

# 1 **Contrasting impacts of humidity on the ozonolysis of** 2 **monoterpenes: insights into the multi-generation** 3 **chemical mechanism**

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8

9 **Abstract.** Secondary organic aerosol (SOA) formed from the ozonolysis of biogenic monoterpenes is a  
10 major source of atmospheric organic aerosol. It has been previously found that relative humidity (RH)  
11 can influence the SOA formation from some monoterpenes, yet most studies only observed the increase  
12 or decrease in SOA yield without further explanations of molecular-level mechanisms. In this study, we  
13 chose two structurally different monoterpenes (limonene with an endocyclic double bond and an  
14 exocyclic double bond,  $\Delta^3$ -carene with only an endocyclic double bond) to investigate the effect of RH  
15 in a set of oxidation flow reactor experiments. We find contrasting impacts of RH on the SOA formation:  
16 limonene SOA yield increases by ~100% as RH increases, while there is a slight decrease in  $\Delta^3$ -carene  
17 SOA yield. Although the complex processes in the particle phase may play a role, we primarily attribute  
18 it to the water-influenced reactions after ozone attack on the exocyclic double bond of limonene, which  
19 leads to the increment of lower volatile organic compounds under high RH condition. However, as  $\Delta^3$ -  
20 carene only has an endocyclic double bond, it cannot undergo such reactions. This hypothesis is further  
21 supported by the SOA yield enhancement of  $\beta$ -caryophyllene, a sesquiterpene that also has an exocyclic  
22 double bond. These results greatly improve our understanding of how water vapor influences the  
23 ozonolysis of biogenic organic compounds and subsequent SOA formation processes.

## 24 **1 Introduction**

25 Secondary organic aerosol (SOA), as an important type of ambient fine particulate matter (PM<sub>2.5</sub>:  
26 aerosols with aerodynamic diameter  $\leq 2.5 \mu\text{m}$ ) (Guo et al., 2014; Huang et al., 2014), has caused a series  
27 of negative impacts on human health (Pye et al., 2021), air quality (Zhang et al., 2016) and global climate  
28 (Levy et al., 2013). SOA produced from the oxidation of biogenic volatile organic compounds (BVOCs)  
29 is a major component of SOA in heavy forest regions during summer (Sindelarova et al., 2014; Ahmadov  
30 et al., 2012), and contributes by a large fraction (~40%-80%) to global OA budget (Cholakian et al.,

31 2019).

32 Monoterpenes, mostly emitted from coniferous trees, account for ~11% in total BVOCs  
33 (Sindelarova et al., 2014; Kanakidou et al., 2005). Limonene is one of the most abundant monoterpenes,  
34 with the annual emission budget of 11.4 Tg yr<sup>-1</sup> (Guenther et al., 2012). Apart from the biogenic source,  
35 limonene can also be released from the indoor emission, mainly from essential oils (Ravichandran et al.,  
36 2018; De Matos et al., 2019; Mot et al., 2022). Limonene has an endocyclic double bond and an exocyclic  
37 double bond, and is thus more reactive than other monoterpenes towards oxidants such as ozone (O<sub>3</sub>),  
38 hydroxyl radical (OH), and nitrate radical (NO<sub>3</sub>) (Chen and Hopke, 2010; Atkinson and Arey, 2003). Δ<sup>3</sup>-  
39 carene is another kind of monoterpene that dominates the monoterpene emission from Scots pine (Bäck  
40 et al., 2012). Different from limonene, Δ<sup>3</sup>-carene contains only one endocyclic double bond, which is  
41 similar to most other monoterpenes.

42 Ozonolysis is an important reaction pathway for limonene and Δ<sup>3</sup>-carene. Although reactions with  
43 OH and NO<sub>3</sub> are faster than that with O<sub>3</sub> for both two monoterpenes (Atkinson, 1991; Khamaganov and  
44 Hites, 2001; Chen et al., 2015; Shaw et al., 2018), the atmospheric concentration of the latter  
45 monoterpene is much higher than that of the former (Sbai and Farida, 2019). The contributions of O<sub>3</sub>-  
46 reactions with limonene and Δ<sup>3</sup>-carene to tropospheric degradation are 47% and 24%, respectively, in  
47 the daytime (Ziemann and Atkinson, 2012). In pristine areas where NO<sub>3</sub> concentration is very low,  
48 ozonolysis is also the dominant fate for limonene and Δ<sup>3</sup>-carene in the nighttime. In addition, it has been  
49 previously found that the ozonolysis of monoterpenes can produce more extremely low volatility  
50 products than OH-initiated oxidation, which contributes by a large fraction to the SOA production  
51 (Jokinen et al., 2015). For either limonene or Δ<sup>3</sup>-carene, the first step for ozonolysis is attacking on the  
52 endocyclic double bond to form two types of stabilized Criegee intermediates (sCI) with low energy (Fig.  
53 S1) (Drozd and Donahue, 2011; Chen et al., 2019). The sCI will then trigger a series of chemical reactions,  
54 like isomerization, decomposition and addition reactions. Correspondingly, the major components in Δ<sup>3</sup>-  
55 carene SOA are caric acid, OH-caronic acid, and caronic acid (Ma et al., 2009; Thomsen et al., 2021),  
56 while the major components from limonene SOA are limonaldehyde, keto-limonon aldehyde, limononic  
57 acid and keto-limononic acid (Pathak et al., 2012; Wang and Wang, 2021).

58 Water is ubiquitous in the atmosphere and can affect the formation mechanism of SOA and its  
59 relevant physical and chemical properties (Sun et al., 2013). A number of field measurements have shown

60 that the average molecular weight of the water/organic phase and activity coefficient of condensed  
61 organics would be changed due to the change of relative humidity (RH) (Seinfeld et al., 2001; Li et al.,  
62 2020). In addition, several laboratory studies have demonstrated that RH can influence the ozonolysis of  
63 monoterpenes in different ways. Most of those studies have reported either an inhibitory effect or a  
64 negligible effect of high RH on the particle formation (Bonn and Moortgat, 2002; Fick et al., 2002; Zhao  
65 et al., 2021; Ye et al., 2018). Nevertheless, few other studies found that high RH can promote SOA  
66 formation from the ozonolysis of limonene (Yu et al., 2011; Gong et al., 2018; Xu et al., 2021), but the  
67 reason of this promotion effect remains unclear.

68 To fully examine the effects of water on SOA formation from the ozonolysis of monoterpenes,  
69 especially the related chemical processes, we used an oxidation flow reactor (OFR) to investigate the  
70 ozonolysis of limonene and  $\Delta^3$ -carene under different RH conditions in this study. An ultra-high  
71 performance liquid chromatography with a quadrupole time-of-flight mass spectrometer (UPLC-Q-TOF-  
72 MS) was deployed to analyze the molecular chemical composition of the SOA, which provided insights  
73 into the physical and chemical processes influenced by the water content. With these state-of-the-art  
74 techniques, we proposed mechanisms that may explain the inhibitory or enhancing RH effects on SOA  
75 formation for different monoterpenes.

## 76 **2 Experimental methods**

### 77 **2.1 Oxidation flow reactor experiments**

78 A series of dark ozonolysis experiments of limonene and  $\Delta^3$ -carene were conducted in a custom-  
79 made oxidation flow reactor (OFR). The OFR is a 602 mm long stainless cylinder with a volume of 2.5  
80 L (Fig. S2) (Liu et al., 2019; Liu et al., 2014). A zero-air generator (XHZ2000B, Xianhe, China) was  
81 used to generate dry clean air as the carrier gas for the OFR. As shown in Fig. S2, there are four gas paths  
82 upstream of the OFR: the first path is the precursor gas channel through which monoterpenes are injected  
83 via a syringe pump (ISPLab 01, Shenchen, China); the second path is for the flow of 300 sccm dry zero  
84 air passing through a mercury lamp ( $\lambda = 185$  nm) to generate  $O_3$ ; the third path is connected to a water  
85 bubbler to generate wet air; the fourth path is the extra dry zero air entering the OFR. The RH in the OFR  
86 was controlled by adjusting the ratio of the wet and dry zero air flows. A water recycle system was  
87 equipped to keep the temperature (T) around at 298 K. The total flow was  $0.9 \text{ L min}^{-1}$ , resulting in an

88 average residence time of 167 s. The RH and T in the OFR were monitored by a T/RH Sensor (HM40,  
 89 VAISALA, Finland). The concentration of ozone and the consumption of the precursor gas were  
 90 measured with an ozone monitor (Model 106L, 2B Technologies, USA) and a gas chromatography with  
 91 flame ionization detector (GC-FID 7890B, Agilent Technologies, USA), respectively. The GC was  
 92 equipped with a DB-624 column (30 m × 0.32 mm, 1.8 μm film thickness) whose temperature was set  
 93 to ramp from 100 °C to 180 °C at a rate of 20 °C min<sup>-1</sup>, and then held at 180 °C for 2 min. Before each  
 94 experiment, O<sub>3</sub> was introduced into the OFR to clean it until the background aerosol mass concentration  
 95 reached < 1 μg m<sup>-3</sup>.

96 The experimental conditions are shown in Table 1. In these OFR experiments, the precursor  
 97 (limonene or Δ<sup>3</sup>-carene) concentration was set to ~320-340 ppb. A high O<sub>3</sub> concentration of ~6 ppm was  
 98 used to realize an equivalent aging time of 0.41 day in the real atmosphere, assuming an average ambient  
 99 O<sub>3</sub> concentration of 28 ppb (Sbai and Farida, 2019) (see Section S1 for the calculation). Under such  
 100 conditions, most of the precursors were consumed, since the residence time was almost five and three  
 101 times of the half-life for limonene and Δ<sup>3</sup>-carene, respectively. Correspondingly, the O<sub>3</sub> consumption for  
 102 limonene and Δ<sup>3</sup>-carene were ~250 ppb and ~100 ppb, respectively. A series of RH conditions ranging  
 103 from dry (1-2%) to 60% with a step of ~10% were used to investigate the effects of water content on  
 104 SOA production and composition (see Table 1). All materials used in the experiments have been  
 105 described in Section S2.

106 **Table 1.** Experimental conditions and results.

Exp.	[Precursor] (ppb)	[O] <sub>3</sub> (ppm)	T (K)	RH (%)	N <sub>(13.8-723.4 nm)<sup>a</sup></sub> (cm <sup>-3</sup> )	M <sub>(13.8-723.4 nm)<sup>b</sup></sub> (μg m <sup>-3</sup> )	D <sub>(mean)<sup>c</sup></sub> (nm)	SOA yield (%)
limonene								
1	321±39	5.7	298	1–2	6.9×10 <sup>5</sup>	980.9	138.2	62.9
2	321±39	6.0	298	10±2	1.3×10 <sup>6</sup>	1377.5	126.8	88.4
3	321±39	5.9	298	20±2	9.0×10 <sup>5</sup>	1573.3	150.9	90.2
4	321±39	5.9	298	30±2	1.4×10 <sup>6</sup>	1573.3	128.9	100.9
5	321±39	6.0	298	40±2	1.7×10 <sup>6</sup>	2051.4	130.7	131.6
6	321±39	5.5	298	50±2	1.5×10 <sup>6</sup>	1962.7	137.8	125.9

7	321±39	5.5	298	60±2	1.5×10 <sup>6</sup>	2211.1	139.0	141.8
$\Delta^3$ -carene								
8	341±28	6.1	298	1–2	9.5×10 <sup>4</sup>	346.0	195.8	19.4
9	341±28	6.4	298	10±2	1.4×10 <sup>5</sup>	300.3	163.4	16.8
10	341±28	6.4	298	20±2	9.4×10 <sup>4</sup>	244.9	176.9	13.7
11	341±28	6.0	298	30±2	5.9×10 <sup>4</sup>	241.2	205.1	13.5
12	341±28	6.3	298	40±2	4.6×10 <sup>4</sup>	205.8	203.2	11.5
13	341±28	6.3	298	50±2	6.8×10 <sup>4</sup>	196.7	180.7	11.0
14	341±28	6.3	298	60±2	5.6×10 <sup>4</sup>	198.5	190.2	11.1

107 <sup>a</sup> N<sub>(14.1-735 nm)</sub> means the total particle number concentration from size 13.8 nm to 723.4 nm. <sup>b</sup> M<sub>(13.8-723.4</sub>  
108 nm) means the total particle mass concentration from size 13.8 nm to 723.4 nm. <sup>c</sup> D<sub>(mean)</sub> means the particle  
109 mean diameter.

## 110 2.2 SOA particle analysis

### 111 2.2.1 SOA yield

112 The SOA particle size distribution was measured with a scanning mobility particle sizer (SMPS),  
113 which consists of a differential mobility analyzer (DMA) (model 3082, TSI Inc., USA) and a  
114 condensation particle counter (CPC) (model 3776, TSI Inc., USA). The samples were measured by SMPS  
115 every 5 minutes with a sampling flow and a sheath flow of 0.3 L min<sup>-1</sup> and 3 L min<sup>-1</sup>, respectively. The  
116 SOA mass concentration was calculated from the volume concentration measured with SMPS and the  
117 aerosol density, which was estimated to be 1.25 cm<sup>-3</sup> for limonene- and 1.09 g cm<sup>-3</sup> for  $\Delta^3$ -carene-SOA  
118 (Thomsen et al., 2021; Watne et al., 2017).

119 The SOA yield (Y) for individual organic gas can be calculated as:

$$120 Y = \frac{\Delta M}{\Delta HC}$$

121 Where  $\Delta M$  is the total mass concentration of SOA,  $\Delta HC$  is the mass concentration of reacted precursor  
122 (Ng et al., 2007; Odum et al., 1996).

### 123 2.2.2 Ultra-high performance liquid chromatography quadrupole time-of-flight mass spectrometry 124 analysis

125 An ultra-high performance liquid chromatography (UPLC, UltiMate 3000, Thermo Scientific)  
126 coupled with a quadrupole time-of-flight mass spectrometry (Q-TOFMS, Bruker Impact HD) was used

127 to analyze the molecular-level chemical composition of SOA. First, the SOA particles were collected on  
128 the PTFE filters (47 mm diameter, 0.22  $\mu\text{m}$  pore size, Jinteng, China). Next, these filters were dissolved  
129 and extracted by 5 mL methanol for two times. Extracts were then filtered through PTFE syringe filters  
130 (0.22  $\mu\text{m}$  pore size), and were concentrated to near dryness by nitrogen-blowing. At last, the samples  
131 were redissolved in a 200  $\mu\text{L}$  solution with 0.1% (v/v) formic acid in 50:50 methanol/ultrapure water  
132 mixture.

133 The parameters of LC-MS were set as follows: capillary voltage 4000 V, nebulizer pressure 0.4 bar,  
134 dry heater temperature 200°C, end plate voltage -500 V, and flow of dry gas 4 L  $\text{min}^{-1}$ . A  $\text{C}_{18}$  column  
135 (100  $\text{\AA}$ , 3 mm particle size, 2.1 mm $\times$ 50 mm, Waters, USA) was used with a column temperature of 35°C.  
136 The mobile phase was 0.1 % formic acid in methanol (A) and 0.1 % formic acid in ultra-high purity  
137 water (B) with a flow of 200  $\mu\text{L min}^{-1}$ . The injection volume was 5  $\mu\text{L}$ . The MS was operated in negative  
138 ion mode, and the detection molecular weight range was from  $m/z$  50 to 1500. The temperature ramp  
139 program was: 0–3min with 0%–3% phase B, 3–25min with 3%–50% phase B, 25–43min with 50%–90%  
140 phase B, 43–48 min with 90%–3% phase B, 48–60min with 3% phase B.

### 141 **3 Results and discussion**

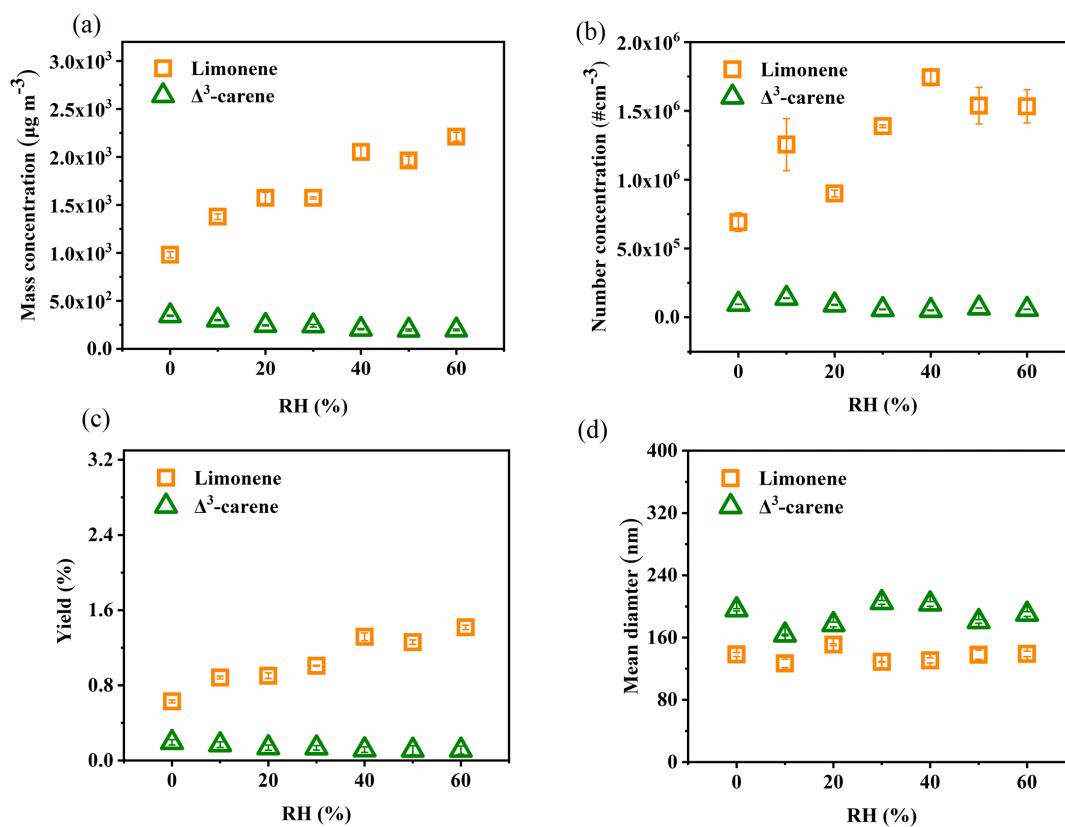
#### 142 **3.1 SOA production under different RH conditions**

143 SOA formation of a representative experiment is shown in Fig. S3. It is found that the formed SOA  
144 are mainly in the size range of 60-200 nm, and the number concentration and mass concentration are  
145 relatively stable during the course of the OFR experiment. SOA formation from limonene and  $\Delta^3$ -carene  
146 in terms of particle number concentration, particle mass concentration, and SOA yield as a function of  
147 RH are illustrated in Fig. 1a-c. We find that all the above-mentioned 3 parameters of limonene-SOA  
148 increase with the increasing RH. The increment of particle mass concentration and SOA yield from the  
149 ozonolysis of limonene is  $\sim$ 100% higher at wet (60% RH) than at dry conditions. In contrast, SOA  
150 formation from  $\Delta^3$ -carene is suppressed by  $\sim$ 40% under high RH. The distinct effects of RH on SOA  
151 formation from the ozonolysis of limonene and  $\Delta^3$ -carene found in this study agree with most previous  
152 studies (Yu et al., 2011; Jonsson et al., 2006b; Bonn et al., 2002; Gong and Chen, 2021; Li et al., 2019b).  
153 As shown in Table 2, Yu et al. (2011) reported a positive correlation between SOA production and RH  
154 for the ozonolysis of limonene in the chamber experiments without OH scavenger. Their experimental

155 condition is similar to that in our study regarding the absence of OH scavenger and, thus, similar results  
156 were observed. However, in the presence of OH scavenger, results are quite different. Jonsson et al. (2006)  
157 observed a similar enhancement effect of high RH on SOA production with 2-butanol as the OH  
158 scavenger, while Bonn et al. (2002) found a negligible or suppressive effect with cyclohexane as the OH  
159 scavenger. It should be noted that the OH scavenger not only has the ability to scavenge OH but also  
160 produces additional products which may influence the reactions of target precursors. For example, there  
161 is no difference between 2-butanol and cyclohexane in the scavenging ability of OH radical, though 2-  
162 butanol will produce more HO<sub>2</sub>· than cyclohexane and, consequently, R· will react with HO<sub>2</sub>· to produce  
163 more hydroxyl acids and hydroxyl per-acid products, most of which have low volatility and, thus high  
164 partitioning into the particle phase. According to previous studies, the influence of different OH  
165 scavengers can vary (Jonsson et al., 2008). This may explain the different findings with and without OH  
166 scavenger for limonene-SOA. With regard to Δ<sup>3</sup>-carene, similar results are found in the absence of OH  
167 scavenger, namely, high RH has negligible or slightly suppressive effect on SOA production (Bonn et al.,  
168 2002; Fick et al., 2002). Same as limonene, the presence of OH scavenger and its different chemical  
169 nature can explain the different results found previously (Jonsson et al., 2006a; Bonn et al., 2002).

170 The enhancement in limonene-SOA production under high RH can be due to several reasons from  
171 either physical or chemical processes. First, the hygroscopic growth of the particles (i.e., absorption of  
172 water content) can lead to higher mass concentration under higher RH, but the enhancement should be  
173 at most ~30% as the growth factor (GF, the ratio of wet and dry diameter:  $D_{\text{wet}}/D_{\text{dry}}$ ) of limonene-SOA is  
174  $\leq 1.1$  (Varutbangkul et al., 2006). However, we do not observe an obvious change in the mean diameter  
175 when comparing dry and wet conditions (Fig. 1d). In addition, hygroscopic growth should also occur for  
176 Δ<sup>3</sup>-carene SOA, but no obvious enhancement in particle mass is observed (Fig. 1a). Therefore, it is  
177 suggested that physical processes regarding hygroscopic growth play a minor role in the enhancement in  
178 limonene-SOA under high RH. As a consequence, we believe that chemical processes are likely the  
179 reason of the enhancement in limonene-SOA under high RH. Water can influence chemical processes in  
180 the gas phase or in the particle phase. Particle-phase reactions can promote the growth of small particles  
181 and, thus, mainly lead to larger particle sizes. As the observed SOA enhancement is mainly from high  
182 number concentration particles rather than the large size particles (Fig. 1b and 1d), it is likely that the  
183 water-participated gas-phase reactions are the most possible reasons for the limonene-SOA enhancement.

184 The reaction mechanism is analyzed below based on the mass spectra information on the SOA.



185

186 **Figure 1.** The effect of RH on the SOA formation: (a) number concentration, (b) mass concentration, (c)

187 SOA yield, (d) mean diameter.

188



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

Precursor	Precursor concentration (ppb)	O <sub>3</sub> concentration (ppb)	Reactor	OH scavenger	T (K)	RH (%)	SOA Mass Concentration ( $\mu\text{g}/\text{m}^3$ )	SOA Yield (%)	M <sup>a</sup>	N <sup>b</sup>	Reference					
1000	1000	1000	flow	cyclohexane	295 $\pm$ 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)					
			reactor		18 $\pm$ 2,	7.0 $\pm$ 0.7;										
320	100 $\pm$ 5	430.9	chamber	N.M. <sup>c</sup>	296 $\pm$ 2	50 $\pm$ 3 and 82 $\pm$ 2	24; 58; 120	17.4 $\pm$ 1.3;	+ <sup>d</sup> (7 times)	+ <sup>d</sup> (8 times)	Yu et al. (2011)					
			flow		298 $\pm$ 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)					
limonene	15 and 30	430.9	reactor	2-butanol	298	10-50	endoicyclic	endoicyclic	endoicyclic	exoicyclic						
							endoicyclic (24.6) and exoicyclic (15.2)	endoicyclic (270) and exoicyclic (12200)	endoicyclic	endoicyclic	exoicyclic (22-51)	exoicyclic (23.8-55.3)	endoicyclic	endoicyclic	N.M. <sup>e</sup>	Gong and Chen (2021)
							endoicyclic	endoicyclic	endoicyclic	exoicyclic						
1085	900 $\pm$ 10	flow	reactor	none	298	3-62	150; 200; 210	N.M.	+ <sup>d</sup>	– <sup>e</sup>	Li et al. (2019)					

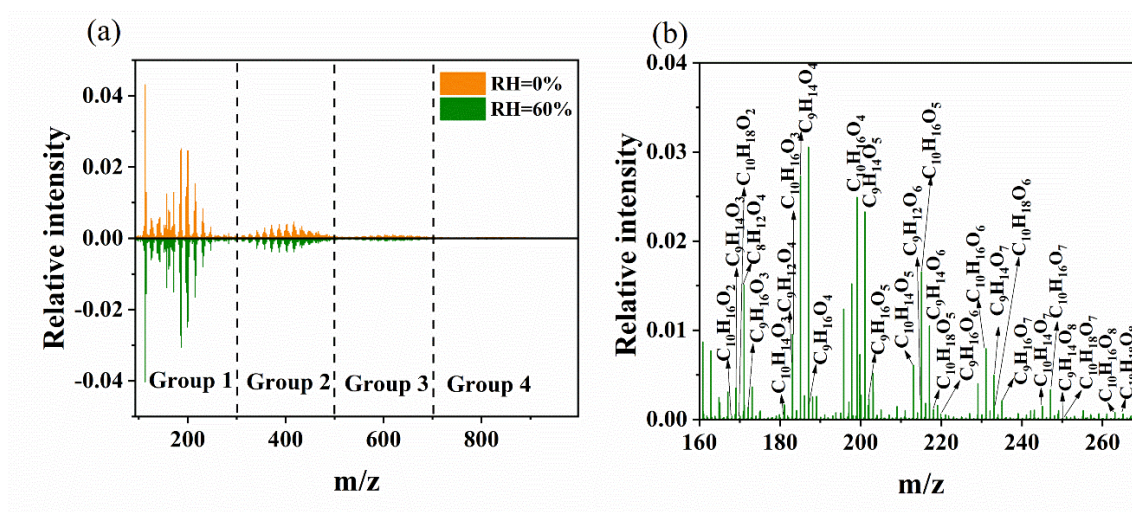
	321±39	5786±203	flow reactor	none	298	0-60	980.9-2211.1	62.9-141.8	+ <sup>d</sup> (2 times)	+ <sup>d</sup> (3 times)	this study
	1000	1000	flow reactor	cyclohexane	295±2	0.02 and 32.5	N.M. <sup>e</sup>	N.M. <sup>e</sup>	no effect	- <sup>e</sup>	Bonn et al. (2002)
	14.2 and 29.4	2300	flow reactor	2-butanol	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>	+ <sup>d</sup>	Jonsson et al. (2006)
Δ <sup>3</sup> -carene	1111	900±10	flow reactor	none	298	3-62	75; 80; 90	N.M	- <sup>e</sup>	- <sup>e</sup>	Li et al. (2019)
	341±28	6257±140	flow reactor	none	298	0-60	346.0-198.5	19.4-11.1	- <sup>e</sup>	no effect	this study

190 <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.

191

192 **3.2 Molecular analysis of SOA particles**

193 The UPLC/ESI-Q-TOF-MS was used to examine the SOA molecular composition under high and  
 194 low RH conditions. As shown in Fig. 2a, the mass spectra of limonene-SOA are divided into four groups:  
 195 monomeric group (<m/z 300), dimeric group (m/z 300-500), trimeric group (m/z 500-700), and  
 196 tetrameric group (m/z 700-1000), corresponding to products containing one, two, three, and four  
 197 oxygenated limonene units, respectively (Bateman et al., 2009). Most of the SOA molecules are  
 198 monomers (>60%) (Fig. 2b) and dimers (~25%), while trimers and tetramers contribute to very small  
 199 fractions (<10% and ~3%) (Table S1). Correspondingly, the distribution of  $\Delta^3$ -carene-SOA can be  
 200 divided into four groups (Fig. S4), comparable to that of limonene-SOA. Most of the SOA molecules are  
 201 monomers (~70%) and dimers (~25%), while trimers and tetramers contribute to smaller proportions (~2%  
 202 and <1%, respectively) (Table S2). Although the SOA mass concentration increases by ~100% under  
 203 high RH condition, the relative intensities of MS peaks do not significantly change with varying RH  
 204 conditions. In other words, we did not observe an obvious change in the overall MS patterns, and the  
 205 fractions of the four groups only slightly differed under different RH conditions, e.g., the fraction of  
 206 monomers was 62% under dry condition and 66% under wet conditions. However, if we take a closer  
 207 look, the intensities and contributions of specific peaks are quite different with varying RH. For example,  
 208 the relative intensity of  $C_{10}H_{16}O_2$ , a possible first-generation product (Gong et al., 2018), decreases by  
 209 ~20% with increasing RH from dry to 60% (Table S3). This is likely due to the multi-generation reactions  
 210 influenced by water vapor concentration, as discussed below with the proposed reaction mechanism of  
 211 limonene ozonolysis.



212

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

215 The proposed reaction mechanism of limonene ozonolysis is shown in Fig. 3 and Fig. 4. The initial  
216 step in the reaction of O<sub>3</sub> with limonene is the attack of the endocyclic double bond to form eCI<sub>1</sub> and  
217 eCI<sub>2</sub> (with branching ratios of 0.35 and 0.65, respectively). In the context of eCI<sub>1</sub>, several complex  
218 reactions occur, with the most dominant reaction being the generation of hydroxyl radicals (OH) and a  
219 reaction pathway known as sCI<sub>1</sub>. The sCI<sub>1</sub> pathway can proceed through three distinct reactions, as  
220 depicted in Fig. 3. The first pathway is the reaction with H<sub>2</sub>O, alcohol or carboxylic acid to form a  
221 carboxylic acid species with hydroxyl, which would subsequently lose a molecule of water to form  
222 limononaldehyde or lose a molecule of hydrogen peroxide to form limononic acid (Grosjean et al., 1992;  
223 Li et al., 2019b). The second and third pathways involve reactions of sCI<sub>1</sub> with carboxylic acids and  
224 carbonyls, respectively, leading to the formation of anhydrides and secondary ozonides. Additionally, the  
225 generated OH radicals can react with limonene, giving rise to another alkyl radical, C<sub>10</sub>H<sub>17</sub>O·. These  
226 alkyl radicals react with O<sub>2</sub> and form peroxy radicals (RO<sub>2</sub>·). The atmospheric fate of produced RO<sub>2</sub>· in  
227 the absence of NO<sub>x</sub> includes the reaction with RO<sub>2</sub>· or HO<sub>2</sub>· (Atkinson and Arey, 2003) and the  
228 unimolecular H shift. The RO<sub>2</sub>·+HO<sub>2</sub>· route mainly form hydroperoxide (ROOH), and the minor fraction  
229 is to form alcohols and carbonyls (Atkinson and Arey, 2003). The products of bimolecular reactions  
230 between RO<sub>2</sub>· and RO<sub>2</sub>· are alcohols, carbonyls, alkoxy radicals, peroxides and ROOR dimers (Hammes  
231 et al., 2019; Peng et al., 2019). The H shift of RO<sub>2</sub>· can form second-generation R· and trigger a main  
232 generation channel of highly oxidized molecules (HOMs), i.e., R· would go through a process of repeated  
233 oxygen addition and hydrogen-atom shift to form HOMs with high O/C ratios of > 0.7–0.8 (Molteni et  
234 al., 2018; Bianchi et al., 2019).

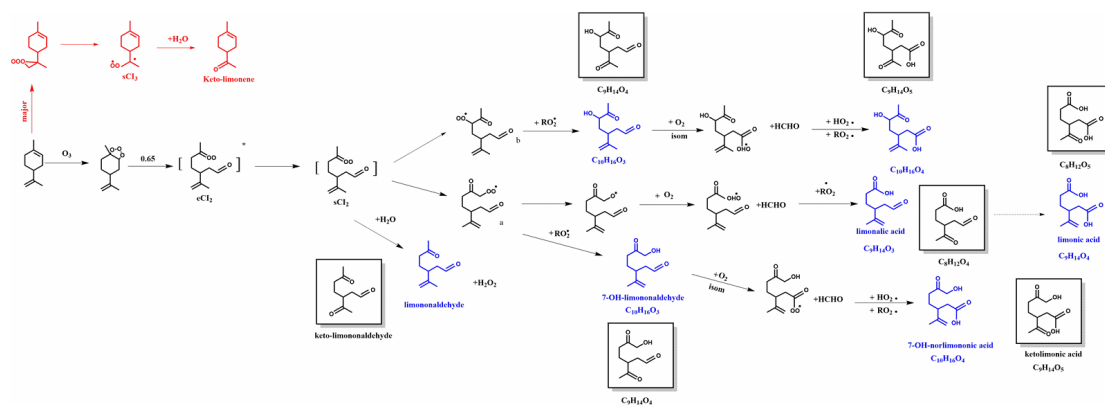
235 In addition to the eCI<sub>1</sub> route, the eCI<sub>2</sub> pathway is also responsible for the generation of various  
236 products (Fig. 4). Since the reaction of the hydroxyl radical (OH) attacking limonene is already depicted  
237 in Fig. 3, our main emphasis in Fig. 4 is on the pathways involved in the generation of SCI. First, sCI<sub>2</sub>  
238 reacts with H<sub>2</sub>O and decomposes to limononaldehyde and H<sub>2</sub>O<sub>2</sub>. Additionally, sCI<sub>2</sub> could experience an  
239 O<sub>2</sub> addition, ·OH loss and isomerization to produce two types of RO<sub>2</sub>·, which can undergo the similar  
240 reactions as the RO<sub>2</sub>· formed from the sCI<sub>1</sub> route, and the major products are also shown in Fig. 4.

241 Since limonene and Δ<sup>3</sup>-carene both have an endocyclic double bond, the similar reactions as

242 mentioned above can occur for the ozonolysis of  $\Delta^3$ -carene (Fig. S5), and most corresponding formula  
243 in Fig. S5 could be identified in Table S4. However, the reactivity of limonene towards  $O_3$  is expected to  
244 be higher owing to its exocyclic double bond. As shown in Fig. 4, the attack of  $O_3$  to the exocyclic double  
245 bond mainly leads to  $sCl_3$  (highlighted in red) with the unpaired electrons outside the ring (Leungsakul  
246 et al., 2005).  $sCl_3$  can react with  $H_2O$  to form a carbonyl called keto-limonene. It should be noted that  
247 this reaction can occur not only for limonene, but also for all the products that retain the exocyclic double  
248 bond. As a result, the compounds that are colored in blue in Fig. 3 and Fig. 4 can undergo further reactions  
249 to generate products with an additional carbonyl (see the boxes in Fig. 3 and Fig. 4). Furthermore, their  
250 molecular formula shown in Table S5 have been identified using the Q-TOF-MS. This mechanism can  
251 well explain the decrease in the relative intensity of  $C_{10}H_{16}O_2$  from high RH to low RH and the increase  
252 in the relative intensity of  $C_9H_{14}O_3$  from low RH to high RH (Table S3).

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





264

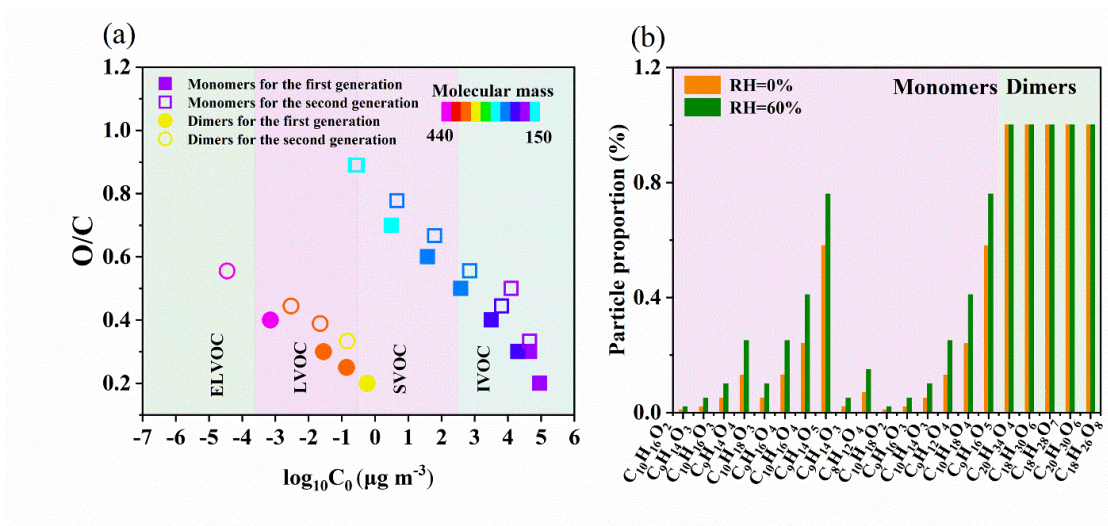
265 **Figure 4.** Proposed formation mechanisms for SOA formation from eCl<sub>2</sub> and exocyclic double bond  
 266 oxidation under high RH. The compounds in blue and in boxes are identified using UPLC/ (-) ESI-Q-  
 267 TOF-MS.

268

269 **3.3 Processes leading to the increase or decrease in SOA formation**

270 Based on the results and mechanisms shown above, we present evidence that high humidity  
 271 enhances limonene-SOA formation. First, the presence of water vapor enhances the formation of  
 272 carbonyls from the reaction of exocyclic double bond, and the oligomerization of these carbonyls  
 273 generates more dimers including hemiacetal (or acetal) formation and aldol condensation (Zhang et al.,  
 274 2022; Kroll et al., 2005; Jang et al., 2003). As shown in Table S6, the intensity of dimers generating from  
 275 multi-carbonyls under high RH is higher than that under low RH, and 54 out of the total 187 dimers were  
 276 exclusively observed for limonene under high humidity conditions, contributing to a corresponding  
 277 intensity of ~19% (Table S7). These dimers can be classified as low-volatile organic compounds (LVOC;  
 278  $3 \times 10^{-4} < C_0 < 0.3 \mu\text{g m}^{-3}$ ) and extremely low-volatile organic compounds (ELVOCs;  $C_0 < 3 \times 10^{-4} \mu\text{g}$   
 279  $\text{m}^{-3}$ ) (Fig. 5a), and thus promote the nucleation and new particle formation in different ways. This finding  
 280 is similar to that from a previous study showing that high RH can promote dimer formation from the  
 281 ozonolysis of  $\alpha$ -pinene (Kristensen et al., 2014). Second, we find that high RH can also promote the  
 282 formation of HOMs, although the mechanism remains unclear. As shown in Table S3, many HOMs  
 283 proposed from the mechanism are detected under high RH condition but not detected under low RH  
 284 condition, including both monomers and dimers. Many HOMs have low volatilities and, thus, can also  
 285 promote new particle formation. Overall, the promoted dimer and HOM formation may greatly enhance  
 286 the new particle number concentration under high RH condition (Fig. 6).



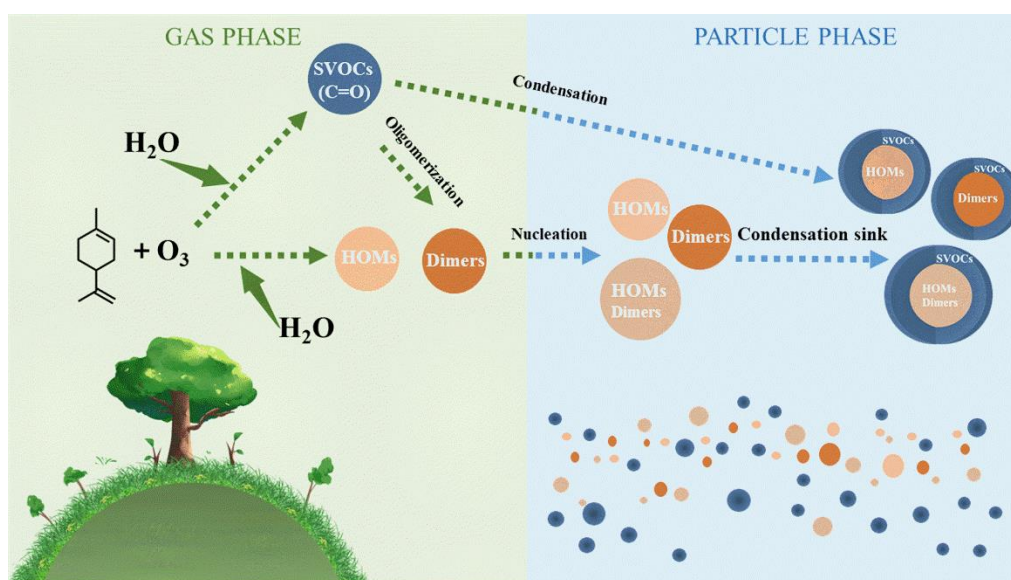


287

288 **Figure 5.** (a) Distribution of the limonene-SOA in the two-dimensional volatility basis set (2D-VBS)

289 space. (b) Partitioning coefficients of limonene monomers and dimers under low and high RH conditions.

290



291

292 **Figure 6.** Schematic diagram of the possible mechanisms for the enhancement of limonene-SOA.

293

294 High particle number concentration generally provides more surface areas for semi-volatile organic  
 295 compounds (SVOCs;  $0.3 < C_0 < 300 \mu\text{g m}^{-3}$ ) to condense on, which results in higher condensation sink  
 296 (CS). In the OFR, the fates of SVOCs include condensing on aerosol, getting lost on the wall, and reacting  
 297 with OH radicals to form functionalization and/or fragmentation products (Palm et al., 2016; Li et al.,  
 298 2019a). The promoted condensation by higher CS leads to a higher fraction of SVOCs getting into the  
 299 particle phase rather than getting lost on the wall or becoming smaller fragments staying in the gas phase,



300 and thus promoting SOA formation (Li et al., 2019a). Furthermore, the transformation from C-C double  
301 bond to carbonyl shown in Fig. 3 and Fig. 4 decreases the volatility of molecules, which can largely  
302 influence the gas-particle partitioning of the monomeric compounds (Fig. 5b). For example, the  $C_0$  values  
303 of  $C_{10}H_{16}O_2$  and  $C_{10}H_{16}O_3$  are 90701 and 19968  $\mu\text{g m}^{-3}$ , corresponding to partitioning coefficients of  
304 0.01 and 0.05, respectively (Fig. 5b and Table S3), with an SOA mass concentration of  $\sim 1000 \mu\text{g m}^{-3}$   
305 under dry condition. When they are converted to carbonyls  $C_9H_{14}O_3$  and  $C_9H_{14}O_4$ , the values of  $C_0$   
306 become 45556 and 6479  $\mu\text{g m}^{-3}$ , corresponding to partitioning coefficients of 0.02 and 0.13, respectively  
307 (Fig. 5b and Table S3), with the same SOA loading. This enhancement in partitioning coefficient can  
308 largely promote the condensation of SVOCs and, thus, enhance the SOA mass concentration. In addition,  
309 the enhanced SOA formation can further influence the equilibrium, e.g., the partitioning coefficient of  
310  $C_{10}H_{16}O_3$  increases from 0.05 to 0.10 when SOA mass concentration increases from  $\sim 1000 \mu\text{g m}^{-3}$  under  
311 dry condition to  $\sim 2000 \mu\text{g m}^{-3}$  under wet condition (Fig. 5b and Table S3). The distribution of saturation  
312 vapor pressure for monomers and dimers identified by MS has also been shown in Fig. 5a. As can be  
313 seen from this figure, around 50% monomers are categorized as SVOCs, thus having the large fraction  
314 in the particle phase when converting from dry to wet conditions. Overall, it is likely that the different  
315 fate and partitioning of SVOCs largely enhance the amount of SVOCs in the particle phase (Fig. 6).

316 Concluding the analysis above, high humidity promotes the SOA formation from the ozonolysis of  
317 limonene in two steps: nucleation of new particles and condensation of SVOCs on them (Fig. 6). While  
318 our study highlights significant changes in gas-phase chemistry, we cannot exclude the possibility of  
319 concurrent reactions occurring in the condensed phase. These two steps are closely related to the multi-  
320 generation reactions of the exocyclic C=C bond, which are unlikely to happen for the ozonolysis of  $\Delta^3$ -  
321 carene. Interestingly, Gong and Chen (2021) have found that high RH can inhibit the SOA formation  
322 from the first-generation oxidation of limonene ozonolysis, but enhance the SOA formation from the  
323 second-generation oxidation (Gong and Chen, 2021), their results agree well with the results and analysis  
324 shown here. In contrast, Li et al. (2019b) found negligible change in dimers and HOMs in limonene- $O_3$   
325 system when changing RH from 0 to 60%. The discrepancy is mainly attributed to the different  
326 experimental conditions. The ozone exposure in this study is  $\sim 18$  times higher than in Li et al. (2019b),  
327 while the limonene concentration in this study is only  $\sim 30\%$  of that in their study. These two conditions  
328 both favor the multi-generation reactions occurred at the exocyclic double bond of limonene and its

329 products. Thus, we believe this leads to the different results regarding the formation of HOMs and dimers.

330 Regarding  $\Delta^3$ -carene, the mechanisms and processes are almost opposite to those of limonene. First,  
331 water vapor reacts with  $s\text{Cl}_1$  or  $s\text{Cl}_2$  to promote the formation of  $\alpha$ -hydroxyalkyl-hydroperoxides (Fig.  
332 S5). Their subsequent products without second ozonolysis of exocyclic double bond have higher  
333 volatility, and may most likely prevail in the gas phase. In addition, it has been found that  $\alpha$ -hydroxyalkyl  
334 hydroperoxides preferentially decompose into aldehydes and  $\text{H}_2\text{O}_2$  (Kumar et al., 2014; Chen et al., 2016),  
335 i.e., 3-caronaldehyde for  $\Delta^3$ -carene, which has higher volatility than the products from other reaction  
336 pathways. Correspondingly, the number and relative intensity of HOMs and dimers detected under high  
337 RH conditions are both lower than those under low RH conditions (Table S8). Furthermore, out of a total  
338 of 178 dimers, 63 dimers were exclusively identified under low RH conditions (Table S7). As a result,  
339 high RH shows an inhibitory effect on the SOA formation from  $\Delta^3$ -carene ozonolysis.

340 To investigate the multi-generation reactions of limonene under low-concentration conditions, we  
341 conducted low-concentration limonene ozonolysis experiments, and the results are shown in Fig. S6. In  
342 these experiments, the limonene and  $\text{O}_3$  concentrations were 20.5 ppb and 5.7 ppm, respectively.  
343 According to the experimental results, the number concentration of SOA formed from limonene  
344 ozonolysis increased by approximately 1.4 times under high RH, which is similar to the increase observed  
345 under high-loading conditions. The mass concentration increased by approximately 1.3 times at a  
346 precursor concentration of 20.5 ppb. The relatively small increase in mass concentration compared to the  
347 high-concentration conditions may be attributed to the less pronounced distribution of SVOCs at low  
348 mass concentrations. This result suggests that the enhancement effect on limonene SOA by high RH is  
349 still valid for low precursor concentrations.

350 To further confirm the assumption that water-influenced multi-generation reactions of the exocyclic  
351 double bond enhance the SOA formation, we conducted two comparative analyses: firstly, we examined  
352 the ozonolysis of the endocyclic double bond in limonene, leaving the exocyclic double bond unreacted.  
353 This was done by applying a low  $\text{O}_3$  concentration ( $\sim 67$  ppb), since the reaction of  $\text{O}_3$  with endocyclic  
354 double bond is  $\sim 30$  times faster than the reaction of  $\text{O}_3$  with exocyclic double bond (Shu and Atkinson,  
355 1994). Interestingly, when limonene was oxidized at only the endocyclic double bond, we observed a  
356 slight decrease in both the number and mass concentrations as the RH increased (Fig. S7). This is similar  
357 to the results obtained for  $\Delta^3$ -carene, which contains only one endocyclic double bond. Secondly, we

358 compared the ozonolysis of structurally similar  $\beta$ -caryophyllene, which has an exocyclic C-C double  
359 bond that can undergo further reactions (Fig. S8). As expected, we observe a large enhancement in SOA  
360 formation under high RH condition (Table S9 and Fig. S9). This implies that monoterpenes,  
361 sesquiterpenes, and other BVOCs with two unsaturation double bonds may follow similar reaction  
362 mechanisms during ozonolysis, and thus have a RH dependency in SOA production.

#### 363 **4 Conclusions**

364 In this study, the effect of humidity on SOA production from the ozonolysis of two monoterpenes  
365 (limonene and  $\Delta^3$ -carene) was investigated with an OFR. Contrasting impacts of RH on the SOA  
366 formation were observed: limonene-SOA yield increases by  $\sim 100\%$  when RH changes from  $\sim 1\%$  to  
367  $\sim 60\%$ , while  $\Delta^3$ -carene-SOA yield slightly decreases. By analyzing the chemical composition of SOA  
368 with ESI-Q-TOF-MS, we find that the multi-generation reactions of the exocyclic C-C double bond are  
369 likely the driving force of the enhancement in limonene-SOA. The presence of water promotes the  
370 formation of carbonyls from the reaction of exocyclic double bond, and further favors the formation of  
371 dimers and HOMs. This leads to promoted new particle formation and subsequent condensation of  
372 SVOCs. These reactions also lower the volatilities of the SVOCs, and further promote the gas-particle  
373 partitioning. Moreover, this hypothesis is supported by a similar behavior of the ozonolysis of  $\beta$ -  
374 caryophyllene (sesquiterpene with an exocyclic double bond) in SOA enhancement under high RH  
375 condition. However, since aerosol dynamics of small clusters and particles are very complex, we do not  
376 rule out a series of reactions that may occur in the particle phase. The results in this study suggest that  
377 multi-generation reactions play an important role in SOA formation from the ozonolysis of BVOCs,  
378 which are significantly influenced by humidity. This impact is largely dependent on the molecular  
379 structure of the SOA precursors (e.g., with or without the exocyclic double bond), thus highlighting the  
380 importance to consider the molecular structure of monoterpenes in modeling and field studies of biogenic  
381 SOA.

382

383 **Data availability.** Experimental data are available upon request to the corresponding authors.

384 **Supplement.** The supplement related to this article is available online.

385 **Author contributions.** LD and SZ designed the experiments and SZ carried them out. SZ performed

386 data analysis with assistance from KL, LD, ZY, and JL. SZ and KL wrote the paper with contributions  
387 from all co-authors.

388 **Declaration.** The authors declare that they have no conflict of interest.

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