Dear Professor Jason Surratt,

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

acp-2021-965-RC1

This manuscript prepared by Han et al. describes an investigation of secondary organic aerosol (SOA) arising from cyclic volatile methyl siloxanes (cVMs). The SOA yield under a variety of atmospheric conditions was investigated using an oxidative flow tube reactor (OFR). The authors provided detailed discussions on the effect of NO_x concentration, presence of seed, and oxidation lifetime. Chemical composition of the resulting SOA was monitored with an aerosol mass spectrometer (AMS). Further, the authors applied the obtained yield in a model to estimate the contribution of cVMS SOA on the global scale. The scope of the study matches that of ACP. The discussion and conclusions of the paper were fully justified, and the literary quality of the manuscript is outstanding. I highly recommend publication in ACP. My comments below can be considered only technical.

Re: We thank you for the positive comments.

One thing that I feel is missing from the current manuscript is a brief discussion on the mechanism of OH reaction with cVMS. This shouldn't take more than a few sentences or a short paragraph. In addition to H-abstraction on the $-CH_3$ groups, does OH undergo any reaction unique to e.g., O-Si bonds? Pieces of mechanistic information are provided in line 265 - 268, but it is hard for the readers to gauge whether that is generic OH chemistry or something unique to cVMS.

Re: The initial step of OH radicals oxidation can be considered as OH abstracting a H atom from the methyl groups on the -Si-O- ring of cVMS to form Si-containing radicals, which may generate OH and CH_2OH substitution products, such as silanol and silyl methanol (Wu and Johnston, *J. Am. Soc. Mass Spectrom.*, 2016, 27, 402-409; Alton and Browne, *Environ. Sci. Technol.*, 2020, 54, 5992-5999). Such Si-containing products may partition into SOA and result in an appearance of $C_xH_yO_zSi_n$ ions in the AMS mass spectra, thereby decreasing the ratio of Si/O (D5: 0.53; D6: 0.72) at initial stage. Notably, one previous study reported that one of oxidation products of D5, 1-hydroxynonamethylcyclopentasiloxane (D_4TOH), has been detected in ambient particulates (Milani et al., *Atmos. Environ.*, 2021, 246, 118078). As the reaction progressed, the Si-O bonds may be cleaved from OH radical attack, which may reduce the number of O atoms, leading to an increase of Si/O with PA. To clearly explain the reaction mechanism of OH with cVMS, the related description has been revised in Lines 281-289 in the revised manuscript.

Figure S6b - It is a little counterintuitive that the Si/O ratio continued to rise during photooxidation. The number of Si in cVMS is fixed, while the molecule should be continuously oxidized. So Si/O should be decreasing as oxidation proceeds? The authors' discussion from line 259 to 270 did not really explain why Si/O was rising continuously.

Re: The generation of OH and CH_2OH substitution products, such as silanol and silyl methanol, may partition into SOA and result in an appearance of $C_xH_yO_zSi_n$ ions in the AMS mass spectra, thereby decreasing the ratio of Si/O (D5: 0.53; D6: 0.72) at initial stage (Wu and Johnston, *J. Am. Soc. Mass Spectrom.*, 2016, 27, 402-409; Alton and Browne, *Environ. Sci. Technol.*, 2020, 54, 5992-5999). As the reaction progressed, the Si-O bonds may be cleaved from OH radical attack, which may reduce the number of O atoms, leading to an increase of Si/O with PA. The related explanation has been given in Lines 283-289 in the revised manuscript.

Line 151 - the acronym, PTR-ToF-MS is already introduced previously.

Re: The acronym of PTR-ToF-MS has been used in Line 156 in the revised manuscript.

acp-2021-965-RC2

Major Comment

The study was conducted to measure the formation of secondary organic aerosols (SOAs) during OH oxidation of cyclic volatile methylsiloxanes (cVMS) in an oxidation flow reactor (OFR). While the measured data of SOA formation was consistent with other published results obtained similar OFRs, the authors assumed that the results of OFRs would be used to determine the SOA formation in the real atmosphere. However, the assumption was proved incorrect by an earlier study by Charan et al. (2021). Their work was cited in Introduction of the current manuscript, but the main result of the paper was completely ignored (not mentioned/discussed). Charan et al. (2021) supported that the yield of SOA depended strongly on OH concentration and organic aerosol mass concentration (related to initial D5 concentration) among several experimental parameters (e.g., OH concentration, OH exposure, aerosol seed, NOx, initial D5 concentration, reactor type). They also claimed that the formation of secondary aerosols is fairly small (<5% or more likely <1%) under environmentally relevant conditions (i.e., low OH and VMS concentrations). Thus, a large chamber might be a good option (rather than OFRs) to maintain environmental-relevant conditions and a low surface-to-volume ratio. Note that all the SOA yields from OFRs were high and in contrast with those from chamber reactors. However, the current manuscript (by Han et al.) did not discussed any of these important findings. They asserted SOA yield was dependent on OH exposure and applied the OFR results for the real atmosphere. Therefore, without providing a strong result against the conclusions of Charan et al. (2021), the current manuscript was built on an incorrect assumption. Accordingly, the estimated SOA production rate is not reliable.

Re: We welcome the opportunity to clarify our paper in this discussion, and respectfully disagree with the comment that "the estimated SOA production rate is not reliable". This comment concerns the suitability of OFR versus chamber for investigating the yields from cVMS oxidation. This is indeed a generally important discussion topic in the community, and the differences between OFRs versus chambers have been the subject of numerous investigations prior to our paper, with varied conclusions with no clear bias towards the relative merits of either approach. But one clear advantage of OFRs is their ability to simulate long OH exposures. We are of the opinion that chamber studies generally have difficulties sustaining long OH exposure times, and as such OFRs are more suitable to address such conditions especially when a compound has relatively long-life time in the atmosphere. In the case of cVMS, low OH exposure versus relatively short period of reaction times, such as in the chamber, may indeed result in a relatively low aerosol yield. However, given the relatively long cVMS life times in the atmosphere and the continued reaction beyond the chamber reaction times, one expects continued aerosol production still proceeding that will result in increased accumulative aerosol yield compared to chamber studies. Such a condition can be experimentally simulated using OFRs but with difficulties using chambers.

This consideration notwithstanding, it should be noted that the ***published version*** of the Charan et al. paper (Charan et al., *Atmos. Chem. Phys*., 2022, 22, 917-928) indicated that at similar OH concentrations and OH exposures, the D5 SOA yields in the Caltech Photooxidation Flow Tube (CPOT) and chamber experiments were consistent. There were previous reports for investigating the differences between chambers and flow reactors. For example, Lambe et al. (*Atmos. Chem. Phys*., 2015, 15, 3063-3075) found small differences between chambers and flow reactors for many systems. Peng et al. (*Atmos. Chem. Phys*., 2019, 19, 813-834) studied these two types of reactors using models, and provided operational recommendations for evaluating the atmospheric relevance of RO_2 chemistry. Our previous study (Li et al., *Atmos. Chem. Phys*., 2019, 19, 9715-9731) made a comparison of SOA yields obtained in ECCC-OFR and other traditional chambers under similar OH exposure, showing that the SOA yields obtained by two types of reactors were in good agreement. Under a low OH exposure (~10^{10}-10^{11} molecules cm^{-3} s), the D5 SOA yield (0.01-0.11) obtained here was similar to that (chamber, 0-0.057; flow tube, 0.018-0.06) measured by Charan et al. (*Atmos. Chem. Phys.*, 2022, 22, 917-928).

Our differences with Charan et al. (*Atmos. Chem. Phys*., 2022, 22, 917-928) are for high OH exposure conditions both using OFRs. Under a high OH exposure of ~10^{11}-10^{12} molecules cm^{-3} s, the D5 SOA yield of 0.46-0.70 was higher than 0.14-0.35 (flow tube) reported by Charan et al. (*Atmos. Chem. Phys*., 2022, 22, 917-928). Here the differences may be attributed to differences in experimental conditions, such as differences in reactors, wall losses, SOA measurement methods, determination of OH concentrations, and initial D5 concentrations (Table S5) (Janechek et al., *Atmos. Chem. Phys.*, 2019, 19, 1649-1664; Charan et al., *Atmos. Chem. Phys.*, 2022, 22, 917-928). Wall losses in particular can be a major factor influencing aerosol yields; our ECCC-OFR uses a sheath flow to minimize such an artefact (Li et al., *Atmos. Chem. Phys.*, 2019, 19, 9715-9731) resulting in higher and more reliable yields than approaches without such a design. In the revision, we have now included a brief discussion to include the results from the Charan et al. paper in Lines 200-208, and further in Table S5 in the revised *Supplement* to show the comparison.

When extrapolating laboratory results to the real atmosphere, the relevant OH concentrations and exposures should be understood carefully, as suggested by Charan et al. (*Atmos. Chem. Phys.*, 2022, 22, 917-928). As we all know, one important advantage of OFR is to simulate up to several weeks of OH exposures. Considering the half-life of cVMS, the OH exposures on the order of 10^{12} molecules cm^{-3} s are also environmentally relevant (Charan et al., *Atmos. Chem. Phys.*, 2022, 22, 917-928). Studies have predicted the SOA formation based on ambient SOA precursors and yields obtained from OFR (Palm et al., *Atmos. Chem. Phys.*, 2018, 18, 467-493; Jokinen et al., *Proc. Natl. Acad. Sci. U S A.*, 2015, 112, 7123-7128), further strengthening the argument in favor of OFRs.

The calculation of cVMS-SOA concentration (in Eq. 4) is not clear. The equation needs the amount of lost of cVMS, but the quantity was not measured or published. See more in Minor Comment below.

Re: The reacted cVMS in the atmospheric environment is estimated from $C_{cVMS}\times\Delta C_{cVMS}/C_{in\text{-}cVMS}$, based on assumptions that the lost cVMS ratio is not affected by the cVMS concentration and the background $C_{cVMS\text{-}SOA}$ is zero. The values of lost cVMS (ΔC_{cVMS}) were obtained by the PTR-MS measurements, and they have been provided in Table S7 (i.e., Table R2) in the revised *Supplement*.

The manuscript states that the number and mass size distribution of aerosols was monitored using a scanning mobility particle sizer (SMPS), but no data was provided and discussed except the statement that the data was used for calculation of effective aerosol densities. The results would be helpful to understand the characteristics of SOA formation under different conditions.

Re: Based on the SPMS data, the number and mass size distributions of aerosols (D5 SOA as an example) were added in Figure S2 (i.e., Figure R1) in the revised *Supplement*. Figure S2 (i.e., Figure R1) shows that small particles dominated in the number, while large ones were prominent in the mass. Compared to the size distributions of D5 SOA in low-NO$_x$ experiments (Figure. S2a), the mode diameters of SOA increased for both number and mass size distributions under high-NO$_x$ conditions (Figure. S2b), which suggests that larger particles are dominant in D5 SOA generated in high-NO$_x$ experiments. The related discussions have been added in Lines 175-180 in the revised manuscript.

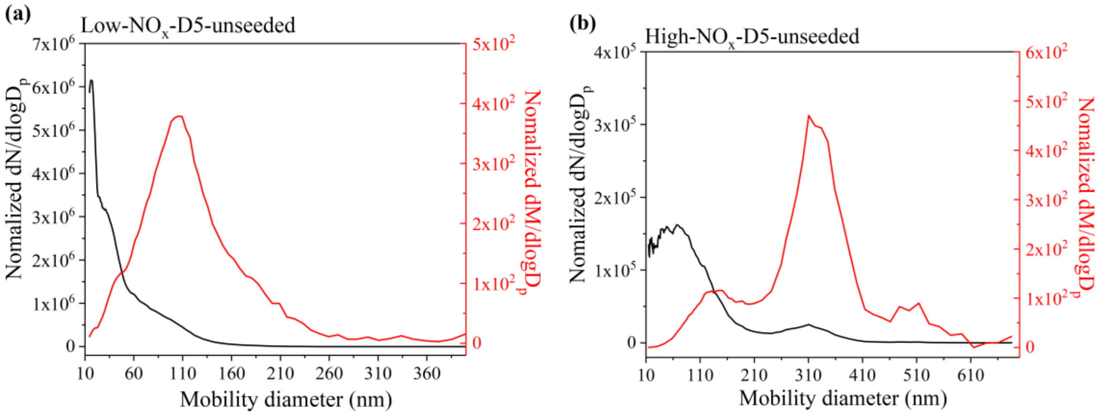

Figure R1. Number and mass size distributions of D5 SOA measured by SMPS at OH exposure of 9.0×10^{11} molecules cm^{-3} s under low-NO$_x$ (**a**) and high-NO$_x$ (**b**) conditions.

Minor Comment

L51-53: Is this (scarce knowledge) still valid? There have been many studies published since the reference you cited.

Re: It has been modified in Lines 51-53 in the revised manuscript as shown below: "The legislative actions notwithstanding, knowledge of environmental behavior of cVMS still needs to be further deepened as compared to their applications and economic significance".

L135 & Table S2: Based on my extra calculations, the initial concentration range (i.e., 20-40 ppb & 20-25 ppb in Table S3) is equivalent to ~10,000 times greater than environmental concentrations or similar to the values of Janecheck et al. (2019). See Table S2. The authors should note that the concentrations are high enough to increase potential uncertainty in the extrapolation to the environmental concentrations. This manuscript does not provide individual initial concentrations for each of the cVMS species, but it would be helpful with the data.

Re: The initial concentrations for each of the cVMS species have been provided in Table S2 (i.e., Table R1) in the revised *Supplement*. It should be noted that these were far greater than environmental concentrations, which may cause potential uncertainty in the extrapolation to the atmospheric conditions. This has been described in Lines 356-360 in the revised manuscript.

Table R1. Initial concentration of cVMS

cVMS	Low-NO_x experiments (ppb)		High-NO_x experiments (ppb)	
	unseeded	seeded	unseeded	seeded
D3	19-21	18-20	38-43	42-46
D4	27-35	30-33	25-31	25-33
D5	18-26	27-30	36-41	30-38
D6	19-28	25-30	24-30	26-32

L190 (&L29): This study claims that the production of SOA is dependent on OH exposure. However, this is partially true in the limit of OFR experiments. In contrast, Charan et al. (2021) discovered that OH radical concentrations are more important than OH exposure considering all experiment results with OFR and chamber reactors. If the latter is valid, it's better to use OH radical concentrations for the x-axis rather than photochemical age as the initial cVMS concentrations were in a relatively narrow range.

Re: It should be pointed out that the comparison on how OH concentration versus exposure affects SOA yields has been removed in the published version of Charan et al. (*Atmos. Chem. Phys*., 2022, 22, 917-928). In fact, the OH exposure (i.e., photochemical age) is positively correlated with the OH concentration due to the constant resident time of gas in the ECCC-OFR. The use of OH exposure (i.e., photochemical age) is a typical way for OFR experiments (Tengyu Liu et al., *Atmos. Chem. Phys*., 2018, 18, 5677-5689; Janechek et al., *Atmos. Chem. Phys.*, 2019, 19, 1649-1664). As for us, it is better to use OH exposure as the x-axis, which is convenient to compare with results from other literatures.

L255-256: This is under unseeded conditions. Please explain why there were more productions under seeded conditions at earlier PAs?

Re: As shown in Figure 3, the initial fractions of C_xH_y in seeded experiments were larger than those in unseeded experiments, which may be related to the volatility of species containing C_xH_y that may be more easily deposited in the presence of seeds. This has been given in Lines 300-301 in the revised manuscript.

L321-322: The estimation would not be valid based on this study that used OFRs. See Charan et al. (2021) for the detailed discussion.

Re: The responses to the first major comment have clarified the validity of the estimation. It should be noted that in the recently ***published version*** of Charan et al. (*Atmos. Chem. Phys*., 2022, 22, 917-928) the CPOT OFR was also used to support their conclusion. Briefly, when extrapolating laboratory results to real atmosphere, the relevant OH concentrations and exposures should be understood carefully, as suggested by Charan et al. (*Atmos. Chem. Phys*., 2022, 22, 917-928). As we all know, one important advantage of OFR is to simulate up to several weeks of OH exposure. Considering the half-life of cVMS, the OH exposures on the order of 10^{12} molecules cm^{-3} s are also environmentally relevant (Charan et al., *Atmos. Chem. Phys*., 2022, 22, 917-928). Additionally, previous studies have predicted the SOA formation based on ambient SOA precursors and yields obtained from OFR (Palm et al., *Atmos. Chem. Phys.*, 2018, 18, 467-493; Jokinen et al., *Proc. Natl. Acad. Sci. U S A.*, 2015, 112, 7123-

7128), further demonstrating the usefulness of OFR in investigating reactions relevant to the atmosphere.

L323,330: There should be differences between C_{cVMS} and ΔC_{cVMS}. I assume SOA concentrations were calculated based on C_{cVMS}, not ΔC_{cVMS}. Eq.4 is valid only when $C_{cVMS} = C_{in\text{-}cVMS}$ and background $C_{cVMS\text{-}SOA}$=0. Thus, there should be more clarification. In addition, extrapolation should be highly uncertain due to 4 orders-of-magnitude differences of concentrations and overestimated SOA yields.

Re: The reacted cVMS in the atmospheric environment is estimated from $C_{cVMS}\times\Delta C_{cVMS}/C_{in\text{-}cVMS}$, based on assumptions that the lost cVMS ratio is not affected by the cVMS concentrations and the background $C_{cVMS\text{-}SOA}$ is zero. Although there may be some uncertainties in extrapolating our results to the real atmosphere, such as larger cVMS concentrations and SOA yields, our extrapolations may provide an upper limit for evaluating cVMS SOA. This has been described in Lines 356-360 in the revised manuscript.

L332-333: Not clear what values were used in this study. The values were not directly measured.

Re: The values of $\Delta C_{cVMS}/C_{in\text{-}cVMS}$ were obtained by the PTR-MS measurements, and they have been provided in Table S7 (i.e., Table R2) in the revised *Supplement*.

Table R2. The values of $C_{in\text{-}cVMS}$ and ΔC_{cVMS} in Equation 4.

cVMS	Low-NO$_x$-unseeded-14.2 d		High-NO$_x$-seeded-8.5 d	
	Initial concentration ($C_{in\text{-}cVMS}$, μg m^{-3})	Lost concentration (ΔC_{cVMS}, μg m^{-3})	Initial concentration ($C_{in\text{-}cVMS}$, μg m^{-3})	Lost concentration (ΔC_{cVMS}, μg m^{-3})
D3	186.83	156.99	392.56	258.27
D4	386.42	327.30	391.84	305.99
D5	371.66	371.66	557.73	445.59
D6	476.12	453.72	566.47	456.72

L617-619: Check this reference: not used.

Re: It has been added in Line 51 in the revised manuscript.

acp-2021-965-RC3

The manuscript by Han et al describes several cVMS aerosol yield experiments in an oxidation flow reactor (OFR). They use their derived yields to make estimates of cVMS-derived SOA at various locations. cVMS chemistry and aerosol yield is an open question in the field and the results are of interest to the community. However, I have several major comments that I would like to see addressed before I could recommend publication.

Re: We welcome the opportunity to further clarify and improve our paper.

Major Comments

The results of this study need to be discussed in the context of Charan et al., (2021). Charan et al. (2021) found that the aerosol yield for D5 oxidation varied with the OH exposure in an unusual way. I note that when considering the Charan et al., (2021) work, it would be prudent to wait for the ACP version of the manuscript as several points of discussion regarding possible explanations of the differing yields were modified following public discussion. A particular result from Charan et al. (2021) that should be discussed in the context of the current study is that OFR experiments led to higher SOA yields than environmental chamber experiments.

Re: The ***published version*** of Charan et al. (*Atmos. Chem. Phys*., 2022, 22, 917-928) showed that at similar OH concentrations and OH exposures, the D5 SOA yields in the Caltech Photooxidation Flow Tube (CPOT) and chamber experiments were consistent.

Under a low OH exposure (~10^{10}-10^{11} molecules cm^{-3} s), the D5 SOA yield (0.01-0.11) obtained here was similar to that (chamber, 0-0.057; flow tube, 0.018-0.06) measured by Charan et al. (*Atmos. Chem. Phys*., 2022, 22, 917-928). However, under a high OH exposure of ~10^{11}-10^{12} molecules cm^{-3} s, the D5 SOA yield of 0.46-0.70 was higher than 0.14-0.35 (flow tube) reported by Charan et al. (*Atmos. Chem. Phys*., 2022, 22, 917-928), respectively, which may be attributed to differences in experimental conditions, such as differences in reactors, wall losses, SOA measurement methods, determination of OH concentrations, and initial D5 concentrations (Table S5) (Janechek et al., *Atmos. Chem. Phys.*, 2019, 19, 1649-1664; Charan et al., *Atmos. Chem. Phys*., 2022, 22, 917-928). The results from Charan et al. (*Atmos. Chem. Phys*., 2022, 22, 917-928) have been cited in Table S5 in the revised *Supplement.* Moreover, a brief discussion has been added in Lines 200-208 in the revised manuscript.

Further details about the radical chemistry need to be included in the manuscript. While information is given on the ratio or RO_2 + NO to RO_2 + HO_2 reactions in the high NO_x experiments, there is no discussion on how prevalent RO_2 + RO_2 reactions were or even the (not atmospherically relevant) RO_2 + OH. Differences in the fate of the peroxy radical in the OFR experiments compared to chamber experiments is one possibility that could explain the Charan et al (2021) results, however, the investigation of RO_2 fate was beyond the scope of that paper. I encourage the authors to describe the radical chemistry of these experiments in more detail as it could aid in understanding the apparent discrepancy between OFR experiments and chambers for this chemical system.

Re: Although RO_2+RO_2 reactions cannot be totally ignored compared to RO_2 + HO_2 and RO_2 + NO reactions, their roles may be minor due to the low concentration of SOA precursors (cVMS, 18-46 ppb) according to the study of Lambe et al. (*Atmos. Meas. Tech.*, 2017, 10, 2283-2298). Peng et al. (*Atmos. Chem. Phys.*, 2019, 19, 813-834) have illustrated that when at low precursor concentrations, the roles of RO_2 + RO_2 are minor or negligible in OFR, where N_2O was used to achieve high-NO_x conditions. Our previous model results have also demonstrated that the dominant fate of RO_2 was the reaction with NO in the ECCC-OFR under high-NO_x conditions (Li et al., *Environ. Sci. Technol.*, 2019, 53, 14420-14429), implying the minimal role of RO_2 + RO_2 reactions. As reported by Peng et al. (*Atmos. Chem. Phys.*, 2019, 19, 813-834), the relative importance of RO_2 + OH is generally negatively correlated with the injection of N_2O in OFR, which may be attributed to the suppressing effect of NO_x on OH and the increasing role of RO_2 + NO. The related discussion about the radical chemistry has been added in Lines 147-152 in the revised manuscript.

Given the prevalence of cVMS, it is easy for contamination to occur. I would like to see more information on control experiments that were performed to check for contamination and possible impacts on cVMS yields. Additionally, I think the manuscript would benefit from including more examples (SI is ok) of the measurements. In particular, I would like to see some examples of the SMPS data and AMS time series absolute values (not in terms of fraction). The SMPS data in particular should be included as it is central in the yield calculation.

Re: Control experiments were performed under both low and high-NO_x conditions, where the aerosol mass concentration (background values) in the absence of cVMS was measured by SMPS, as shown in Table S3 (i.e., Table R3) in the revised *Supplement*. The background values were subtracted when calculating the cVMS SOA yields. The revised descriptions have been added in Lines 171-172 in the revised manuscript.

Taking D5 in low-NO_x experiments as an example, the mass concentrations of D5 SOA measured by SMPS under unseeded conditions were shown in Table S4 (i.e., Table R4) in the revised *Supplement*. Moreover, the number and mass size distributions of D5 SOA measured by SMPS were added in Figure S2 (i.e., Figure R1) in the revised *Supplement*. The related discussions have been added in Lines 175-180. The AMS time series of D5 SOA in low-NO_x experiments under unseeded conditions were also shown in Figure S3 (i.e., Figure R2) in the revised *Supplement*. This has been described in Lines 180-182 in the revised manuscript.

Table R3. Background values of SMPS at different OH exposures in low and high-NO_x experiments without cVMS.

Low-NO_x experiments			High-NO_x experiments			
OH exposure	Equivalent photochemic	Background (μg/m^3)	OH exposure	Equivalent photochemic	Background (μg/m^3)-	Background (μg/m^3)-

($\times 10^{12}$ molecules cm^{-3} s)	al age (days)		($\times 10^{12}$ molecules cm^{-3} s)	al age (days)	unseeded	seeded
0.05	0.42	0.51	0.08	0.63	0.15	2.74
0.14	1.10	1.55	0.22	1.71	0.33	5.37
0.26	2.00	2.01	0.34	2.64	0.32	6.84
0.35	2.67	2.38	0.45	3.45	0.39	7.44
0.43	3.28	2.25	0.61	4.69	0.37	10.91
0.50	3.86	2.70	0.82	6.36	0.58	12.34
0.60	4.66	3.50	0.90	6.94	0.41	12.21
0.69	5.30	3.73	1.10	8.46	0.98	13.61
0.90	6.95	3.86				
1.16	8.96	5.19				
1.32	10.15	6.17				
1.67	12.88	7.24				
1.85	14.24	7.81				

Table R4. The mass concentrations of D5 SOA at different OH exposures under unseeded conditions in low-NO_x experiments.

OH exposure ($\times 10^{12}$ molecules cm^{-3} s)	Equivalent photochemical age (days)	Low-NO_x-unseeded-D5 SOA ($\mu g/m^3$)
0.05	0.42	0.49
0.14	1.10	1.83
0.26	2.00	8.92
0.35	2.67	16.95
0.43	3.28	25.76
0.50	3.86	48.86
0.60	4.66	68.65

0.69	5.30	97.70
0.90	6.95	169.74
1.16	8.96	228.76
1.32	10.15	253.56
1.67	12.88	282.73
1.85	14.24	273.61

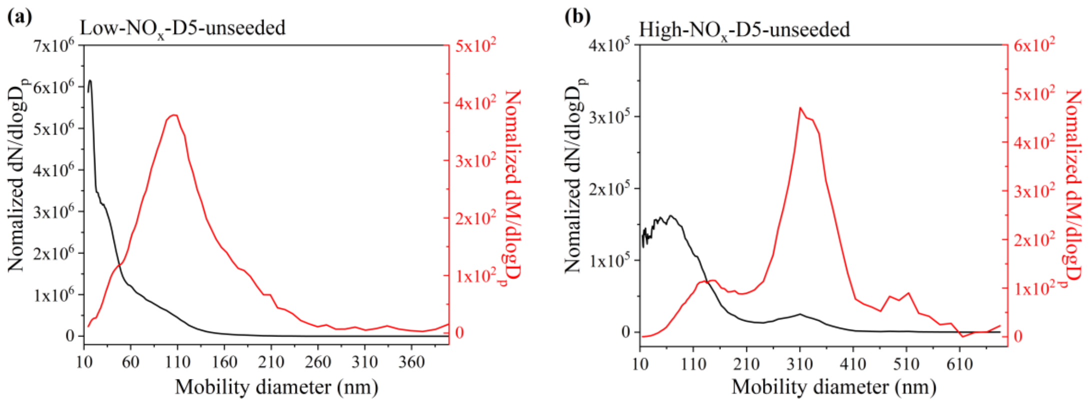

Figure R1. Number and mass size distributions of D5 SOA measured by SMPS at OH exposure of 9.0 × 10^{11} molecules cm^{-3} s under low-NO$_x$ (**a**) and high-NO$_x$ (**b**) conditions.

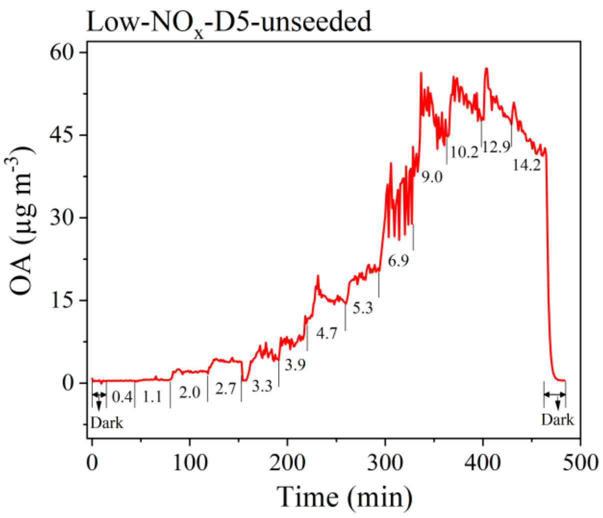

Figure R2. The AMS time series of D5 SOA in low-NO$_x$ experiments under unseeded conditions. The numbers represent the equivalent photochemical age.

The back of the envelope calculations for the cVMS SOA loadings need to be better justified. For instance, why is 8.5 days selected for the urban sites? That seems long considering typical transport times. There should also be discussion of the results of Milani et al., (2021) and Pennington et al., (2021) and the consistency or not of these back of the envelope estimates with those studies.

Re: The atmospheric half-lives of D3-D6 were 6-30 days. The yield at 8.5 equivalent days was selected to provide an upper limit for evaluating cVMS SOA. This has been described in Lines 349-350 and 356-360 in the revised manuscript.

A discussion with the results of Milani et al. (*Atmos. Environ.*, 2021, 246, 118078) and Pennington et al. (*Atmos. Chem. Phys.*, 2021, 21, 18247-18261) has been added in Lines 388-394 in the revised manuscript and presented below.

"It was noted that the D5 SOA concentration (13.38-683.57 ng/m^3) estimated here is far more than that (0.016-0.206 ng/m^3) reported by Milani et al., (2021), who obtained their data using semi-quantified concentrations of D_4TOH (first-generation D5 SOA product) extracted from $PM_{2.5}$ samples in Atlanta and Houston. The difference may be mainly attributed to the missing analysis of multi-generation SOA products or dimers (Wu and Johnston, 2016, 2017). Pennington et al., (2021) utilized the developed CMAQ model to investigate the concentration of D5 SOA in the urban area of Los Angeles, and the model data (21 ng/m^3) was within these values here."

Minor Comments

Figure 2 (and analogous SI figure for high NO_x). Given that the cVMS precursors only differ in the number of (C_2H_6OSi) units, I would have expected to see somewhat more similar mass spectra from their oxidation products. I find it intriguing how different the MS are between the experiments and find some of the ions unexpected. For instance, $C_{12}H_{11}O_2Si_5^+$ from D5 oxidation is intriguing given the addition of C and loss of O from the parent species. I recognize the electron ionization spectra of complex mixtures can be challenging and non-intuitive to interpret, but I wonder if the authors have considered possible explanations for some of these ions and what they might imply for the identify of oxidation products. Additionally, I wonder if the PTR provides any information on gas-phase oxidation products that is useful.

Re: We thank the reviewer for this thoughtful comment. Indeed, information buried in the MS can be very meaningful for understanding the mechanisms of cVMS oxidation by OH radicals. We have tried to provide possible explanations for these ions when analyzing mass spectra. However, due to the complexity of the fragments caused by electron ionization, we admit that it is hard to establish a correlation between these special fragments and oxidation products only based on the AMS results. Gas-phase species in PTR-MS are still being analyzed in our further investigation to complete a study about the kinetics and gas-phase products of the reaction between cVMS and OH radicals. The PTR-MS may provide some information about the gas-phase species, as shown in Figure R3. The focus of the current manuscript is on the yields and compositions of cVMS SOA, rather than gas-phase products and mechanisms of cVMS oxidated by OH radicals, which are the subject of a continued investigation. Therefore, the PTR-MS results are not presented in our manuscript.

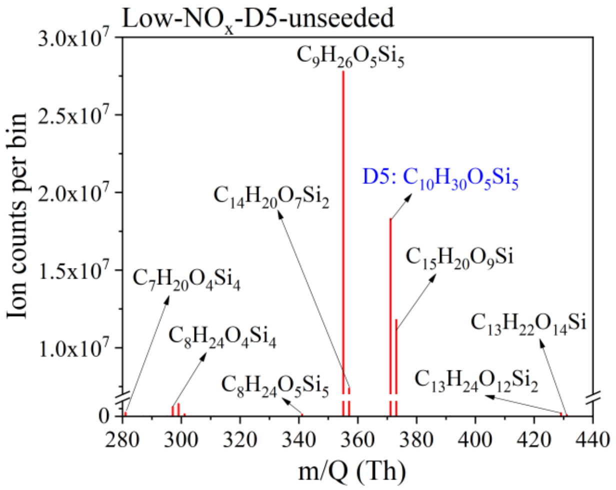

Figure R3. The mass spectrum of the gas-phase oxidation products of D5 measured by PTR-MS under low-NO$_x$ and unseeded conditions.

Lines 268-270: I would think that continued breaking of Si-O bonds would lead to more volatile products since after the first bond breaking, it would lead to fragmentation and thus smaller molecules.

Re: We agree with your opinion. The related explanation has been modified in Lines 290-291 in the revised manuscript.

Technical Comments

Line 70: The conclusion of Alton and Browne, (2020) is more subtle than suggested here. They suggest that while Cl is minor globally, loss locally (for instance in Los Angeles) could be more important given the spatial and temporal overlap of cVMS emissions and sources of Cl (i.e. from $ClNO_2$). This is an important distinction if cVMS yields are high as suggested by this work.

Re: The text has been modified in Lines 70-71 in the revised manuscript and shown below: “The loss of cVMS in the atmosphere is slight through O_3 and NO_3 due to their small reaction rates, and by Cl atoms on account of its low concentration except for the spatial and temporal overlaps of cVMS emissions and Cl sources.”

Lines 84-85: “…indicating necessary conditions when extrapolating SOA yields to the ambient atmosphere.” This sentence does not make sense. Pleas reword.

Re: This sentence has been rewritten in Lines 84-86 in the manuscript as “…emphasizing the importance of the relevant OH concentrations and exposures when extrapolating these laboratory results or comparing with other studies…”.

Table S2: Please keep D5 in the same units for all the studies.

Re: The unit of D5 in Table S5 has been uniformly changed to “ppbv” in the revised *Supplement*.

Line 229: Alton and Browne (2020) did not state anything about the relative volatility of different cVMS oxidation products. The only discussion on volatility concerned wall loss and that one of the first-generation oxidation products had a lower vapor pressure than the parent cVMS. Moreover, that vapor pressure is still high enough that it is unlikely to contribute to SOA except at high loadings. Additionally, they did not report D6 results.

Re: This reference has been deleted in Line 245 in the revised manuscript.

The use of n/z and n/z rather than Si/C and Si/O adds complexity to the paper that I think is unnecessary. I think it would be easier for the reader to understand the results if Si/C and Si/O are used.

Re: "Si/C" and "Si/O" have been used in Lines 276-280 and 331-333 in the revised manuscript.

Lines 265-266: This discussion of oxidation as occurring by substitution of one functional group for another is confusing and misleading. I suggest editing to be more clear about the chemistry occurring (OH abstracting a H, etc.).

Re: This discussion has been modified into "The initial step of OH radical oxidation can be considered as OH abstracting a H atom from the methyl groups on the -Si-O-ring of the cVMS to form Si-containing radicals, which may generate OH and CH_2OH substitution products, such as silanol and silyl methanol (Wu and Johnston, 2016; Alton and Browne, 2020)", as shown in Lines 281-284 in the revised manuscript.

References

Alton, M. W. and Browne, E. C.: Atmospheric Chemistry of Volatile Methyl Siloxanes: Kinetics and Products of Oxidation by OH Radicals and Cl Atoms, Environ. Sci. Technol.,

54, 5992–5999, https://doi.org/10.1021/acs.est.0c01368, 2020.

Charan, S. M., Huang, Y., Buenconsejo, R. S., Li, Q., Cocker III, D. R., and Seinfeld, J. H.: Secondary Organic Aerosol Formation from the Oxidation of Decamethylcyclopentasiloxane at Atmospherically Relevant OH Concentrations, Atmospheric Chem. Phys. Discuss., 1–17, https://doi.org/10.5194/acp-2021-353, 2021.

Milani, A., Al-Naiema, I. M., and Stone, E. A.: Detection of a secondary organic aerosol tracer derived from personal care products, Atmos. Environ., 246, 118078, https://doi.org/10.1016/j.atmosenv.2020.118078, 2021.

Pennington, E. A., Seltzer, K. M., Murphy, B. N., Qin, M., Seinfeld, J. H., and Pye, H. O. T.: Modeling secondary organic aerosol formation from volatile chemical products, Atmospheric Chem. Phys., 21, 18247–18261, https://doi.org/10.5194/acp-21-18247-

2021, 2021.

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

Sincerely yours,

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