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.

Anonymous referee #2

Although the revision has been improved, I am not still fully convinced that the results can be applied to the environmentally relevant conditions. Charan et al. (2022) claimed that the yield of SOA depended strongly on OH concentration rather than OH exposure. Since the authors used a fixed residence time of 2 min in the OFR, the exposure reported was a directly proportional to OH concentration, which should be the governing factor for SOA formation. The OH exposure (OH concentration multiplied by exposure duration) and photochemical age can be used interchangeably using an assumption of a constant OH concentration. Under an ideal condition, a low OH concentration for a long exposure time and a high OH concentration for a short exposure time can achieve the same degree of degradation of the parent compound. However, that is not for the formation of SOA as Charan et al. (2022) asserted. Since OH concentrations in the OFR were >1,000 times greater than the average OH concentration in air, the result of SOA formation yield should not be applied to the prediction in the real atmosphere. The predicted SOA concentrations were overestimated when compared with other predictions in the literature. Thus, the current section of 4 Conclusions and implications should be properly revised.

Re: We agree that the SOA yield depends on the OH concentration. Charan et al. also claimed that the SOA yield varied in a small range (0-6%) at the OH concentration $\leq 5 \times 10^8$ molecules cm^{-3} (Atmos. Chem. Phys., 2022, 22, 917-928). It was assumed that the SOA yields at environmentally relevant OH concentrations ($\sim 10^6$ molecules cm^{-3}) were similar to those at the lowest OH concentrations ($\sim 10^8$ molecules cm^{-3}) used here. Thus, the high-NO_x SOA yields (D3: 0.038; D4: 0.001; D5: 0.011; D6: 0.000) under the seeded conditions at the OH concentration of 6.83×10^8 molecules cm^{-3} (0.63 equivalent days) were employed in the calculation of cVMS SOA concentrations at urban sites, while the low-NO_x SOA yields (D3:

0.041; D4: 0.013; D5: 0.023; D6: 0.004) under the unseeded conditions at the OH concentration of 4.57×10^8 molecules cm^{-3} (0.42 equivalent days) were used to estimate cVMS SOA at background and polar sites.

It was noted that the time-integrated consumption over the lifetime of a precursor compound in the atmosphere should be suitable for evaluating the SOA formation. As you stated, under an ideal condition, a low OH concentration for a long exposure time and a high OH concentration for a short exposure time can achieve the same degree of degradation of the precursor compound. Accordingly, when considering half-lives (6-30 days) of cVMS in the atmosphere, the $\Delta C_{cVMS}/C_{in-cVMS}$ values in low-NO_x and unseeded experiments at 14.2 equivalent days (Table S7) are used to calculate cVMS SOA at background and polar sites. Due to a short residence time of airmass over urban areas, the $\Delta C_{cVMS}/C_{in-cVMS}$ values in high-NO_x and seeded experiments at 0.63 equivalent days (Table S7) are employed to estimate cVMS SOA at urban sites.

The related descriptions have been given in Lines 371-377, 379-382 and 384-392 in the revised manuscript. The section of conclusions and implications has been properly modified on the basis of the updated data in Figure 4 in the revised manuscript, and in Tables S6-7 in the revised *Supplement*.

Anonymous referee #3

Main Points

1) I thank the authors for their additional text regarding the back of the envelope calculations on cVMS SOA concentrations. I think these types of calculations are valuable. However, I am still unconvinced by the arguments regarding the choice of 8.5 days. I agree that the SOA formation will occur as the airmass is transported and that for this type of calculation simplification is required. I disagree though that 8.5 days is the appropriate choice. As the airmass is transported it will undergo dilution in addition to chemical processing. For the equations used here, the aerosol is being calculated in terms of ng/m^3 and the dilution would not be taken into account when using 8.5 days and measured gas-phase concentrations near the

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60   **Re**: There is a short residence time of airmass over urban areas. The cVMS SOA yields (D3:

61   0.038; D4: 0.001; D5: 0.011; D6: 0.000) and the $\Delta C_{cVMS}/C_{in\text{-}cVMS}$ values in high-NO_x and

62   seeded experiments at 0.63 equivalent days have been employed in the calculation of cVMS

63   SOA concentrations at urban sites. The dilution of cVMS would occur during the transportation

64   in the atmosphere, leading to an uncertainty of cVMS concentrations (C_{cVMS}) in the Equation

65   4. To simplify the estimation process, the effect of dilution on C_{cVMS} would not be taken into

66   account, and the reported C_{cVMS} values were directly used. The related descriptions have been

67   given in Lines 368-371, 375-377 and 387-389 in the revised manuscript. The section of

68   conclusions and implications has been properly modified on the basis of the updated data in

69   Figure 4 in the revised manuscript, and in Tables S6-7 in the revised *Supplement*.

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71   2) Si/O and Si/C ratio calculation. I thank the authors for the additional text clarifying the

72   calculation of the Si/O and Si/C ratios. However, I think the text requires a bit more elaboration

73   to make the procedure clearer. From the way the calculation is written, it appears that the

74   number of Si or O in each ion is being used rather than the mass of Si and O. I think it is also

75   more appropriate to calculate the mass of Si and the mass of O separately then calculate the

76   Si/O making the appropriate adjustments for atomic ratios (Aiken et al., 2007). It is also unclear

77   to me why in equation S1 max is used in the denominator rather than sum if the fraction is

78   being calculated. Additionally, uncertainty in this calculation goes beyond simply uncertainty

79   in assigned peaks, but also includes fragmentation (see Aiken et al paper referenced above).

80   **Re**: The calculation methods of Si/O and Si/C ratios have been modified as follows:

81   (1) The peak intensity of $C_xH_yO_zSi_n$ ($C_{x1}H_{y1}O_{z1}Si_{n1}$, $C_{x2}H_{y2}O_{z2}Si_{n2}$ …$C_{xi}H_{yi}O_{zi}Si_{ni}$) is obtained

82   from the HR-ToF-AMS, which is named as A_1, A_2…A_i, respectively.

83   (2) The fraction of each $C_xH_yO_zSi_n$ ion (F_1, F_2, F_3…F_i) is calculated by Equation S1,

84    $$F_i = A_i / \text{SUM}(A_1, A_2, A_3…A_i) \tag{S1}$$

85   (3) The Si/O and Si/C ratio of $C_xH_yO_zSi_n$ ions at each equivalent day are calculated by Equation

S2-S6,

$$m_{Si} = \text{SUM}(F_i \times n_i \times M_{Si} / M_{C_{xi}H_{yi}O_{zi}Si_{ni}}) \tag{S2}$$

$$m_O = \text{SUM}(F_i \times z_i \times M_O / M_{C_{xi}H_{yi}O_{zi}Si_{ni}}) \tag{S3}$$

$$m_C = \text{SUM}(F_i \times x_i \times M_C / M_{C_{xi}H_{yi}O_{zi}Si_{ni}}) \tag{S4}$$

$$n/z = \frac{m_{Si}}{M_{Si}} \Big/ \frac{m_O}{M_O} \tag{S5}$$

$$n/x = \frac{m_{Si}}{M_{Si}} \Big/ \frac{m_C}{M_C} \tag{S6}$$

where M is the molar mass of one specific element (Si, O, C and H) or $C_xH_yO_zSi_n$ ions; m is the total mass of Si, O or C in all $C_xH_yO_zSi_n$ ions. The related descriptions have been given in Text S1 in the revised *Supplement*.

For the calculation results, there may be some uncertainties due to the assignments of peaks in the HR-ToF-AMS and the fragmentation processes of the AMS ionization. The revised Si/O and Si/C mass ratios have been updated in Figure S8 and S11. The related descriptions have been revised in Lines 287-288 in the revised manuscript.

Technical: Line numbers refer to track changes version.

Line 305: I believe this should be Si-C, not S-C.

Re: The S-C has been modified into Si-C in Line 299 in the revised manuscript.

Line 256-257: This statement is incorrect. The Alton and Browne papers say the opposite – the products measured there are predicted to have high vapor pressures that wouldn't partition to aerosol under most ambient conditions (assuming absorptive partitioning). Wu and Johnston also show that a significant fraction of the products have a logC* >2 making them also volatile.

Re: The original statement "In fact, most D5 oxidation products have been shown to be nearly non-volatile" has been deleted in the revised manuscript.

Line 433-435: The Pennington et al results were for aerosol from multiple different siloxanes,

Re: The results of Pennington et al. (*Atmos. Chem. Phys.*, 2021, 21, 18247-18261) have been compared with total cVMS SOA at urban sites, as shown in Lines 396-399 in the revised manuscript.

References

Aiken, A. C., DeCarlo, P. F., and Jimenez, J. L.: Elemental Analysis of Organic Species with Electron Ionization High-Resolution Mass Spectrometry, Anal. Chem., 79, 8350–8358, https://doi.org/10.1021/ac071150w, 2007.

Re: We thank the reviewer for providing this literature. It has been cited properly in the revised *Supplement*.

Sincerely yours,

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