

1 Dear Professor Jason Surratt,

2 We welcome the opportunity to revise and clarify our manuscript for publication in  
3 *Atmospheric Chemistry and Physics*. Below is a point-by-point response to the comments of  
4 reviewers.

## 5 **Anonymous referee #2**

6 I understand the experiments with the oxidation flow reactor (OFR) were conducted well.  
7 However, I am not fully convinced that the results can be applied to the environmentally  
8 relevant conditions. Charan et al. (2022) claimed that the yield of SOA depended strongly on  
9 OH concentration, not OH exposure. The OH exposure (OH concentration multiplied by  
10 exposure duration) and photochemical age can be used interchangeably using an assumption  
11 of a constant OH concentration. OH exposure can be used to determine the degree of  
12 degradation of a parent compound. A low OH concentration for a long exposure time and a  
13 high OH concentration for a short exposure time can achieve the same degree of degradation  
14 of the parent compound. However, that is not for the formation of SOA as Charan et al. (2022)  
15 asserted. The current experiments were conducted with a fixed residence time of 2 minutes  
16 while OH concentrations were varied. Thus, the main independent variable should be OH  
17 concentration, but not OH exposure nor photochemical age.

18 **Re:** As you suggested, the OH concentration has been used as a variable in Figures 1, 3, S5,  
19 S6, S8, S10 and S11 in the revised manuscript and *Supplement*.

20  
21 In addition, the SOA yields from the experiments cannot be used to predict the formation of  
22 SOA for various monitoring sites if the claim of Charan et al. (2022) is accepted. Unless the  
23 authors fully discuss why the results from an OFR study can be applied to the environmental  
24 conditions, all the predictions of SOA formation in the real world are already unreliable.

25 **Re:** We agree that OH concentrations and exposures have different effects on the reaction  
26 systems, leading to different SOA yields. OH concentration determines the cVMS+OH reaction  
27 rate and therefore the instantaneous cVMS SOA yield. In contrast, OH exposure of cVMS  
28 determines the time-integrated, or cumulative, cVMS SOA yield. For any OH concentration, if  
29 a cVMS is exposed to the OH for a short period of time, the cumulative SOA yield over the

30 short exposure time will be small. From this perspective, exposure is a more relevant factor to  
31 atmospheric conditions because SOA yield under such conditions should be an integration of  
32 instantaneous yields over the lifetime of a precursor compound in the atmosphere. Hence, one  
33 can argue that exposure experiments such as ours, simulating exposure in the real atmosphere,  
34 that were conducted using OFR, should be more suitable for application to the ambient  
35 atmosphere.

36 As Charan et al. described, the interchanges between OH concentrations and exposures  
37 have to be considered due to experimental limitations, especially an inability to carry out long-  
38 time (multiple days) experiments (Charan et al., *Atmos. Chem. Phys.*, 2022, 22, 917-928).  
39 When extrapolating the laboratory data to the real atmosphere, it is necessary to consider  
40 atmospherically relevant OH concentrations and exposures. Charan et al. have claimed that D5  
41 SOA yields are strongly dependent on both OH concentrations and exposures (*Atmos. Chem.*  
42 *Phys.*, 2022, 22, 917-928), implying the simultaneous effects of OH concentrations and  
43 reaction time on SOA yields. OH exposures in our work are  $0.05\text{-}1.85 \times 10^{12}$  molecules  $\text{cm}^{-3}$  s,  
44 which is within atmospheric OH exposure range of cVMS when considering half-lives (6-30  
45 days) of cVMS and average OH concentration ( $1.5 \times 10^6$  molecules  $\text{cm}^{-3}$ ) in the atmosphere.  
46 Therefore, these experimental data is used to predict the SOA formation in real environments,  
47 which would provide an estimation for understanding the SOA potential of cVMS. The related  
48 descriptions have been stated in Lines 373-392 in the revised manuscript.

49

50 I also observed that the concentrations of cVMS at the exit of the reactor were not clearly  
51 presented and discussed although they were measured according to the manuscript. The results  
52 would indicate how deep reactions went under different conditions.

53 **Re:** The concentrations of each cVMS at the exit of the reactor have been added in Table S2  
54 (i.e., Table R1) in the revised *Supplement*. The related descriptions have been stated in Lines  
55 140-142 in the revised manuscript.

56

Table R1. The concentration of cVMS at the reactor inlet and outlet.

cVMS	Low-NO <sub>x</sub> experiment (ppb)		High-NO <sub>x</sub> experiment (ppb)	
	unseeded	seeded	unseeded	seeded
[D3] <sub>i</sub>	19.91	20.06	41.20	42.90
[D3] <sub>o</sub>	3.28	3.14	13.03	14.76
[D4] <sub>i</sub>	30.89	29.83	27.05	28.56
[D4] <sub>o</sub>	4.87	4.51	5.95	7.08
[D5] <sub>i</sub>	21.51	28.45	38.50	35.99
[D5] <sub>o</sub>	0	0.12	7.31	7.39
[D6] <sub>i</sub>	24.40	27.08	26.92	28.67
[D6] <sub>o</sub>	1.23	1.16	5.73	6.03

57 Note: ‘i’ and ‘o’ means the reactor inlet and outlet, respectively; the OH exposure is  $1.85 \times 10^{12}$   
 58 and  $1.10 \times 10^{12}$  molecules  $\text{cm}^{-3} \text{ s}$  in low and high-NO<sub>x</sub> experiments, respectively.

59

60 [Another minor additional comment is that the effect of seasons and climate changes on cVMS](#)  
 61 [reaction should be discussed briefly in Introduction although not extensively since OH radical](#)  
 62 [formation is dependent on solar illumination.](#)

63 **Re:** The related discussion has been given in Lines 70-72 in the revised manuscript: “Different  
 64 OH concentrations can partly explain the seasonal variation of cVMS lifetimes that was  
 65 characterized by longer during winter than in summer (Rücker and Kümmerer, 2015)”.

66

### Anonymous referee #3

67 [I thank the authors for their consideration and response to my prior comments. I think that the](#)  
 68 [manuscript is improved; however, I believe it would benefit from further consideration of the](#)  
 69 [points below. Line numbers refer to the track changes version of the manuscript.](#)

70 **Re:** Thank you for your comments.

71

### 72 Main comments

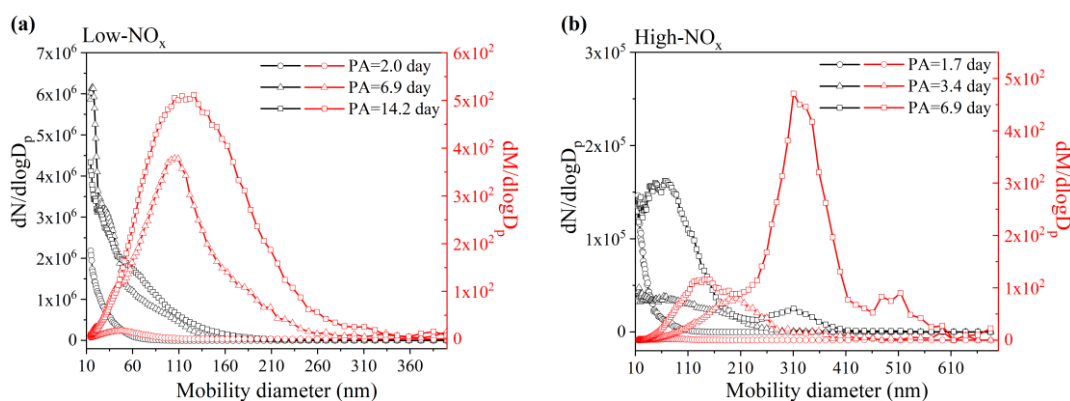
73 1) Thank you for the additional text describing the peroxy radical fate in the high NO<sub>x</sub>

74 conditions. I think that the same consideration should be given to the low NO<sub>x</sub> conditions.  
 75 Based on line 145, it appears that a model was used to determine the RO<sub>2</sub> fate for the high NO<sub>x</sub>  
 76 experiment. Including the general output of that model (for instance, the model estimates over  
 77 x% of RO<sub>2</sub> reacts with HO<sub>2</sub>) for the low-NO<sub>x</sub> simulations would be more convincing to the  
 78 reader than the current statements.

79 **Re:** The reaction ratio of RO<sub>2</sub> with HO<sub>2</sub> was estimated to be larger than 99% under low-NO<sub>x</sub>  
 80 conditions. The related description has been given in Lines 159-161 in the revised manuscript.

81  
 82 2) Lines 177-179 (in reference to the SMPS data in Fig. S2): I don't think this statement is fully  
 83 supported by the information available to me as a reader. For instance, couldn't the distribution  
 84 be different because of different starting conditions? From table S2, low NO<sub>x</sub> unseeded D5  
 85 experiments had 18-26 ppb D5 whereas high-NO<sub>x</sub> had 36-41 ppb D5. The different starting  
 86 concentrations would affect the distributions. With regards to figure S2, please clarify the  
 87 meaning of "normalized" in the axes. It is not readily apparent to me how these values were  
 88 normalized. It is also unclear to me how representative these SMPS distributions are.

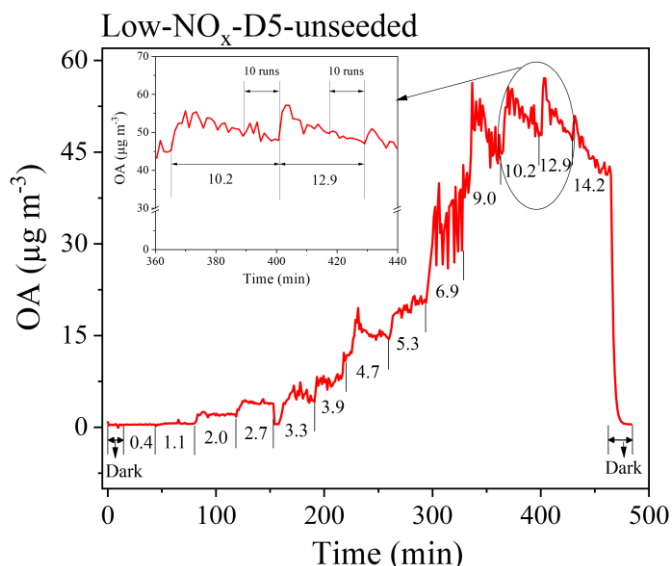
89 **Re:** We have presented three sets of SPMS data at low, medium and high photochemical age  
 90 (PA) in low and high-NO<sub>x</sub> experiments, as shown in Figure S3 (i.e., Figure R1) in the revised  
 91 *Supplement*. The mass mode diameter of SOA for mass size distributions increased with PA  
 92 under low and high-NO<sub>x</sub> conditions. The related descriptions have been modified in Lines 184-  
 93 188 in the revised manuscript. With regards to Figure S3 (i.e., Figure R1), the data was not  
 94 normalized, and the word "normalized" in the Y-axes has been deleted.



95  
 96 Figure R1. Number and mass size distributions of D5 SOA from SMPS under (a) low-NO<sub>x</sub>  
 97 (PA=2.0, 6.9 and 14.2 days) and (b) high-NO<sub>x</sub> (PA=1.7, 3.4 and 6.9 days) conditions.

98 3) Figure S3: I think the data presented in this figure warrants further discussion and a more  
99 transparent consideration of how experimental variability/error influences the results.  
100 Particularly at the higher OH exposures, the OA loading doesn't plateau during an experiment,  
101 meaning that the yields calculated will be extremely dependent upon which data was used in  
102 the calculation. I think some discussion on why the mass loading fails to stabilize under the  
103 high OH conditions and how this impacts the derived quantities and interpretation is essential.  
104 Moreover, there should be variability/error bars reported on the values. This discussion and  
105 error analysis is particularly important given the discussion in the literature about the sensitivity  
106 to this chemical system to high OH exposures (e.g. the Charan paper).

107 **Re:** The AMS results presented in this work were derived from the average values in the last  
108 10 runs (~10 minutes) for each OH exposure, as shown in the inset of Figure S2 (i.e., Figure  
109 R2) in the revised *Supplement*. At high OH exposures, unstable SOA loadings may be mainly  
110 attributed to the fragmentation reactions, leading to the difficulty in the deposition of products  
111 on SOA. The yields were calculated from the average data of SMPS and AMS in the last 10  
112 minutes for each OH exposure. The error bars of the SOA yields have been given in Figure 1  
113 in the revised manuscript, and Figure S5 in the revised *Supplement*. The related descriptions  
114 have been stated in Lines 179-181 and 190-191 in the revised manuscript.



115  
116 Figure R2. The AMS time series of D5 SOA in low-NO<sub>x</sub> experiments under unseeded  
117 conditions. The numbers represent the equivalent photochemical age, and the inset is an  
118 enlarged view at 10.2 and 12.9 PA.

119 4) I am not convinced by the discussion of why the Si/O increases with photochemical age (text  
120 added on lines 288-291). The added text is hand-wavy and doesn't explain why the Si/O would  
121 increase at the lowest photochemical ages where siloxane loss (and thus generation of higher  
122 oxidation products) is low. Furthermore, the Si-O bond is an incredibly strong bond (> 110  
123 kcal/mol). This can be compared to Si-C, C-C, or C-O bonds (all <90 kcal/mol). Bond energies  
124 are from (Rücker and Kümmerer, 2015). What support in the literature is there for this idea of  
125 Si-O bond breaking, particularly at the low OH exposures? I wonder what the role of  
126 fragmentation in the AMS detection and/or uncertainty in peak assignment could be to the  
127 reported Si/O values. Elemental ratios derived from AMS measurements typically require at  
128 least some sort of correction. Given the variability in the MS pattern b/w siloxane precursor (as  
129 mentioned in my minor comment #1 from the initial review and the associated author response),  
130 fragmentation may play a significant role in the observed Si/O. Some further discussion on the  
131 uncertainty associated with the Si/O calculation is warranted.

132 **Re:** At low OH exposure, some oxygen-containing functional groups (-CH<sub>2</sub>OH/-COOH/-OH)  
133 can be formed by the reaction of methyl groups in cVMS with OH, which resulted in a smaller  
134 Si/O ratio compared to that (1.0) in cVMS. With increasing OH exposure, these functional  
135 groups (-CH<sub>2</sub>OH/-COOH/-OH) may dissociate, leading to an increase in the Si/O ratio. The  
136 Si-O bond breaking may mainly happen at high OH exposures, and it may occur after the  
137 cleavage of S-C bonds (69 kcal/mol) (Rücker and Kümmerer, *Chem. Rev.*, 2015, 115, 466-524).  
138 According to the previous study of Wu and Johnston (*Environ. Sci. Technol.*, 2017, 51, 4445-  
139 4451), some ring-opened products were generated from the reaction of D5 with OH radicals,  
140 necessarily requiring the cleavage of Si-O bonds. Thus, the Si-O bonds may be cleaved from  
141 the OH radical attack, which may reduce the number of O atoms, leading to an increase of Si/O  
142 at high PA. More detailed descriptions have been added in Lines 297-308 in the revised  
143 manuscript.

144 The calculation processes of the Si/O and Si/C ratios at each PA are shown as follows:

145 (1) The normalized peak intensity of each C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>Si<sub>n</sub> ion (C<sub>x1</sub>H<sub>y1</sub>O<sub>z1</sub>Si<sub>n1</sub>,  
146 C<sub>x2</sub>H<sub>y2</sub>O<sub>z2</sub>Si<sub>n2</sub> ... C<sub>xi</sub>H<sub>yi</sub>O<sub>zi</sub>Si<sub>ni</sub>) is obtained from HR-ToF-AMS, which is named as A<sub>1</sub>, A<sub>2</sub>...A<sub>i</sub>,  
147 respectively.

148 (2) The fraction of each C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>Si<sub>n</sub> ion (F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub>...F<sub>i</sub>) is calculated by Equation S1,

149 
$$F_i = A_i / \text{MAX} (A_1, A_2, A_3 \dots A_i) \quad (\text{S1})$$

150 (3) The  $\text{C}_x\text{H}_y\text{O}_z\text{Si}_n$  ions with  $F_i \geq 0.01$  are used to calculate the ratio of Si/O and Si/C at each  
151 equivalent day by Equation S2 and S3, respectively.

152 
$$n/z = \text{SUM} (F_i \times n_i/z_i) / \text{SUM} (F_i) \quad (\text{S2})$$

153 
$$n/x = \text{SUM} (F_i \times n_i/x_i) / \text{SUM} (F_i) \quad (\text{S3})$$

154 When assigning molecular formulas to ion fragments, there are many candidates at one m/z.  
155 The final molecular formula was determined based on the possible reaction process of cVMS  
156 and OH radicals. Thus, the assignment of peaks may lead to the uncertainty of the results. The  
157 related descriptions have been stated in Line 288 in the revised manuscript and in Text S1 in  
158 the revised *Supplement*.

159

160 5) I thank the authors for their consideration of my previous comment regarding the back of  
161 the envelope calculations for the cVMS SOA loadings and for the addition of the discussion  
162 regarding the Milani and Pennington papers. However, I feel that my question regarding the  
163 choice of 8.5 days for urban sites was not sufficiently addressed. I agree with the authors that  
164 8.5 days is within the lifetime of siloxanes, however, 8.5 days is longer than an airmass would  
165 remain in an urban area and thus I think these numbers are biased extremely high. The  
166 Pennington et al data quoted in the paper (21 ng/m<sup>3</sup>) is much lower than the urban values  
167 reported in this paper and thus I am unsure of how the conclusion that the Pennington et al  
168 results are within the results reported here (lines 392-394) was reached. In my opinion, using  
169 8.5 days is biasing the results extremely high and this choice needs to be both better justified  
170 and the implications of the choice (including biases) needs to be more transparently addressed  
171 (including the in the abstract).

172 **Re:** We agree that 8.5 days are longer for the residence time of an airmass in an urban area. It  
173 is reasonable that the SOA yields under high-NO<sub>x</sub> and seeded conditions are employed in the  
174 calculation of cVMS SOA concentrations at urban sites. The SOA formation from the reaction  
175 of cVMS with OH would always occur when the airmass is transported from urban areas to  
176 low-NO<sub>x</sub> sites such as rural, forested, and polar regions. As shown in Figure 1 in the revised  
177 manuscript, the SOA yields under high-NO<sub>x</sub> conditions were generally smaller than those at  
178 similar OH exposures under low-NO<sub>x</sub> conditions. To simplify the estimation process, the SOA

179 yields at the maximum equivalent days (i.e., 8.5 days) here were used for the calculation of  
180 SOA generated by cVMS from urban areas. It should be noted that these estimations may have  
181 large deviations, and they can still predict the SOA production from cVMS. The related  
182 descriptions have been stated in Lines 32-34, 368-372 and 389-392 in the revised manuscript.

183 The concentrations of D5 SOA in 14 urban sites have been estimated in our work. D5 SOA  
184 concentrations ranged from 13.4 to 684 ng/m<sup>3</sup>, which covered the D5 SOA concentration (21  
185 ng/m<sup>3</sup>) reported by Pennington et al (*Atmos. Chem. Phys.*, 2021, 21, 18247-18261). Therefore,  
186 it was stated that the model data (21 ng/m<sup>3</sup>) of Pennington et al (*Atmos. Chem. Phys.*, 2021, 21,  
187 18247-18261) was within the results reported here. The related descriptions have been  
188 modified in Lines 433-435 in the revised manuscript.

189

#### 190 **Technical Comments**

191 [Line 70-71: I thank the authors for their addition to the manuscript in response to my earlier](#)  
192 [comment. For the reader not familiar with the siloxane literature though, the addition could be](#)  
193 [difficult to follow. I encourage the authors to consider revising to something perhaps bigger](#)  
194 [picture about how O<sub>3</sub> and NO<sub>3</sub> loss pathways are low, but Cl needs to be evaluated more](#)  
195 [thoroughly due to potential spatial and temporal overlap.](#)

196 **Re:** The loss of cVMS in the atmosphere is negligible through O<sub>3</sub> and NO<sub>3</sub> due to their small  
197 reaction rates (Atkinson, 1991). The global loss by the reaction with Cl atoms is less than 5 %  
198 on account of low Cl concentrations, although it may be higher in some regions where cVMS  
199 emissions and Cl sources overlap in both space and time (Alton and Browne, 2020). The related  
200 descriptions have been modified in Lines 72-76 in the revised manuscript.

201

202 [Line 149: I believe the reference here should be to \(Peng et al., 2018\) for the high NO<sub>x</sub>](#)  
203 [conditions.](#)

204 **Re:** We have checked carefully the reference in Line 156 in the revised manuscript, and it  
205 indeed refers to Peng et al (*Atmos. Chem. Phys.*, 2019, 19, 813-834).

206

207 [Line 246-247: I think this sentence would benefit from more nuance. Not all of the D5](#)  
208 [oxidation products are non-volatile. In fact, the early generation ones are volatile enough that](#)



209 they do not partition to aerosol in any significant way (e.g. Alton and Browne, 2020, 2022)

210 **Re:** The description has been modified into “In fact, most D5 oxidation products have been  
211 shown to be nearly non-volatile”, and these two references above have been cited in Lines 256-  
212 257 in the revised manuscript.

213

214 Lines 316-317: I did not notice this in my initial review, but on this reading it appears to me  
215 that this sentence is implying the formation of organic nitrates rather than inorganic nitrates.  
216 How is the formation of some form of inorganic nitrate ruled out? There are no NH<sub>4</sub><sup>+</sup> peaks in  
217 Fig. S9, but it is unclear if that is because they were not measured, or just not included in the  
218 figure. Are the ratios of NO<sup>+</sup>/NO<sub>2</sub><sup>+</sup> different than an ammonium nitrate standard?

219 **Re:** According to previous studies, the ratio of NO<sub>2</sub><sup>+</sup> (m/z 46) to NO<sup>+</sup> (m/z 30) in the mass  
220 spectra detected by AMS can be used to distinguish organic or inorganic nitrates (Zhao et al.,  
221 *Atmos. Chem. Phys.*, 2018, 18, 1611-1628; Fry et al., *Atmos. Chem. Phys.*, 2018, 18, 11663-  
222 11682; Boyd et al., *Environ. Sci. Technol.* 2017, 51, 7831-7841; Ng et al., *Atmos. Chem. Phys.*,  
223 2007, 7, 5159-5174). Organic nitrates are usually considered to have a NO<sub>2</sub><sup>+</sup>/NO<sup>+</sup> of ~0.1-0.175,  
224 which is typically 2-3 times lower than that for NH<sub>4</sub>NO<sub>3</sub> (0.31-0.85) (Zhao et al., *Atmos. Chem.*  
225 *Phys.*, 2018, 18, 1611-1628; Fry et al., *Atmos. Chem. Phys.*, 2018, 18, 11663-11682; Fry et al.,  
226 *Atmos. Chem. Phys.*, 2009, 9, 1431-1449; Boyd et al., *Environ. Sci. Technol.* 2017, 51, 7831-  
227 7841; Fry et al., *Atmos. Chem. Phys.*, 2013, 13, 8585-8605). In our study, taking D3-D6 SOA  
228 at PA of 6.9 d in high-NO<sub>x</sub> experiments as examples, NO<sub>2</sub><sup>+</sup>/NO<sup>+</sup> ranged from 0.015 to 0.66,  
229 indicating that both inorganic and organic nitrates may be generated in high-NO<sub>x</sub> experiments.  
230 The related description has been modified in Line 336 in the revised manuscript. There are no  
231 NH<sub>4</sub><sup>+</sup> peaks in Figure. S9, because they were not measured.

232

233 Table S4: Are the mass concentrations based on SMPS + density or AMS. Granted, they should  
234 agree, but I think it should be specified. Given the results in Fig. S3 showing the variability  
235 within an experiment, some indication of variability in these mass concentrations should be  
236 included.

237 **Re:** The mass concentrations of D5 SOA in Table S4 were obtained on the basis of SMPS and  
238 effective aerosol density. In addition, the mass concentrations of cVMS SOA are the average

239 data of SMPS in the last 10 minutes for each OH exposure. The related description has been  
240 specified in the title of Table S4 in the revised *Supplement*.

241

## 242 **References**

243 Alton, M. W. and Browne, E. C.: Atmospheric Chemistry of Volatile Methyl Siloxanes:  
244 Kinetics and Products of Oxidation by OH Radicals and Cl Atoms, *Environ. Sci. Technol.*, 54,  
245 5992–5999, <https://doi.org/10.1021/acs.est.0c01368>, 2020.

246 Alton, M. W. and Browne, E. C.: Atmospheric Degradation of Cyclic Volatile Methyl Siloxanes:  
247 Radical Chemistry and Oxidation Products, *ACS Environ. Au*,  
248 <https://doi.org/10.1021/acsenvironau.1c00043>, 2022.

249 Peng, Z., Palm, B. B., Day, D. A., Talukdar, R. K., Hu, W., Lambe, A. T., Brune, W. H., and  
250 Jimenez, J. L.: Model Evaluation of New Techniques for Maintaining High-NO Conditions in  
251 Oxidation Flow Reactors for the Study of OH-Initiated Atmospheric Chemistry, *ACS Earth*  
252 *Space Chem.*, 2, 72–86, <https://doi.org/10.1021/acsearthspacechem.7b00070>, 2018.

253 Rucker, C. and Kummerer, K.: Environmental Chemistry of Organosiloxanes, *Chem. Rev.*, 115,  
254 466–524, <https://doi.org/10.1021/cr500319v>, 2015.

255 **Re:** We thank the reviewer for providing these literatures. We have read them carefully and  
256 some of them have been cited and discussed properly in the revised manuscript.

257

258 Sincerely yours,

259

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