

1 **Calibrating adsorptive and reactive losses of monoterpenes and sesquiterpenes in**  
2 **dynamic chambers using deuterated surrogates**

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10 **Abstract**

11 Accurately measuring the emissions of monoterpenes (MTs) and sesquiterpenes (SQTs) using dynamic  
12 chambers requires careful consideration of their adsorptive and reactive losses, which are often overlooked  
13 and difficult to assess in situ. This study evaluated the effectiveness of deuterated surrogates,  $\alpha$ -pinene-d3  
14 and  $\beta$ -caryophyllene-d2, in tracing these losses in a dynamic chamber system. Using standard gas mixtures  
15 of 10 MTs and 10 SQTs, we characterized adsorptive losses across varying concentrations, temperatures, and  
16 humidity levels, as well as reactive losses with ozone. Results indicated that adsorptive losses were  
17 significantly influenced by concentration and temperature, with species-specific variations particularly under  
18 low concentrations and low temperatures, while relative humidity had negligible impact. Reactive losses with  
19 ozone exhibited substantial species-specific variability. Key MTs ( $\alpha$ -pinene,  $\beta$ -pinene, 3-carene, limonene,  
20 and 1,8-cineole) and SQTs ( $\beta$ -caryophyllene and  $\alpha$ -humulene) demonstrated consistent adsorptive and  
21 reactive behavior with their respective deuterated surrogates  $\alpha$ -pinene-d3 and  $\beta$ -caryophyllene-d2, suggesting  
22 that these surrogates are effective for correcting losses in in-situ emission measurements using dynamic  
23 chambers. However, due to varied adsorptive and reactive losses, additional deuterated MTs and SQTs are  
24 recommended, particularly selected according to their O<sub>3</sub> reactivities, to cover a broader range of MTs and  
25 SQTs for loss correction. A strong correlation between adsorptive capacity and ozone reactivity was observed,  
26 underscoring the need to carefully address losses of highly reactive MTs and SQTs during emission  
27 measurements. This study also emphasizes that ozone-free circulating air should be used for accurately  
28 measuring emissions of highly reactive SQTs, such as  $\beta$ -caryophyllene and  $\alpha$ -humulene, especially when loss  
29 correction methods are unavailable.

30

## 31 1 Introduction

32 Monoterpenes (MTs) and sesquiterpenes (SQTs) emitted from terrestrial vegetation account for about 18%  
33 of global biogenic volatile organic compound (BVOC) emissions, with even higher contributions in certain  
34 ecosystems (Guenther et al., 2012). These reactive organic gases can rapidly react with atmospheric oxidants  
35 such as ozone (O<sub>3</sub>), hydroxyl radicals (OH), and nitrate radicals (NO<sub>3</sub>) (Di Carlo et al., 2004; Jardine et al.,  
36 2011; Edwards et al., 2017; He et al., 2021), influencing atmospheric oxidation capacity and leading to the  
37 formation of organic aerosols, which, as significant components of fine particles, can scatter solar radiation  
38 and act as cloud condensation nuclei (Yli-Juuti et al., 2021), directly and indirectly affecting air quality and  
39 climate (Peñuelas and Staudt, 2010; Unger, 2014; Scott et al., 2017).

40 Despite their importance, current BVOC emission models carry large uncertainties, largely due to inaccurate  
41 emission factors (Guenther et al., 2006, 2012). Common BVOC emission measurement techniques, such as  
42 leaf cuvettes and dynamic branch chambers (Niinemets et al., 2011; Šimpraga et al., 2019), are prone to  
43 adsorptive and reactive losses, particularly for the less volatile MTs and SQTs (Ortega et al., 2008). Their  
44 adsorptive losses, which can vary with conditions like temperature and concentration, may lead to significant  
45 underestimation of emission rates (Niinemets et al., 2011; Zeng et al., 2022a). For example, Helmig et al.  
46 (2004) reported that, after a 5-hour equilibrium, only 80% of SQTs and 60% of oxygenated SQTs were  
47 recovered in a leaf cuvette, requiring 5-10 hours to purge to background levels. Additionally, MTs and SQTs  
48 have short atmospheric lifetimes (from minutes to hours) due to their high reactivity with OH and O<sub>3</sub>  
49 (Atkinson and Arey, 2003). Field studies have shown significant in-canopy losses of SQTs (up to 61%) due  
50 to O<sub>3</sub> in the Amazonian rainforest (Jardine et al., 2011). These findings highlight the risk of underestimating  
51 the emissions of reactive terpenes using existing methods, especially in dynamic chambers where adsorptive  
52 and reactive losses remain a challenge (Niinemets et al., 2011).

53 Dynamic chambers, commonly made from chemically inert materials like Teflon or Tedlar, minimize but do  
54 not eliminate these losses (Niinemets et al., 2011; Materic et al., 2015). Previous studies have reported that  
55 adsorptive losses of MTs and SQTs in such chambers can exceed 30%, even with residence times of the  
56 chamber under one minute (Zeng et al., 2022a). Field studies also revealed that adsorptive losses in Tedlar  
57 bags reached 20-30% for MTs and ranged 10-80% for SQTs (Ortega et al., 2008). Temperature plays a critical  
58 role, with more substantial adsorptive losses at lower temperatures (Schaub et al., 2010). The adsorbed  
59 compounds may re-emit at higher temperatures, leading to potential overestimation (Ruuskanen et al., 2005;  
60 Schaub et al., 2010). Meanwhile, the presence of O<sub>3</sub> complicates measurements, as it both influences BVOC  
61 emissions from plants and reacts with MTs and SQTs (Feng et al., 2019; Zeng et al., 2022b). Some studies  
62 have used O<sub>3</sub>-free circulating air to mitigate the reactive losses (Helmig et al., 2007; Ortega et al., 2008;  
63 Hellén et al., 2021), but this may neglect the impact of O<sub>3</sub> on BVOC emissions. In contrast, the use of ambient  
64 air can reflect real-world conditions (Kuhn et al., 2002; Boursoukidis et al., 2012; Zeng et al., 2022b), but  
65 the reactive loss exists~~ed~~. Despite reducing residence time by increasing flow rate of circulating air can lower

66 the reactive losses (Zeng et al., 2022a), it may still not be suitable for highly reactive MTs and SQTs  
67 (Pollmann et al., 2005; Niinemets et al., 2011).

68 Addressing these issues is crucial for improving BVOC emission measurements. While previous laboratory  
69 studies have evaluated adsorptive losses in empty chambers (Kolari et al., 2012; Hohaus et al., 2016; Helin  
70 et al., 2020; Ghirardo et al., 2020; Zeng et al., 2022; He et al., 2024) and proposed correction methods for  
71 simplified chamber systems (Ghirardo et al., 2020; Zeng et al., 2022; He et al., 2024), variations in chamber  
72 design, plant species and environmental conditions introduce additional complexities. To address these  
73 challenges, internal surrogates are recommended for evaluating and correcting such losses in dynamic  
74 chambers (Ortega et al., 2008; Zeng et al., 2022a). While internal surrogates like aromatic compounds have  
75 been used to assess adsorptive losses, their suitability as surrogates for MTs and SQTs remains debated  
76 (Helmig et al., 2007; Ortega et al., 2008). More importantly, the reactivity of these compounds with O<sub>3</sub> in  
77 dynamic chambers has not been thoroughly evaluated (Pollmann et al., 2005; Helin et al., 2020; Zeng et al.,  
78 2022a), and this reactive loss for individual MT and SQT species cannot be assessed by using surrogates like  
79 aromatic compounds ~~that have~~<sup>with</sup> quite different reactivity with O<sub>3</sub>.

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80 This study investigates the potential of using deuterated  $\alpha$ -pinene-d<sub>3</sub> and  $\beta$ -caryophyllene-d<sub>2</sub> to quantify the  
81 adsorptive and reactive losses of individual MTs and SQTs in dynamic chambers, taking advantage of the  
82 almost identical adsorption and reaction behaviors of these deuterated compounds as their counterpart MTs  
83 and SQTs. We evaluated these losses of  $\alpha$ -pinene-d<sub>3</sub> and  $\beta$ -caryophyllene-d<sub>2</sub>, along with target MTs and  
84 SQTs, under varying concentration, temperature, and humidity, and analyzed the gas-phase reactive losses  
85 with O<sub>3</sub> at different concentrations.

## 86 2 Materials and methods

### 87 2.1 Lab evaluation

88 A cylindrical dynamic chamber, which is made of polymethyl methacrylate with inner surface coated with  
89 fluorinated ethylene propylene (FEP) Teflon film (FEP 100, Type 200A, DuPont, Witton, USA), was used  
90 for lab evaluation. It has a diameter of 25 cm and a height of 28 cm, yielding a volume of 13.7 L. Detailed  
91 information about the design and initial characterization of this dynamic chamber was described in our  
92 previous study (Zeng et al., 2022a). Here, we used standard gas mixtures of  $\alpha$ -pinene-d<sub>3</sub>,  $\beta$ -caryophyllene-  
93 d<sub>2</sub>, ten species of MTs, and ten species of SQTs to simulate their emissions from enclosed leaves in the  
94 chamber. Detailed description of the preparation of the standard gas mixtures can be found in Zeng et al.  
95 (2022a), and the information of standards were provided in Table S1. As shown in Fig. S1, when the chamber  
96 reached a steady state offline samples were collected simultaneously from inlet ( $C_i$ ) and outlet ( $C_o$ ) by  
97 commercial adsorbent cartridges (Tenax TA/Carbograph 5TD, Markes International Ltd, Bridgend, UK)  
98 connected onto a portable dual-channel sampler (ZC-QL, Zhejiang Hengda Instrumentation Ltd., Zhejiang,

99 China) at a rate of 200 mL min<sup>-1</sup> for 5 min. Therefore, the recovery was expressed as  $C_1/C_0$  in percentage  
100 (Fig. S1). More detail descriptions of the experiment are provided in Text S1.

101 The effect of concentration on adsorptive losses was evaluated under four concentration levels, with total  
102 mixing ratios of MTs and SQTs of 0.23 and 0.26, 0.37 and 0.47, 0.68 and 0.94, and 2.26 and 3.16 ppb,  
103 respectively. These experiments were conducted in O<sub>3</sub>-free air at a temperature of approximately 25 °C and  
104 a relative humidity of about 50%. The temperature effect was tested at two MTs and SQTs concentration  
105 levels: a low concentration of 0.22 and 0.28 ppb and a high concentration of 2.26 and 3.16 ppb. In these  
106 experiments, the relative humidity was about 50% but varied slightly with temperature, while the circulating  
107 air was O<sub>3</sub>-free. For the low-concentration experiments, the temperature ranged from 15 °C to 40 °C in 5 °C  
108 increments, whereas the high-concentration experiments started at 10 °C and ended at 45 °C, also in 5 °C  
109 increments. Humidity effect was tested under both low and high concentration levels, similar to the  
110 temperature experiments. These humidity experiments were conducted at low (5%), mid (50%), and high  
111 (95%) relative humidity (RH) levels, with a constant temperature of about 25 °C and O<sub>3</sub>-free circulating air.  
112 Additionally, the ozone effect was assessed at six ozone mixing ratios of 0, 30, 45, 60, 100, and 200 ppb,  
113 with temperature of about 25 °C and RH of approximately 50%. For each experimental setting, three  
114 replicates were performed, and the recovery for a single compound is shown as the mean of these replicates,  
115 with error bars representing the standard deviations.

## 116 2.2 Lab analysis

117 Cartridge samples were analyzed by an automatic thermal desorption system (TD-100, Markes International  
118 Ltd, Bridgend, UK) coupled to a mode 7890 gas chromatography (GC) with a model 5975 mass selective  
119 detector (MSD) (Agilent Technologies, Inc., CA, USA). The adsorbent cartridges were thermally desorbed  
120 by the TD-100 at 280 °C for 10 minutes and then the desorbed analytes were transferred by pure helium into  
121 a cryogenic trap (U-T11PGC-2S, Markes International Ltd, Bridgend, UK) at -10 °C. Then the trap was  
122 rapidly heated to transfer the analytes to the GC/MSD system with an HP-5MS capillary column (30 m ×  
123 0.25 mm × 0.25 μm, Agilent Technologies, Inc., CA, USA). The GC oven temperature was programmed to  
124 be initially at 35 °C (held for 3 minutes), increased to 100 °C at 5 °C min<sup>-1</sup> and held for 1 minute, then to  
125 120 °C at 10 °C min<sup>-1</sup> and held for 12 minutes, and then to 260 °C with a final hold time of 2 minutes. The  
126 MSD was operated simultaneously under scan mode and selected ion monitoring mode with electron  
127 impacting ionization at 70 eV. Target compounds were identified by comparing their retention times with  
128 authentic standards (Table S1), and were quantified with the standard calibration curves. More detailed  
129 descriptions of the identification and quantification can ~~refer to be found in~~ our previous studies (Zeng et al.,  
130 2022b; Zeng et al., 2023; Zeng et al., 2024) and in Text S2. Method detection limits (MDLs) were determined  
131 by seven parallel analyses of the lowest concentration of calibration standards. Based on a sample volume of  
132 1 L, the MDLs varied from 8 to 92 ng m<sup>-3</sup> for MTs and from 2 to 92 ng m<sup>-3</sup> for SQTs, and the measurement  
133 precision ranged from 2.3 to 4.8 % for MTs and from 1.1 to 3.4 % for SQTs (Table S2).

## 134 3 Results and discussion

### 135 3.1 Concentration effect

136 The adsorptive behaviors of different MTs and SQTs varied significantly across concentration levels (Fig. 1).  
137 At low concentrations, recoveries ranged from 59% for  $\gamma$ -terpinene to 81% for  $\alpha$ -pinene among MTs and  
138 from 40% for  $\alpha$ -humulene to 71% for longicyclene among SQTs (Fig. 1a). In contrast, under high  
139 concentration levels, recoveries were more consistent, ranging from 75% for  $\beta$ -myrcene to 87% for  $\beta$ -pinene  
140 among MTs and from 74% for  $\beta$ -chamigrene to 84% for  $\alpha$ -longipinene for SQTs (Fig. 1d). Overall, recoveries  
141 were higher at elevated concentrations (Figs. S3 and S4), with average recoveries of  $68\pm 9\%$ ,  $75\pm 7\%$ ,  $78\pm 5\%$ ,  
142 and  $84\pm 2\%$  for all MTs, and  $58\pm 8\%$ ,  $63\pm 5\%$ ,  $71\pm 4\%$ , and  $82\pm 1\%$  for all SQTs across four concentration  
143 levels (Fig. S5).

144 Despite using chemically inert materials in chamber construction, significant adsorptive losses of MTs and  
145 SQTs persist (Ortega et al., 2008; Niinemets et al., 2011; Kolari et al., 2012; Zeng et al., 2022a). Our findings  
146 corroborate previous studies (Ortega et al., 2008; Niinemets et al., 2011), demonstrating that low  
147 concentrations lead to higher relative losses (Fig. 1). In steady-state conditions, the amount of adsorbed MTs  
148 and SQTs is constant, implying that lower concentration results in a greater proportion of total loss (Figs. S3  
149 and S4). This suggests that low-emitting plants, especially for SQTs, may experience substantial adsorptive  
150 losses.

151 We observed species-specific recovery differences at low concentrations (Fig. 1a), likely due to their  
152 physicochemical properties (Niinemets et al., 2004, 2011). Less reactive MTs like  $\alpha$ -pinene-d3,  $\alpha$ -pinene,  $\beta$ -  
153 pinene, and 1,8-cineole exhibited stable recoveries regardless of concentration changes. In contrast, more  
154 reactive MTs, such as  $\beta$ -myrcene,  $\alpha$ -phellandrene,  $\gamma$ -terpinene, and terpinolene, showed significant recovery  
155 variations (Fig. S3). This pattern also applies to SQTs, with highly reactive compounds, like  $\beta$ -caryophyllene,  
156  $\beta$ -caryophyllene-d2, and  $\alpha$ -humulene, being more affected than others (Fig. S4). This compound-specific  
157 adsorptive losses indicate that  $\alpha$ -pinene-d3 and  $\beta$ -caryophyllene-d2 cannot serve as surrogates for all MTs  
158 and SQTs, respectively.

### 159 3.2 Temperature effect

160 Overall recoveries of MTs and SQTs were higher at elevated temperatures, with a smaller absolute effect  
161 observed at high concentrations compared to low concentrations (Figs. 2 and S6). At the high concentration,  
162 mean recoveries increased from  $80\pm 4\%$  to  $91\pm 1\%$  for MTs and from  $73\pm 3\%$  to  $89\pm 3\%$  for SQTs as  
163 temperature rose from 10 to 45 °C (Figs. S7 and S8). At the low concentration, temperature influenced  
164 recoveries more significantly (Fig. 2), with mean values rising from  $70\pm 12\%$  to  $85\pm 4\%$  for MTs and from  
165  $50\pm 21\%$  to  $77\pm 6\%$  for SQTs as temperature increased from 15°C to 40°C. At low concentration and low  
166 temperatures (e.g., 15 °C), the standard deviation of recoveries was greater, such as 12% for MTs and 21%

167 for SQTs, indicating variability among species (Fig. 2). However, at low concentration but high temperatures  
168 (e.g., 40°C), recoveries became more consistent, with reduced standard deviation of 4% for MTs and 6% for  
169 SQTs (Fig. 2).

170 The temperature effect on recovery was compound-specific. Among MTs,  $\beta$ -myrcene,  $\alpha$ -phellandrene,  $\gamma$ -  
171 terpinene, terpinolene, and linalool showed greater sensitivity (Fig. 2a), while  $\beta$ -caryophyllene,  $\beta$ -  
172 caryophyllene-d2, and  $\alpha$ -humulene showed greater sensitivity among SQTs (Fig. 2b). We categorized MTs  
173 and SQTs into two groups based on their adsorptive behaviors (Fig. 3). MTs in group 1 included  $\alpha$ -pinene-  
174 d3,  $\alpha$ -pinene,  $\beta$ -pinene, 3-carene, limonene, and 1,8-cineole, while MTs in group 2 consisted of  $\beta$ -myrcene,  
175  $\alpha$ -phellandrene,  $\gamma$ -terpinene, terpinolene, and linalool. SQTs in group 1 comprised  $\alpha$ -longipinene,  
176 longicyclene,  $\alpha$ -copaene,  $\alpha$ -gurjunene, thujopsene, aromadendrene, alloaromadendrene, and  $\beta$ -chamigrene,  
177 whereas SQTs in group 2 included  $\beta$ -caryophyllene,  $\beta$ -caryophyllene-d2, and  $\alpha$ -humulene. Under the high  
178 concentration, temperature changes minimally affected recoveries, with slopes of  $0.37\pm 0.07\%$  °C<sup>-1</sup> for all  
179 MTs and  $0.43\pm 0.08\%$  °C<sup>-1</sup> for all SQTs (Fig. 3). However, under the low concentration, sensitivity varied  
180 significantly between groups, with slopes of  $0.27\pm 0.06\%$  °C<sup>-1</sup> for MTs and  $0.53\pm 0.05\%$  °C<sup>-1</sup> for SQTs in  
181 group 1 much lower than those  $1.12\pm 0.12\%$  °C<sup>-1</sup> for MTs and  $2.51\pm 0.19\%$  °C<sup>-1</sup> for SQTs in group 2 (Fig. 3).

182 Our results demonstrate that adsorptive losses of MTs and SQTs are influenced by both concentration and  
183 temperature. Elevated temperatures facilitate evaporation and diffusion, reducing adsorptive losses  
184 (Niinemets et al., 2004; Ortega and Helmig, 2008). Field measurements on *Picea pungens* have similarly  
185 shown increased recoveries at high temperatures (Ortega et al., 2008). At low concentrations, the pronounced  
186 sensitivity to temperature results in greater recovery differences among species particularly at lower  
187 temperatures (Fig. 3), indicating that  $\alpha$ -pinene-d3 and  $\beta$ -caryophyllene-d2 may not effectively calibrate  
188 adsorptive losses across all MTs and SQTs. Since the inter-group adsorptive behaviors (e.g., MTs in group 1  
189 vs. in group 2) differ significantly but the intra-group adsorptive behaviors for both MTs and SQTs remain  
190 consistent (Fig. 3), suggesting that  $\alpha$ -pinene-d3 and  $\beta$ -caryophyllene-d2 instead can be used to calibrate the  
191 adsorptive losses for MTs in group 1 ( $\alpha$ -pinene,  $\beta$ -pinene, 3-carene, limonene, and 1,8-cineole) and SQTs in  
192 group 2 ( $\beta$ -caryophyllene and  $\alpha$ -humulene), respectively.

### 193 3.3 Humidity effect

194 The impact of humidity on the adsorptive losses of MTs and SQTs was examined at three RH levels: 5%,  
195 50%, and 95%. Overall recoveries were slightly higher at 95% RH compared to lower RH levels (Fig. 4). For  
196 low-concentration experiments, mean recoveries of MTs and SQTs were  $72\pm 9\%$  and  $64\pm 20\%$  at 5% RH,  
197  $72\pm 10\%$  and  $62\pm 13\%$  at 50% RH, and  $80\pm 6\%$  and  $70\pm 15\%$  at 95% RH, respectively (Fig. 4a), while for  
198 high-concentration experiments, they were  $77\pm 2\%$  and  $76\pm 2\%$  at 5% RH,  $79\pm 5\%$  and  $82\pm 2\%$  at 50% RH,  
199 and  $82\pm 2\%$  and  $82\pm 2\%$  at 95%, respectively (Fig. 4b), with recoveries more consistent across RH levels.

200 The results suggests that humidity has a minor impact on adsorptive loss, aligning with previous findings  
201 (Hohaus et al., 2016; Helin et al., 2020; Zeng et al., 2022a). The relationship between adsorptive losses and  
202 humidity is complex, as water molecules can compete with MTs and SQTs for adsorption sites, potentially  
203 reducing the adsorption of hydrophobic MTs and SQTs (Kolari et al., 2012; Zeng et al., 2022a). These results  
204 indicate that the effect of humidity on the adsorptive loss of MTs and SQTs in dynamic chambers can be  
205 considered negligible during field studies.

### 206 3.4 Ozone effect

207 The impact of O<sub>3</sub> on the reactive loss of MTs and SQTs was evaluated at six mixing ratio levels: 0, 30, 45,  
208 60, 100, and 200 ppb. Recoveries of  $\alpha$ -pinene-d<sub>3</sub>,  $\alpha$ -pinene,  $\beta$ -pinene, 3-carene, and 1,8-cineole remained  
209 stable across O<sub>3</sub> levels. However, recoveries of  $\beta$ -myrcene, limonene, and  $\gamma$ -terpinene declined slightly with  
210 elevated O<sub>3</sub> levels, and more pronounced losses were observed for  $\alpha$ -phellandrene and terpinolene, with  
211 recoveries of 70±3% and 78±2% at an O<sub>3</sub> mixing ratio of 60 ppb, respectively (Fig. S9). For SQTs,  
212 longicyclene,  $\alpha$ -copaene, aromadendrene, and alloaromadendrene exhibited relatively stable recoveries,  
213 while  $\alpha$ -longipinene,  $\alpha$ -gurjunene, thujopsene, and  $\beta$ -chamigrene suffered significant losses (Fig. 5). Notably,  
214 the recoveries of  $\beta$ -caryophyllene,  $\beta$ -caryophyllene-d<sub>2</sub>, and  $\alpha$ -humulene dropped sharply with increasing O<sub>3</sub>  
215 levels, with recoveries as low as 41±3%, 36±6%, and 30±4%, respectively, even at a low O<sub>3</sub> level of 30 ppb  
216 (Fig. 5).

217 Given ozone's role in reactive losses, some studies have used O<sub>3</sub>-free circulating air during field  
218 measurements to mitigate these effects (Ortega et al., 2008; Helmig et al., 2013). However, it is also critical  
219 to understand ozone's role in affecting emissions of MTs and SQTs (Bourtsoukidis et al., 2012; Feng et al.,  
220 2019; Zhang et al., 2022). Since the measured emissions may not reflect real-world emissions if O<sub>3</sub> is cleaned,  
221 some studies have used ambient air as circulating air during field measurements (Kuhn et al., 2002;  
222 Bourtsoukidis et al., 2012; Zeng et al., 2022b). The relationship between reactive loss and O<sub>3</sub> concentration  
223 can be modelled by:

$$224 \quad C_t = C_0 \cdot \exp(-k \cdot t \cdot [\text{O}_3]) \quad (1)$$

225 where  $C_0$  (molecule cm<sup>-3</sup>) and  $C_t$  (molecule cm<sup>-3</sup>) are the initial and time  $t$  concentrations in the chamber,  
226 respectively;  $k$  (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) is the reaction rate constant;  $t$  (s) is the reaction time of the compound in  
227 the chamber; [O<sub>3</sub>] (molecule cm<sup>-3</sup>) represents the concentration of O<sub>3</sub>. In this study, when the  $C_t$  reached to  
228 equilibrium concentration ( $C_s$ ) with a reaction time of the residence time, Eq. 1 can be rewritten as:

$$229 \quad -\ln(C_s/C_0) = k \cdot \frac{V}{F} \cdot [\text{O}_3] \quad (2)$$

230 where  $V$  (L) is the volume of the chamber and  $F$  (L s<sup>-1</sup>) is the flow rate of circulating air. As a result, through  
231 the application of a linear regression between  $-\ln(C_s/C_0)$  and [O<sub>3</sub>], we can derive  $k$  values for MTs and SQTs,



232 as illustrated in Fig. S10. However,  $k$  values for some less reactive MTs and SQTs cannot be obtained this  
233 way and Table 1 presents the  $k$  values of some highly reactive species, while literature-reported  $k$  values are  
234 shown in Table S3. In present study, the  $k$  values of  $\beta$ -myrcene,  $\alpha$ -phellandrene, limonene, and terpinolene  
235 were  $5.93 \pm 0.17$ ,  $28.15 \pm 1.11$ ,  $3.06 \pm 0.14$ , and  $19.21 \pm 1.20$  ( $\times 10^{-16}$ )  $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , respectively, which are  
236 in agreement with those reported in literatures (Table 1). For SQTs, the  $k$  values were  $20.17 \pm 0.98$ ,  $14.56 \pm 0.15$ ,  
237  $115.33 \pm 3.83$ ,  $129.14 \pm 4.42$ ,  $8.64 \pm 0.16$ ,  $147.04 \pm 3.87$ , and  $15.14 \pm 0.16$  ( $\times 10^{-16}$ )  $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  for  $\alpha$ -  
238 longipinene,  $\alpha$ -gurjunene,  $\beta$ -caryophyllene,  $\beta$ -caryophyllene-d2, thujopsene,  $\alpha$ -humulene, and  $\beta$ -chamigrene,  
239 respectively. The  $k$  values for the most important  $\beta$ -caryophyllene and  $\alpha$ -humulene were consistent with those  
240 reported previously (Table 1). The good consistency of  $k$  values with literatures proves that the assessment  
241 of reactive losses with  $\text{O}_3$  in the dynamic chamber used here is reliable.

242 The compound-specific reactive losses due to their varying reactivity with  $\text{O}_3$  (Table 1) necessitates their  
243 consideration during field measurements, particularly for highly reactive species like  $\beta$ -caryophyllene and  
244  $\alpha$ -humulene. Reactive loss caused by  $\text{O}_3$  can be reduced by shortening the residence time through increasing  
245 the flow rate of circulating air. For the chamber in this study, with a flow rate of  $9 \text{ L min}^{-1}$  for circulating air  
246 ( $\sim 1.5$  minutes of residence time), the reactive losses of all tested MTs, except for  $\alpha$ -phellandrene and  
247 terpinolene, were less than 10%, even at a high  $\text{O}_3$  mixing ratio of 100 ppb (Fig. S9). This suggests that the  
248 effect of  $\text{O}_3$  on the reactive losses of main MTs (e.g.,  $\alpha$ -pinene,  $\beta$ -pinene, limonene) can be disregarded during  
249 field measurements. For SQTs, although the reactive losses for longicyclene,  $\alpha$ -copaene, aromadendrene, and  
250 alloaromadendrene were less than 10% at 100 ppb  $\text{O}_3$ , more than 60% of the critical species like  $\beta$ -  
251 caryophyllene and  $\alpha$ -humulene were consumed by  $\text{O}_3$  even at a low mixing ratio of 30 ppb (Fig. 5). As shown  
252 in Fig. S11, to limit the reactive loss of  $\beta$ -caryophyllene within 15%, the flow rate needs to exceed  $42 \text{ L min}^{-1}$   
253 while  $\text{O}_3$  mixing ratio should be kept below 30 ppb. Although the detection of instrument is not a problem  
254 even under this high flow rate (Zeng et al., 2022a), the requirement for an  $\text{O}_3$  mixing ratio below 30 ppb  
255 poses practical challenges, as this level is already lower than those observed in most background regions  
256 worldwide (Lu et al., 2018; Wang et al., 2019). This suggests that using  $\text{O}_3$ -free circulating air may be more  
257 suitable when measuring emissions of highly reactive SQTs in the field, as a short-term  $\text{O}_3$  scavenge during  
258 measurements could have negligible impact on the BVOC emissions as demonstrated by Niinemets et al.  
259 (2011).

### 260 3.5 Implications for field measurements

261 As discussed above and illustrated in Fig. 6, the effects of concentration, temperature, and  $\text{O}_3$  on the losses  
262 of MTs and SQTs are compound-specific. The adsorptive and reactive losses in group 2 are generally greater  
263 than those in group 1, reflecting their different physicochemical properties (Niinemets et al., 2011). Notably,  
264 we observed a positive correlation between adsorptive capacity and  $\text{O}_3$  reactivity (Fig. 7), suggesting that  
265 compounds with higher  $\text{O}_3$  reactivity experience greater temperature- and concentration-driven adsorptive  
266 losses. These findings underscore the importance of accounting for both reactive and adsorptive losses in

267 accurately measuring emissions of highly reactive MTs and SQTs.

268 Furthermore, findings here demonstrate temperature as a crucial factor in influencing the adsorptive losses  
269 of terpenes especially SQTs in dynamic chambers. For instance, assuming leaves with a dry mass of 10 g are  
270 enclosed in the chamber, the lowest concentration evaluated here, equivalent to emission rates of  $0.07 \mu\text{g g}^{-1}$   
271  $\text{h}^{-1}$  for MTs and  $0.12 \mu\text{g g}^{-1} \text{h}^{-1}$  for SQTs, represents a low MT-emitting but high SQT-emitting plant (Duhl et  
272 al., 2008; Ortega et al., 2008). Despite being a low MT emitter, at temperatures below  $30^\circ\text{C}$ , the adsorptive  
273 losses for MTs in group 1 are only about 20%, while those in group 2 exceed 30%. In contrast, adsorptive  
274 losses for SQTs in groups 1 and 2 can be greater than 30% and 45%, respectively, even for a high SQT-  
275 emitting plant. This suggests that in high-latitude regions with relatively cold weather, while adsorptive losses  
276 of some key MTs, such as those in group 1, may be acceptable, losses can be significant for SQTs especially  
277 the most important  $\beta$ -caryophyllene and  $\alpha$ -humulene, thus needing loss corrections during measurements.  
278 Moreover, in tropical and subtropical regions characterized by hot weather, high daytime temperatures and  
279 strong sunlight can cause temperatures in dynamic chambers to exceed  $35^\circ\text{C}$ , even surpassing  $45^\circ\text{C}$  during  
280 heat events (Zeng et al., 2022b; Doughty et al., 2023). Under these conditions, adsorptive losses can be  
281 reduced to within 20% for most MTs and 25% for most SQTs, regardless of changes in concentration and  
282 humidity. This indicates that adsorptive losses of MTs and SQTs may not pose a significant issue for dynamic  
283 chambers used in hot regions; however, the reactive losses of highly reactive compounds must still be  
284 carefully considered to ensure accurate measurement of their emission rates.

285 Although species-specific variabilities in adsorptive and reactive losses existed, we demonstrated that MTs  
286 in group 1, including  $\alpha$ -pinene,  $\beta$ -pinene, 3-carene, limonene, and 1,8-cineole, exhibit consistent adsorptive  
287 behavior with  $\alpha$ -pinene-d3, regardless of changes in concentration, temperature, or humidity, and the reactive  
288 losses of these MTs are minimally affected by ambient-level  $\text{O}_3$ . This consistency makes  $\alpha$ -pinene-d3 a  
289 suitable surrogate. Similarly,  $\beta$ -caryophyllene-d2 aligns well with  $\beta$ -caryophyllene and  $\alpha$ -humulene, and is a  
290 suitable surrogate for these compounds. However, MTs in group 2 and SQTs in group 1 exhibit significant  
291 differences in adsorptive and reactive behaviors compared to  $\alpha$ -pinene-d3 and  $\beta$ -caryophyllene-d2,  
292 respectively, and therefore cannot be calibrated using these two deuterated surrogates. Given the strong  
293 correlation between adsorptive capacity and  $\text{O}_3$  reactivity (Fig. 7), we recommend considering other  
294 deuterated MTs and SQTs that share similar adsorptive and reactive behaviors with those in group 2 and  
295 SQTs in group 1 as internal surrogates for loss correction.

#### 296 **4 Conclusions**

297 In this study, lab evaluations identified significant species-specific variability in the adsorptive and reactive  
298 losses of MTs and SQTs in dynamic chambers, influenced by their distinct physicochemical properties.  
299 Adsorptive losses were notably influenced by concentration and temperature, with pronounced variability at  
300 low concentrations and low temperatures. The reactive losses were also species-specific, with highly reactive

301 compounds like  $\beta$ -caryophyllene and  $\alpha$ -humulene exhibiting significant losses. This emphasizes the  
302 importance of using O<sub>3</sub>-free circulating air during emission measurement to minimize these losses for highly  
303 reactive SQTs.

304 This study supports the use of  $\alpha$ -pinene-d<sub>3</sub> and  $\beta$ -caryophyllene-d<sub>3</sub> as effective surrogates for loss correction.  
305 These surrogates showed consistent adsorptive and reactive behaviors with corresponding target compounds  
306 (e.g.,  $\alpha$ -pinene,  $\beta$ -pinene, 3-carene, limonene, and 1,8-cineole for MTs, and  $\beta$ -caryophyllene and  $\alpha$ -humulene  
307 for SQTs), enabling more accurate calibration of losses during in-situ measurements. Additionally, the  
308 observed correlation between adsorptive capacity and ozone reactivity indicates that other deuterated MTs  
309 and SQTs could be employed to expand coverage for loss correction.

310 Our study demonstrates that adsorptive losses in dynamic chambers are highly temperature dependent. In  
311 tropical and subtropical regions, higher temperatures potentially reduce adsorptive losses of MTs and SQTs  
312 to acceptable levels. Conversely, low temperatures typical of high-latitude regions could lead to significant  
313 adsorptive losses, particularly for SQTs, necessitating careful correction.

314 To ensure accurate emission measurements, it is crucial to account for both adsorptive and reactive losses of  
315 MTs and SQTs, especially those with high reactivity. For highly reactive SQTs like  $\beta$ -caryophyllene and  $\alpha$ -  
316 humulene, O<sub>3</sub>-free circulating air should be used to avoid substantial reactive losses. Furthermore, selecting  
317 internal surrogates that closely match the adsorptive and reactive properties of target compounds is vital for  
318 precise loss correction.

319 It is important to note that, in addition to adsorptive losses on chamber walls, deuterated surrogates may also  
320 be adsorbed on plant surfaces (especially leaf surfaces of broad-leaf species) through passive deposition or  
321 active uptake. The relative contributions of wall and plant surface losses to the adsorptive loss are not always  
322 known, which may limit the applicability of deuterium-labeled compounds for assessing adsorptive losses.  
323 However, a larger wall-to-plant surface area ratio and shorter residence times in the chamber (Zeng et al.,  
324 2022a) would make the surrogate method more applicable.

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#### 325 ***Data availability***

326 All data used in this study are provided in the manuscript and/or the supplement.

327

#### 328 ***Supplement***

329 The supplement related to this article may be available online.

330

331 ***Author contributions***

332 JZ designed and carried out the experiments with the support of XW, YZ, WS, and HG. JZ, HR, WP, and ZM  
333 analyzed the samples in the lab. JQZ analyzed the data and prepared the original manuscript. XMW and YLZ  
334 revised the manuscript.

335

336 ***Competing interests***

337 The authors declare that they have no conflict of interest.

338

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345

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485

486 **Figure captions**

487 Figure 1. Recoveries of MT and SQT species under four different concentration levels. Total MTs and SQTs  
488 mixing ratios are 0.23 and 0.26 ppb (a), 0.37 and 0.47 ppb (b), 0.68 and 0.94 ppb (c), and 2.26 and 3.16 ppb  
489 (d), respectively.

490 Figure 2. Recoveries of different MT (a) and SQT (b) species under different temperatures under the low  
491 concentration level.

492 Figure 3. Variations of recoveries of MTs and SQTs along with temperature under low and high concentration  
493 levels. MTs group 1 includes  $\alpha$ -pinene-d3,  $\alpha$ -pinene,  $\beta$ -pinene, 3-carene, limonene, and 1,8-cineole, while  
494 MTs group 2 includes  $\beta$ -myrcene,  $\alpha$ -phellandrene,  $\gamma$ -terpinene, terpinolene, and linalool.  $\alpha$ -Longipinene,  
495 longicyclene,  $\alpha$ -copaene,  $\alpha$ -gurjunene, thujopsene, aromadendrene, and alloaromadendrene belong to SQTs  
496 group 1, while  $\beta$ -caryophyllene,  $\beta$ -caryophyllene-d2, and  $\alpha$ -humulene belong to SQTs group 2.

497 Figure 4. Recoveries of different MT and SQT species under different relative humidity levels; (a) low  
498 concentration level, (b) high concentration level.

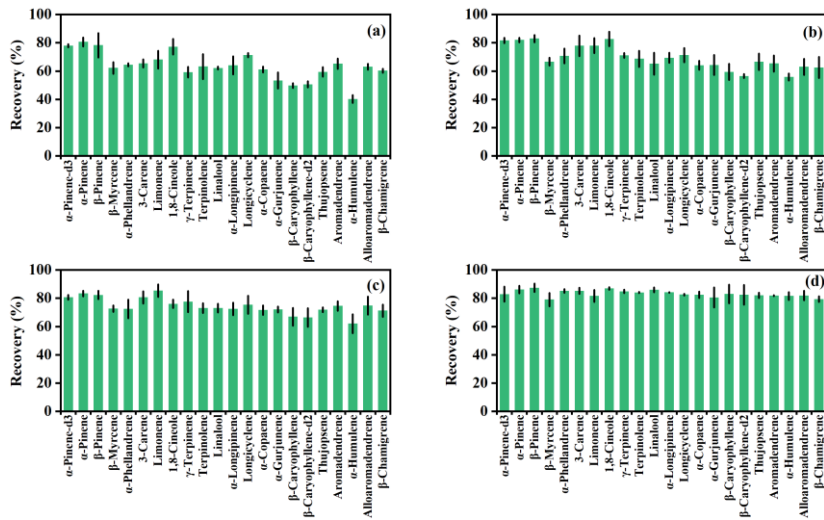
499 Figure 5. Reactive losses of SQT species under different O<sub>3</sub> mixing ratios.

500 Figure 6. The relationships between loss ratio of different MTs and SQTs groups with concentration,  
501 temperature, and ozone mixing ratio.

502 Figure 7. Relationship of ozone reactivity with the effects of concentration (a) and temperature (b); The conc.  
503 effect represents the absolute change of adsorptive loss per ppb (|a|) by fitting the loss ratio and the total  
504 mixing ratios of MTs or SQTs using  $y = a \cdot \ln(x) + b$  as in Fig. 6; The temp. effect represents the absolute change  
505 of adsorptive loss per degree Celsius (|a|) by fitting the loss ratio and the temperature using  $y = a \cdot x + b$  as in  
506 Fig. 6; Each point represents an individual MT or SQT species.

507

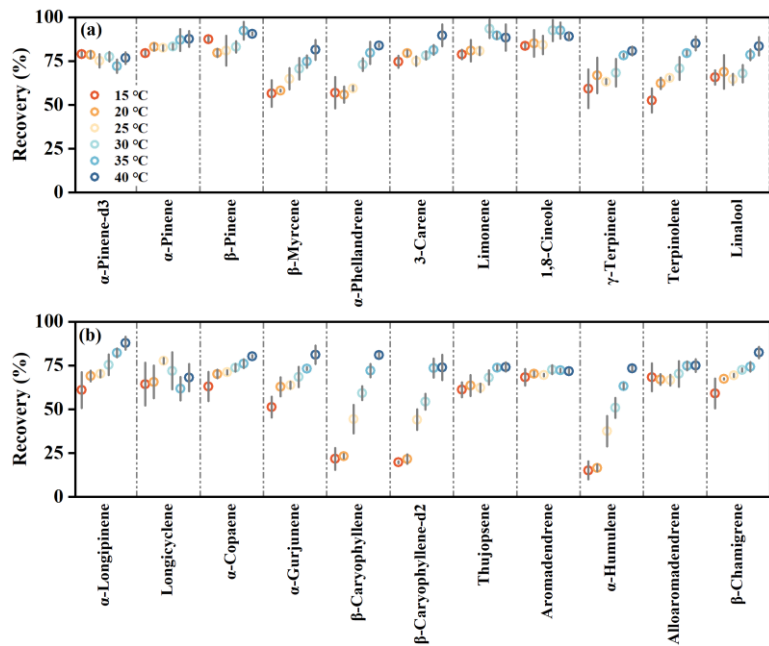




508

509 **Figure 1.** Recoveries of MT and SQT species under four different concentration levels. Total MTs and  
 510 SQTs mixing ratios are 0.23 and 0.26 ppb (a), 0.37 and 0.47 ppb (b), 0.68 and 0.94 ppb (c), and 2.26 and  
 511 3.16 ppb (d), respectively.

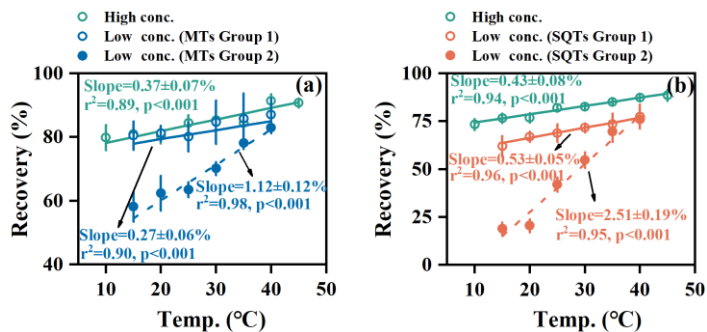
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514 **Figure 2.** Recoveries of different MT (a) and SQT (b) species under different temperatures under the low  
 515 concentration level.

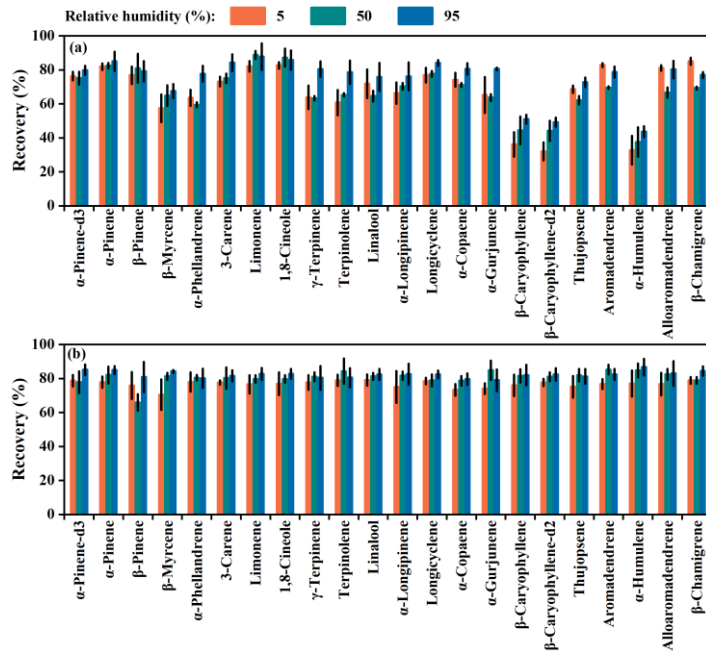
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517

518 **Figure 3.** Variations of recoveries of MTs and SQTs along with temperature under low and high concentration  
 519 levels. MTs group 1 includes  $\alpha$ -pinene-d3,  $\alpha$ -pinene,  $\beta$ -pinene, 3-carene, limonene, and 1,8-cineole, while  
 520 MTs group 2 includes  $\beta$ -myrcene,  $\alpha$ -phellandrene,  $\gamma$ -terpinene, terpinolene, and linalool.  $\alpha$ -Longipinene,  
 521 longicyclene,  $\alpha$ -copaene,  $\alpha$ -gurjunene, thujopsene, aromadendrene, and alloaromadendrene belong to SQTs  
 522 group 1, while  $\beta$ -caryophyllene,  $\beta$ -caryophyllene-d2, and  $\alpha$ -humulene belong to SQTs group 2.

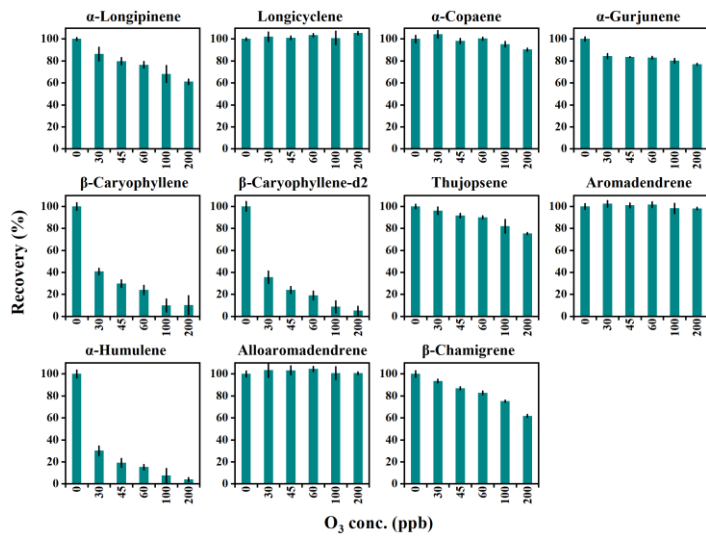
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524

525 **Figure 4.** Recoveries of different MT and SQT species under different relative humidity levels; (a) low  
 526 concentration level, (b) high concentration level.

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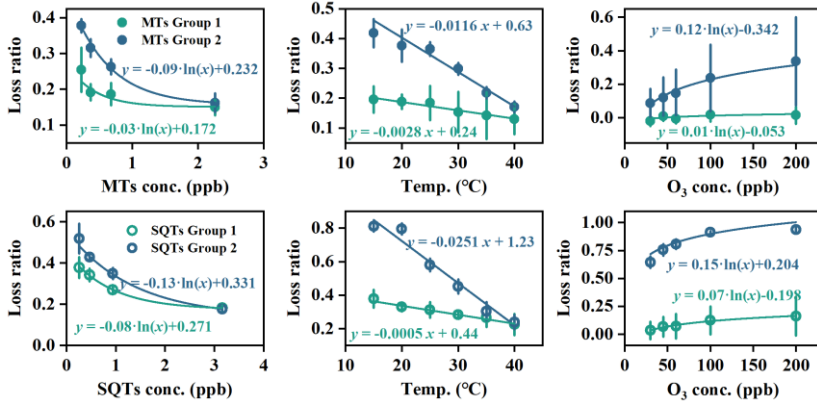


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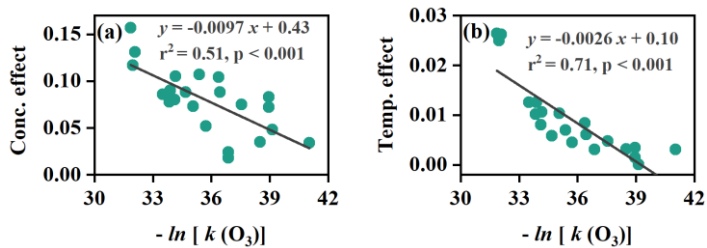
Figure 5. Reactive losses of SQT species under different O<sub>3</sub> mixing ratios.



531

532 **Figure 6.** The relationships between loss ratio of different MTs and SQTs groups with concentration,  
 533 temperature, and ozone mixing ratio.

534



535

536 **Figure 7.** Relationship of ozone reactivity with the effects of concentration (a) and temperature (b); The conc.  
 537 effect represents the absolute change of adsorptive loss per ppb (|a|) by fitting the loss ratio and the total  
 538 mixing ratios of MTs or SQTs using  $y = a \cdot \ln(x) + b$  as in Fig. 6; The temp. effect represents the absolute change  
 539 of adsorptive loss per degree Celsius (|a|) by fitting the loss ratio and the temperature using  $y = a \cdot x + b$  as in  
 540 Fig. 6; Each point represents an individual MT or SQT species.

541

542 **Table 1.** The measured and literature reported rate constants ( $k$ ,  $\times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) of MTs and SQTs  
 543 with ozone.

Species	This study	Atkinson, 1997	Hoffmann et al., 1997	IUPAC* (298K)	Pollmann et al., 2005
$\beta$ -Myrcene	5.93 $\pm$ 0.17	4.70		4.7	
$\alpha$ -Phellandrene	28.15 $\pm$ 1.11	29.8		29	
Limonene	3.06 $\pm$ 0.14	2	2	2.2	
Terpinolene	19.21 $\pm$ 1.20	18.8		16	
$\alpha$ -Longipinene	20.17 $\pm$ 0.98				
$\alpha$ -Gurjunene	14.56 $\pm$ 0.15				
$\beta$ -Caryophyllene	115.33 $\pm$ 3.83	116	116	120	110 $\pm$ 5.1
$\beta$ -Caryophyllene-d2	129.14 $\pm$ 4.42				
Thujopsene	8.64 $\pm$ 0.16				
$\alpha$ -Humulene	147.04 $\pm$ 3.87	117		120	140 $\pm$ 8.8
$\beta$ -Chamigrene	15.14 $\pm$ 0.16				

544 \*IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation (<http://iupac.pole-ether.fr>)