trimer and tetramer in the overall mass spectrometry spectrum of  $\Delta^3$ -carene.

The responses are listed below in blue color text and the associated revisions to the manuscript are shown in red color text.

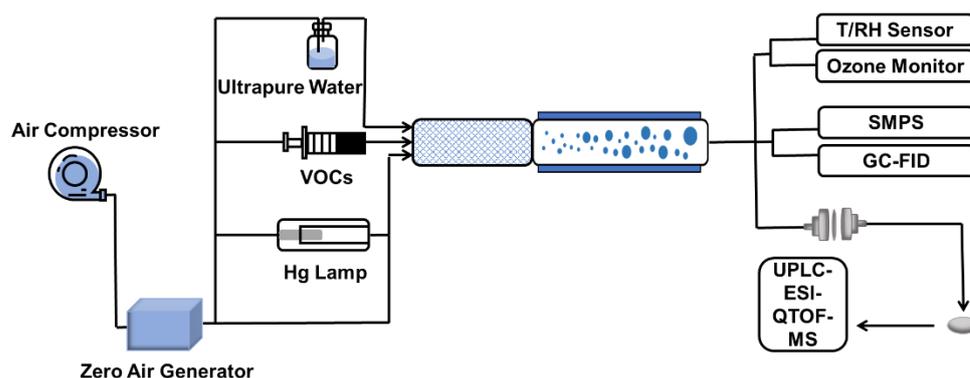
Major comments:

1. As I understand, this is the first publication using the custom-made oxidation flow

reactor (OFR). With a length of 6.02 meters, have the authors validated that measurements of e.g. ozone, RH, temperature and VOC performed at the end of the OFR represent initial conditions at the point of injection and thus initial oxidation? Other OFRs, such as in Jonsson et al., (2006) and Li et al., (2019), is designed to ensure proper mixing of injected oxidant (e.g. O<sub>3</sub>) and VOCs at the initial stage of the OFR. When using OFRs the uniform distributions of O<sub>3</sub>, VOCs and H<sub>2</sub>O in the tube should be confirmed by measuring O<sub>3</sub>, VOC and RH at the different locations prior to the experiments. A particular concern is that the O<sub>3</sub>: VOC ratio and maybe RH may be different at the point of injection compared to the end of the 6.02 meter tube.

Response: We are sorry for the oversight in labeling the dimensions of the oxidation flow reactor. It should have been specified as 602 mm, and we have made the correction in the revised version of the manuscript, as indicated by the highlighted yellow text (Page 3, Line 80). This OFR is similar to the design shown in previous studies (Liu et al., 2019; Liu et al., 2014), containing a mixing tank and a reacting tube, which has been proved to have good mixing ability. We have added more descriptions of OFR (Fig. S2) and related references in the revised manuscript.

“The OFR is a 602 mm long stainless cylinder with a volume of 2.5 L (Fig. S2) (Liu et al., 2014; Liu et al., 2019)”



**Figure S2.** Schematic description of the experiment.

2. The authors report SOA mass concentrations of 980-2200  $\mu\text{g}/\text{m}^3$  from the oxidation of 321 ppb of limonene by 6 ppm of O<sub>3</sub> with corresponding yields of 63-142% (table 1). These values are very high in comparison with other studies which should be made apparent by the authors. E.g. for clarification, please add mass concentrations and yields of all studies in table 2. Any explanation for these high yields?

Response: We have added O<sub>3</sub> concentration, SOA mass concentration and yield in Table 2. As a comparison, the ozonolysis of 13.2 ppb of limonene ( $\Delta\text{org}$ ) with 430 ppb of O<sub>3</sub> resulted in concentration ranges of 62-229  $\mu\text{g}/\text{m}^3$ , and the corresponding yields ranged from 77.4% to 285.7% (Jonsson et al., 2006). In addition, the SOA potential of the exocyclic bond was found to be relatively high. Specifically, the SOA yield from the exocyclic bond was up to eight times higher compared to the endocyclic bond, with corresponding yields of approximately 23.8%-55.3% and 7.4%, respectively (Gong and Chen, 2021). Due to high limonene and O<sub>3</sub> concentrations, the SOA yields in this study are relatively high, but still in the range that was previously reported.

**Table 2.** Comparison with previous studies on the effect of RH.

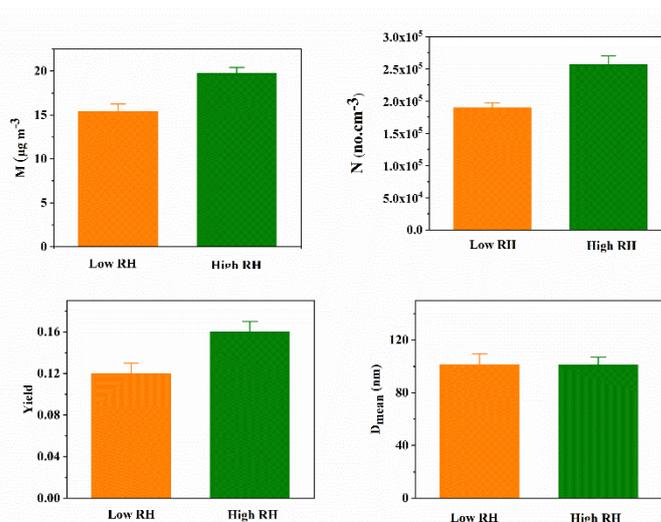
Precursor concentration (ppb)	Precursor concentration (ppb)	O <sub>3</sub> concentration (ppb)	Reactor	OH scavenger	T (K)	RH (%)	SOA Mass		M <sup>a</sup>	N <sup>b</sup>	Reference
							Concentration	SOA Yield (%)			
1000	1000	1000	flow reactor	cyclohexane	295±2	0.02 and 32.5	N.M. <sup>c</sup>	N.M. <sup>c</sup>	no effect	- <sup>e</sup>	Bonn et al. (2002)
320	100±5		chamber	N.M. <sup>c</sup>	296±2	18±2, 50±3 and 82±2	24; 58; 120	7.0 ± 0.7; 17.4±1.3; 53.4±1.9	+ <sup>d</sup> (7 times)	+ <sup>d</sup> (8 times)	Yu et al. (2011)
15 and 30	430.9		flow reactor	2-butanol	298±0.4	< 2-85	2.7-10.5 and 62-229	6.8-26.4 and 77.4-285.7	+ <sup>d</sup>	+ <sup>d</sup>	Jonsson et al. (2006)
endocyclic (24.6) and exocyclic	endocyclic (270) and exocyclic		flow reactor	2-butanol	298	10-50	endocyclic (~11) and exocyclic	endocyclic (~7.4) and exocyclic	exocyclic (+ <sup>d</sup> ) and endocyclic	N.M. <sup>c</sup>	Gong and Chen (2021)

(15.2)	(12200)			(22-51)	(23.8-55.3)	( <sup>-c</sup> )		
1085	900±10	flow reactor	298	3-62	150; 200; 210	N.M	+ <sup>d</sup>	Li et al. (2019)
321±39	5786±203	flow reactor	298	0-60	980.9-2211.1	62.9-141.8	+ <sup>d</sup> (2 times)	this study
1000	1000	flow reactor	295±2	0.02 and 32.5	N.M <sup>c</sup>	N.M <sup>c</sup>	no effect	Bonn et al. (2002)
14.2 and 29.4	2300	flow reactor	298±0.4	< 2-85	0.78-3.8 and 15.3-94;	2.1-10.1 and 19.8- 116.7	+ <sup>d</sup>	Jonsson et al. (2006)
1111	900±10	flow reactor	298	3-62	75; 80; 90	N.M	- <sup>e</sup>	Li et al. (2019)
341±28	6257±140	flow reactor	298	0-60	346.0-198.5	19.4-11.1	- <sup>e</sup>	this study

<sup>a</sup> M means the change trend total particle mass concentration. <sup>b</sup> N means total particle number concentration. <sup>c</sup> N.M. means not mentioned. <sup>d</sup> Positive sign (+) means the mass or number concentration increases with RH. <sup>e</sup> Negative sign (-) means the mass or number concentration decreases with RH.

3. Also, I think the author should discuss the feasibility of extrapolating their flow tube results to the real environment. Limonene mixing ratios are at the sub-ppb level for forest and urban environments, thus the conditions applied in the current study seems far from atmospheric relevant. Could the authors explain the rationale for using such high concentrations?

Response: To get enough SOA particles to analyze, many lab studies use VOC concentrations that are much higher than the ambient concentration. According to Table 2, the limonene concentration applied in previous studies was in the range of ~15-1000 ppb. The limonene concentration in this study (321 ppb) is within this range, but relatively high because we need to collect enough particles for off-line MS analysis with a small sampling flow through the OFR ( $0.9 \text{ L min}^{-1}$ ). To examine the feasibility of extrapolating our results to lower concentrations, we have performed a low-concentration limonene ozonolysis experiment. In this experiment, the limonene concentration was 20.5 ppb, ~16 times lower than previously used and close to the lower limit of the range applied in previous lab studies (i.e., ~15 ppb). According to the experimental results (Fig. S6), the number concentration of SOA formed from limonene ozonolysis increased by approximately 1.4 times under high RH, which is similar to the increase observed under high-loading conditions. The mass concentration increased by approximately 1.3 times at a precursor concentration of 20.5 ppb. The relatively small increase in mass concentration compared to the high-concentration conditions may be attributed to the less pronounced distribution of SVOCs at low mass concentrations. This result indicates that the enhancement effect on limonene SOA by high RH is still valid for low precursor concentrations. We have revised this at Page 18, Line 339-348: “To investigate the multi-generation reactions of limonene under low-concentration conditions, we conducted low-concentration limonene ozonolysis experiments, and the results are shown in Fig. S6. In these experiments, the limonene and  $\text{O}_3$  concentrations were 20.5 ppb and 5.7 ppm, respectively. According to the experimental results, the number concentration of SOA formed from limonene ozonolysis increased by approximately 1.4 times under high RH, which is similar to the increase observed under high-loading conditions. The mass concentration increased by approximately 1.3 times at a precursor concentration of 20.5 ppb. The relatively small increase in mass concentration compared to the high-concentration conditions may be attributed to the less pronounced distribution of SVOCs at low mass concentrations. This result indicates that the enhancement effect on limonene SOA by high RH is still valid for low precursor concentrations.”



**Figure S6.** The SOA formation of low-concentration limonene under low and high RH (a) mass concentration (b) number concentration (c) SOA yield (d) mean diameter.

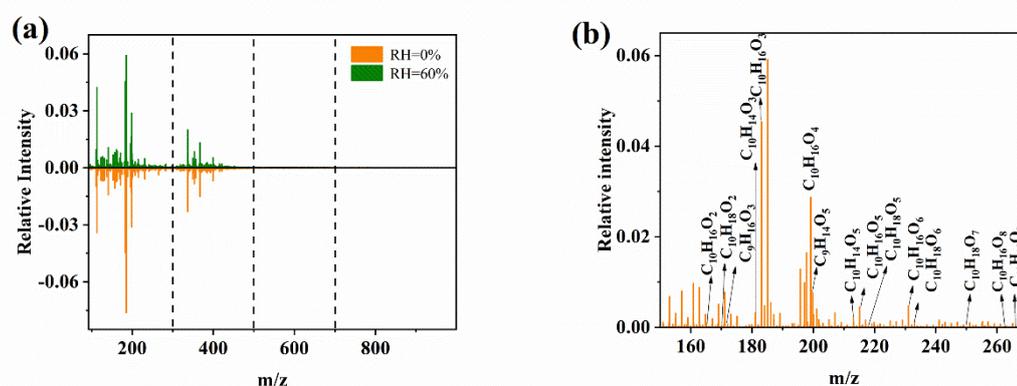
4. Looking at Table 1, it seems that more O<sub>3</sub> is consumed in limonene experiments than in Δ<sup>3</sup>-carene experiments (if reported O<sub>3</sub> concentrations relates to measurement performed during the oxidation). To examine this, could the authors maybe report on the consumed O<sub>3</sub> (ppb) in all experiments (e.g. concentration before and after the OFR). In relation, have the authors considered the influence of OH-radicals as possible explanation for the differences in SOA formation from limonene and Δ<sup>3</sup>-carene? I wonder to what extent the resulting SOA from limonene and Δ<sup>3</sup>-carene can be ascribed to oxidation by OH vs O<sub>3</sub>. I would expect that reaction with O<sub>3</sub> is the dominating oxidation pathway for limonene, whilst reactions with OH-radicals may be more significant in Δ<sup>3</sup>-carene experiments. Espec no such RH effect was observed for O<sub>3</sub>+limonene. Consequently, although all experiments in the current study are conducted as dark ozonolysis of limonene and Δ<sup>3</sup>-carene, it might be important to address that this does not rule out the influence of other oxidation pathways (e.g. OH-radical reactions) which may be less effective at producing SOA compared to ozonolysis and which also could exhibit different response to RH. For instance, it may be that the Δ<sup>3</sup>-carene + OH reaction is unaffected (or enhanced relative to Δ<sup>3</sup>-carene + O<sub>3</sub> reactions) by RH (e.g. Bonn et al 2002) in contrast to the Limonene + O<sub>3</sub> reaction. The authors spend much effort on presenting and discussing the results related to the limonene experiments. However, in comparison, discussions on the Δ<sup>3</sup>-carene results seems lacking. In particular, results on the molecular analysis of the Δ<sup>3</sup>-carene SOA is lacking, e.g. comparison of mass spectrums recorded at different RH (such as in Figure 2), number and intensity proportion of the monomers, dimers, trimers and tetramers (as in Table S1).

Response: Following the Referee's suggestion, we have measured the O<sub>3</sub> consumptions, which are ~250 ppb for limonene experiments and ~100 ppb for Δ<sup>3</sup>-carene experiments. The text has been added in Page 4, Line 102-103: "Correspondingly, the O<sub>3</sub>

consumption for limonene and  $\Delta^3$ -carene were  $\sim 250$  ppb and  $\sim 100$  ppb, respectively.”

Molar OH radical yields were reported as  $0.65 \pm 0.10$  (Hantschke et al., 2021),  $0.86 \pm 0.11$  (Aschmann et al., 2002) and 0.56 to 0.59 (Wang et al., 2019) for  $\Delta^3$ -carene, while for limonene, the reported yields were  $0.67 \pm 0.10$  (Aschmann et al., 2002) and  $0.76 \pm 0.06$  (Herrmann et al., 2010). It seems that the OH radicals produced from limonene and  $\Delta^3$ -carene are quite similar within the range of uncertainties. Therefore, the increased ozone consumption by limonene is primarily attributed to the presence of its exocyclic double bond. We have also updated this in the revised manuscript (Page 13, Line 254-261), “In such progress, we cannot rule out the possibility that relative humidity (RH) may influence the generation of other free radicals (Ma et al., 2009), thereby impacting the formation of secondary organic aerosols (SOA), such as, OH-radical reactions (Bonn et al., 2002; Fick et al., 2002). However, Molar OH radical yields were reported as  $0.65 \pm 0.10$  (Hantschke et al., 2021),  $0.86 \pm 0.11$  (Aschmann et al., 2002) and 0.56 to 0.59 (Wang et al., 2019) for  $\Delta^3$ -carene, while for limonene, the reported yields were  $0.67 \pm 0.10$  (Aschmann et al., 2002) and  $0.76 \pm 0.06$  (Herrmann et al., 2010). It seems that the OH radicals produced from limonene and  $\Delta^3$ -carene are quite similar within the range of uncertainties. Therefore, the increased ozone consumption by limonene is primarily attributed to the presence of its exocyclic double bond.”

Additionally, we have included the mass spectra of SOA from  $\Delta^3$ -carene ozonolysis (Fig. S4) and the quantification of monomers, dimers, trimers, and tetramers of  $\Delta^3$ -carene, along with their corresponding number and intensity proportions in Table S2. The distribution of  $\Delta^3$ -carene SOA is similar to that of limonene-SOA, i.e., most of the SOA molecules are monomers ( $\sim 70\%$ ) and dimers ( $\sim 25\%$ ), while trimers and tetramers contribute to very small fractions ( $\sim 2\%$  and  $< 1\%$ ). The corresponding discussion was changed in the revised manuscript (Page 11, Line 200-203): “Correspondingly, the distribution of  $\Delta^3$ -carene-SOA can be divided into four groups (Fig. S4), comparable to that of limonene-SOA. Most of the SOA molecules are monomers ( $\sim 70\%$ ) and dimers ( $\sim 25\%$ ), while trimers and tetramers contribute to smaller proportions ( $\sim 2\%$  and  $< 1\%$ , respectively) (Table S2).”



**Figure S4.** UPLC/(-) ESI-Q-TOF-MS mass spectra of SOA from  $\Delta^3$ -carene ozonolysis. (a) MS under high and low RH conditions; (b) the identification of monomers under low RH condition.

**Table S2.** The number and intensity proportion of four groups for  $\Delta^3$ -carene

<b>Groups</b>	<b>Monomers</b>	<b>Dimers</b>	<b>Trimers</b>	<b>Tetramers</b>
<b>Number (L)<sup>a</sup></b>	239	178	76	4
<b>Number (H)<sup>b</sup></b>	216	151	26	1
<b>Intensity proportion (L)<sup>a</sup></b>	69.8%	28.6%	1.6%	0.5%
<b>Intensity proportion (H)<sup>b</sup></b>	72.5%	26.9%	2.0%	0.2%

<sup>a</sup>L means under low RH. <sup>b</sup>H means under high RH.

5. In relation, the observed increase in SOA mass in limonene experiments at elevated RH is proposed to arise from increased particle number concentration from nucleation promoted by low-volatile compounds such as dimers. To support this, the authors report 25 more dimers (187 vs 162) in limonene SOA formed at higher RH compared to low RH. This relatively small increase in LVOC species seems unlikely to account for the observed enhancements of SOA particle formation at high RH. At least the authors need to show that these extra dimers indeed contribute significantly to the formed SOA. Also, Could the authors please provide similar results from  $\Delta^3$ -carene experiments; i.e. how many dimers were found in  $\Delta^3$ -carene SOA and do the number of dimers change with changes in RH?

Response: To clarify the contribution of extra dimers, we conducted a reanalysis of the mass spectra for limonene SOA, specifically focusing on the dimers obtained under high RH conditions (Table S6). Among the 187 dimers observed, 54 (~19%) dimers were exclusively detected under high (RH) conditions. Note that some of the 162 dimers under low RH conditions were found under high RH conditions, so the number of newly formed dimers under high RH conditions (54) is larger than the absolute number difference (25). These particular dimers contribute to enhanced nucleation under high RH.

According to Table S2 (see our response above), the number of dimers in  $\Delta^3$ -carene SOA decreased under high RH conditions. As shown in Table S6, we observed 63 dimers exclusively under low humidity conditions, with a corresponding intensity of ~35%.

We have added the following text in the revised manuscript

Page 15, Line 275-277:

“As shown in Table S6, 54 out of the total 187 dimers were exclusively observed for limonene under high humidity conditions, contributing to a corresponding intensity of ~19%.”

Page 18, Line 335-337:

“Correspondingly, the number and relative intensity of HOMs and dimers detected under high RH conditions are both lower than those under low RH conditions (Table S7). Furthermore, out of a total of 178 dimers, 63 dimers were exclusively identified under low RH conditions (Table S6).”

**Table S6.** Dimers: RH-dependent discoveries for limonene and  $\Delta^3$ -carene.

<b>54 dimers exclusively detected under high RH (limonene)</b>		<b>63 dimers exclusively detected under low RH (<math>\Delta^3</math>-carene)</b>	
<b>Molecular formula</b>	<b>Absolute intensity (High RH)</b>	<b>Molecular formula</b>	<b>Absolute intensity (Low RH)</b>
C <sub>18</sub> H <sub>26</sub> O <sub>4</sub>	4.66×10 <sup>2</sup>	C <sub>17</sub> H <sub>24</sub> O <sub>5</sub>	1.59×10 <sup>3</sup>
C <sub>16</sub> H <sub>20</sub> O <sub>6</sub>	7.24×10 <sup>2</sup>	C <sub>10</sub> H <sub>14</sub> O <sub>11</sub>	3.90×10 <sup>3</sup>
C <sub>13</sub> H <sub>18</sub> O <sub>9</sub>	3.36×10 <sup>2</sup>	C <sub>14</sub> H <sub>14</sub> O <sub>8</sub>	4.02×10 <sup>3</sup>
C <sub>17</sub> H <sub>22</sub> O <sub>6</sub>	6.63×10 <sup>3</sup>	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	4.60×10 <sup>3</sup>
C <sub>18</sub> H <sub>26</sub> O <sub>5</sub>	6.28×10 <sup>2</sup>	C <sub>12</sub> H <sub>10</sub> O <sub>10</sub>	4.00×10 <sup>3</sup>
C <sub>19</sub> H <sub>32</sub> O <sub>4</sub>	1.58×10 <sup>3</sup>	C <sub>13</sub> H <sub>16</sub> O <sub>9</sub>	8.34×10 <sup>3</sup>
C <sub>15</sub> H <sub>18</sub> O <sub>8</sub>	1.65×10 <sup>3</sup>	C <sub>19</sub> H <sub>26</sub> O <sub>4</sub>	4.96×10 <sup>3</sup>
C <sub>13</sub> H <sub>12</sub> O <sub>10</sub>	8.85×10 <sup>3</sup>	C <sub>17</sub> H <sub>22</sub> O <sub>6</sub>	1.05×10 <sup>3</sup>
C <sub>14</sub> H <sub>20</sub> O <sub>9</sub>	8.44×10 <sup>2</sup>	C <sub>13</sub> H <sub>12</sub> O <sub>10</sub>	5.46×10 <sup>3</sup>
C <sub>16</sub> H <sub>28</sub> O <sub>7</sub>	9.89×10 <sup>3</sup>	C <sub>13</sub> H <sub>18</sub> O <sub>10</sub>	4.68×10 <sup>3</sup>
C <sub>15</sub> H <sub>26</sub> O <sub>8</sub>	2.18×10 <sup>3</sup>	C <sub>15</sub> H <sub>12</sub> O <sub>9</sub>	4.22×10 <sup>3</sup>
C <sub>10</sub> H <sub>8</sub> O <sub>13</sub>	6.33×10 <sup>3</sup>	C <sub>10</sub> H <sub>12</sub> O <sub>13</sub>	5.00×10 <sup>3</sup>
C <sub>18</sub> H <sub>24</sub> O <sub>6</sub>	6.06×10 <sup>2</sup>	C <sub>22</sub> H <sub>28</sub> O <sub>3</sub>	8.88×10 <sup>3</sup>
C <sub>11</sub> H <sub>14</sub> O <sub>12</sub>	7.70×10 <sup>2</sup>	C <sub>19</sub> H <sub>26</sub> O <sub>6</sub>	1.54×10 <sup>3</sup>
C <sub>21</sub> H <sub>22</sub> O <sub>4</sub>	4.80×10 <sup>3</sup>	C <sub>16</sub> H <sub>20</sub> O <sub>9</sub>	1.64×10 <sup>3</sup>
C <sub>20</sub> H <sub>34</sub> O <sub>4</sub>	2.53×10 <sup>3</sup>	C <sub>15</sub> H <sub>18</sub> O <sub>10</sub>	5.00×10 <sup>3</sup>
C <sub>23</sub> H <sub>32</sub> O <sub>2</sub>	2.12×10 <sup>3</sup>	C <sub>16</sub> H <sub>22</sub> O <sub>9</sub>	1.69×10 <sup>3</sup>
C <sub>18</sub> H <sub>32</sub> O <sub>6</sub>	3.68×10 <sup>2</sup>	C <sub>18</sub> H <sub>22</sub> O <sub>8</sub>	3.32×10 <sup>3</sup>
C <sub>17</sub> H <sub>30</sub> O <sub>7</sub>	7.46×10 <sup>3</sup>	C <sub>12</sub> H <sub>16</sub> O <sub>13</sub>	4.00×10 <sup>3</sup>
C <sub>14</sub> H <sub>22</sub> O <sub>10</sub>	4.04×10 <sup>3</sup>	C <sub>20</sub> H <sub>32</sub> O <sub>6</sub>	8.21×10 <sup>3</sup>
C <sub>21</sub> H <sub>36</sub> O <sub>4</sub>	1.36×10 <sup>4</sup>	C <sub>16</sub> H <sub>18</sub> O <sub>10</sub>	4.50×10 <sup>3</sup>
C <sub>17</sub> H <sub>30</sub> O <sub>8</sub>	4.68×10 <sup>2</sup>	C <sub>16</sub> H <sub>20</sub> O <sub>10</sub>	5.20×10 <sup>3</sup>
C <sub>12</sub> H <sub>16</sub> O <sub>13</sub>	2.43×10 <sup>3</sup>	C <sub>19</sub> H <sub>24</sub> O <sub>8</sub>	8.21×10 <sup>3</sup>
C <sub>11</sub> H <sub>14</sub> O <sub>14</sub>	4.46×10 <sup>2</sup>	C <sub>20</sub> H <sub>28</sub> O <sub>7</sub>	2.38×10 <sup>3</sup>
C <sub>18</sub> H <sub>30</sub> O <sub>8</sub>	4.46×10 <sup>2</sup>	C <sub>17</sub> H <sub>20</sub> O <sub>10</sub>	4.16×10 <sup>3</sup>
C <sub>16</sub> H <sub>26</sub> O <sub>10</sub>	7.44×10 <sup>2</sup>	C <sub>21</sub> H <sub>36</sub> O <sub>6</sub>	8.03×10 <sup>3</sup>
C <sub>17</sub> H <sub>20</sub> O <sub>10</sub>	2.12×10 <sup>3</sup>	C <sub>16</sub> H <sub>26</sub> O <sub>11</sub>	1.16×10 <sup>3</sup>
C <sub>16</sub> H <sub>24</sub> O <sub>11</sub>	1.48×10 <sup>3</sup>	C <sub>17</sub> H <sub>26</sub> O <sub>11</sub>	1.32×10 <sup>3</sup>
C <sub>20</sub> H <sub>24</sub> O <sub>8</sub>	3.96×10 <sup>3</sup>	C <sub>18</sub> H <sub>18</sub> O <sub>11</sub>	4.02×10 <sup>3</sup>
C <sub>17</sub> H <sub>22</sub> O <sub>11</sub>	2.48×10 <sup>3</sup>	C <sub>18</sub> H <sub>22</sub> O <sub>11</sub>	4.54×10 <sup>3</sup>
C <sub>21</sub> H <sub>34</sub> O <sub>8</sub>	1.28×10 <sup>4</sup>	C <sub>18</sub> H <sub>26</sub> O <sub>11</sub>	1.49×10 <sup>3</sup>
C <sub>13</sub> H <sub>22</sub> O <sub>15</sub>	4.06×10 <sup>2</sup>	C <sub>22</sub> H <sub>28</sub> O <sub>8</sub>	4.62×10 <sup>3</sup>
C <sub>19</sub> H <sub>32</sub> O <sub>10</sub>	5.30×10 <sup>2</sup>	C <sub>15</sub> H <sub>18</sub> O <sub>14</sub>	4.08×10 <sup>3</sup>

C <sub>22</sub> H <sub>32</sub> O <sub>8</sub>	5.90×10 <sup>3</sup>	C <sub>20</sub> H <sub>32</sub> O <sub>10</sub>	5.97×10 <sup>3</sup>
C <sub>20</sub> H <sub>28</sub> O <sub>10</sub>	1.53×10 <sup>3</sup>	C <sub>17</sub> H <sub>22</sub> O <sub>13</sub>	5.10×10 <sup>3</sup>
C <sub>18</sub> H <sub>18</sub> O <sub>13</sub>	4.49×10 <sup>3</sup>	C <sub>21</sub> H <sub>28</sub> O <sub>10</sub>	4.25×10 <sup>3</sup>
C <sub>19</sub> H <sub>24</sub> O <sub>12</sub>	1.49×10 <sup>4</sup>	C <sub>19</sub> H <sub>22</sub> O <sub>12</sub>	5.44×10 <sup>3</sup>
C <sub>19</sub> H <sub>30</sub> O <sub>12</sub>	6.10×10 <sup>2</sup>	C <sub>22</sub> H <sub>34</sub> O <sub>9</sub>	7.52×10 <sup>3</sup>
C <sub>15</sub> H <sub>18</sub> O <sub>16</sub>	1.14×10 <sup>3</sup>	C <sub>21</sub> H <sub>34</sub> O <sub>10</sub>	2.12×10 <sup>3</sup>
C <sub>23</sub> H <sub>38</sub> O <sub>9</sub>	4.34×10 <sup>2</sup>	C <sub>14</sub> H <sub>24</sub> O <sub>16</sub>	4.80×10 <sup>3</sup>
C <sub>32</sub> H <sub>44</sub> O <sub>2</sub>	8.96×10 <sup>2</sup>	C <sub>15</sub> H <sub>22</sub> O <sub>16</sub>	4.04×10 <sup>3</sup>
C <sub>21</sub> H <sub>36</sub> O <sub>11</sub>	3.74×10 <sup>2</sup>	C <sub>17</sub> H <sub>30</sub> O <sub>14</sub>	3.51×10 <sup>3</sup>
C <sub>14</sub> H <sub>26</sub> O <sub>17</sub>	1.00×10 <sup>3</sup>	C <sub>22</sub> H <sub>36</sub> O <sub>10</sub>	4.02×10 <sup>3</sup>
C <sub>20</sub> H <sub>26</sub> O <sub>13</sub>	1.26×10 <sup>4</sup>	C <sub>18</sub> H <sub>24</sub> O <sub>14</sub>	4.44×10 <sup>3</sup>
C <sub>22</sub> H <sub>34</sub> O <sub>11</sub>	1.92×10 <sup>3</sup>	C <sub>19</sub> H <sub>28</sub> O <sub>13</sub>	6.68×10 <sup>3</sup>
C <sub>20</sub> H <sub>30</sub> O <sub>13</sub>	9.36×10 <sup>2</sup>	C <sub>20</sub> H <sub>22</sub> O <sub>13</sub>	3.90×10 <sup>3</sup>
C <sub>18</sub> H <sub>24</sub> O <sub>15</sub>	2.05×10 <sup>3</sup>	C <sub>21</sub> H <sub>26</sub> O <sub>12</sub>	4.48×10 <sup>3</sup>
C <sub>21</sub> H <sub>38</sub> O <sub>12</sub>	9.16×10 <sup>2</sup>	C <sub>22</sub> H <sub>30</sub> O <sub>11</sub>	2.29×10 <sup>3</sup>
C <sub>24</sub> H <sub>38</sub> O <sub>10</sub>	3.78×10 <sup>3</sup>	C <sub>15</sub> H <sub>24</sub> O <sub>17</sub>	4.70×10 <sup>3</sup>
C <sub>16</sub> H <sub>24</sub> O <sub>17</sub>	1.26×10 <sup>3</sup>	C <sub>25</sub> H <sub>38</sub> O <sub>9</sub>	5.24×10 <sup>3</sup>
C <sub>21</sub> H <sub>24</sub> O <sub>14</sub>	4.80×10 <sup>3</sup>	C <sub>17</sub> H <sub>26</sub> O <sub>16</sub>	5.18×10 <sup>3</sup>
C <sub>20</sub> H <sub>34</sub> O <sub>4</sub>	4.98×10 <sup>2</sup>	C <sub>21</sub> H <sub>26</sub> O <sub>13</sub>	4.82×10 <sup>3</sup>
C <sub>18</sub> H <sub>30</sub> O <sub>6</sub>	2.74×10 <sup>3</sup>	C <sub>22</sub> H <sub>30</sub> O <sub>12</sub>	2.47×10 <sup>3</sup>
C <sub>18</sub> H <sub>28</sub> O <sub>7</sub>	1.53×10 <sup>4</sup>	C <sub>16</sub> H <sub>24</sub> O <sub>17</sub>	5.16×10 <sup>3</sup>
		C <sub>17</sub> H <sub>28</sub> O <sub>16</sub>	6.58×10 <sup>3</sup>
		C <sub>29</sub> H <sub>44</sub> O <sub>6</sub>	5.82×10 <sup>3</sup>
		C <sub>17</sub> H <sub>30</sub> O <sub>16</sub>	2.06×10 <sup>3</sup>
		C <sub>22</sub> H <sub>38</sub> O <sub>12</sub>	3.86×10 <sup>3</sup>
		C <sub>16</sub> H <sub>32</sub> O <sub>17</sub>	7.04×10 <sup>3</sup>
		C <sub>23</sub> H <sub>30</sub> O <sub>12</sub>	1.26×10 <sup>3</sup>
		C <sub>24</sub> H <sub>34</sub> O <sub>11</sub>	6.82×10 <sup>3</sup>
		C <sub>20</sub> H <sub>30</sub> O <sub>10</sub>	4.14×10 <sup>3</sup>
		C <sub>20</sub> H <sub>32</sub> O <sub>11</sub>	3.41×10 <sup>3</sup>

6. What is the detection limit of the analytical method i.e. could the observation of the additional dimers (and HOMs) merely be due to higher filter mass loadings in high RH experiments. Excluding dimers and HOMs not found in low RH conditions, very little evidence is presented showing increased dimer and HOM formation at high RH. Also, despite more than 160 dimers found in LC-MS analysis of collected SOA, intensities are only reported for 5 dimers in limonene SOA and 7 dimers in  $\Delta^3$ -carene SOA (table S2 and S5). At least it would be beneficial to report how the intensities of these dimers change as a function of RH (not only high vs low RH). Particularly in Limonene experiments performed at 30, 40, 50 and 60 % RH where the particle number do not seem to changes significantly between experiments

Response: The absolute intensities of most monomers and dimers are relatively high (>10<sup>3</sup>, see Table S3 and S7), which are much higher than the intensities of trimers and

tetramers that can still be detected by the LC-MS (Fig. 2). This indicates that the intensities of these dimers and HOMs are likely much higher than the detection limit.

In the original version of the manuscript, we specifically focused on reporting the products with proposed molecular structures, containing 5 dimers in limonene SOA and 7 dimers in  $\Delta^3$ -carene SOA. In the current version, we have added the molecular formulas of more dimers in Table S6. See our response above.

Due to the uncertainties related to filter collection and processing and the LC-MS itself, off-line analysis under every different RH is highly challenging. Thus, similar to the way applied in most of the previous off-line studies (Zhao et al., 2022; Li et al., 2020), we only collected and analyzed samples under the most extreme different conditions, i.e., the highest and lowest RH.

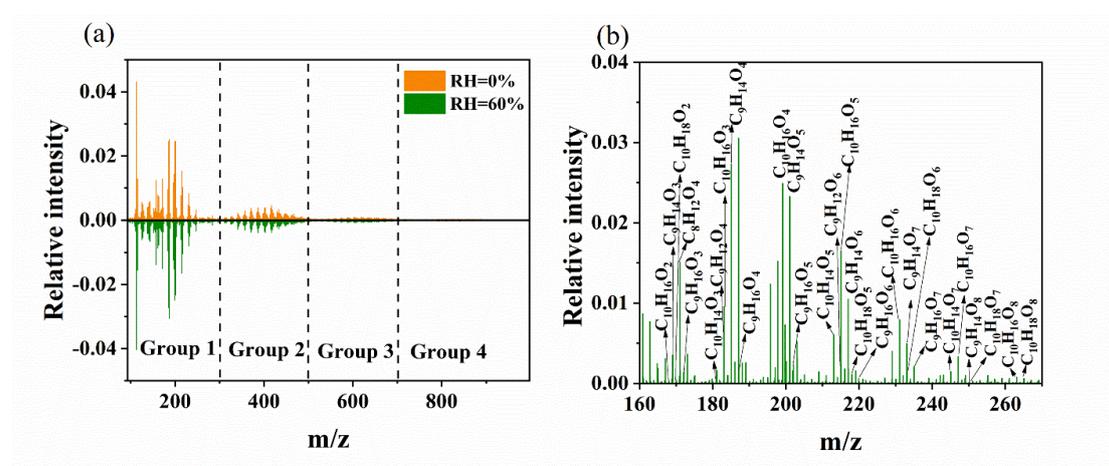
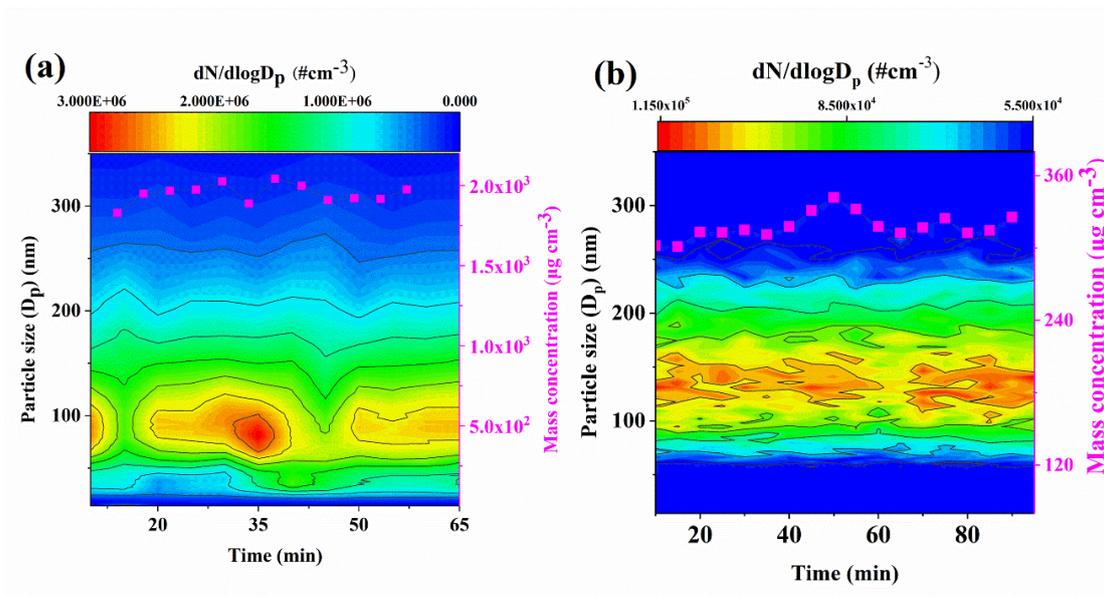


Fig. 2. UPLC/(-) ESI-Q-TOF-MS mass spectra of SOA from limonene ozonolysis. (a) MS under high and low RH conditions; (b) the identification of monomers under high RH condition.

Other comments and suggestions:

7. Please add to Figure S3 time evolution of SOA size and mass concentration from all  $\Delta^3$ -carene/O<sub>3</sub> and limonene/O<sub>3</sub> experiments to validate the stable conditions of the OFR.  
 Response: We have added the time evolution of SOA size and mass concentration from limonene/O<sub>3</sub> experiments in Fig. S3.



**Fig. S3.** Time evolution of SOA size (electromobility diameter) and mass concentration obtained from limonene/ $O_3$  and  $\Delta^3$ -carene/ $O_3$  experiments (Exp. 6 and Exp. 11).

8. Line 103-104: No description of materials are found in S2 (Figure?)

Response: S2 meant “Section S2. Materials” in the Supplement. We have changed “S2” into “Section S2” (Supplement, Page 2)

9. Line 259-260: Note that HOMs are not all considered low-volatile (see Kurtén et al. (2016), entitled “ $\alpha$ -Pinene Autoxidation Products May Not Have Extremely Low Saturation Vapor Pressures Despite High O:C Ratios”)

Response: We agree with the Referee that not all HOMs are considered low-volatile. We have changed this sentence into “Many HOMs have low volatilities (Donahue et al., 2011; Ehn et al., 2014)”

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