

We appreciate the anonymous reviewers for their thoughtful reviews and comments. We have carefully considered their suggestions and revised the manuscript accordingly. In addition to changes arising from the reviewers, we have made edits to correct figure references in the text and the figures themselves.

Key changes from the previous version are the separation of the gas and particle-phase chemical aging rate coefficients in the aging-VBS model and the addition of model sensitivity evaluations. With the revised model, we regenerate the model figures. We also include an ensemble of optimized parameter sets to provide a range of potential fit values and show the root mean square errors of the models against the data. Accordingly, the text has been updated so $k_{\text{age,particle}}$ is not tied to being 10 % of $k_{\text{age,gas}}$, including the abstract.

The reviewer comments are in blue, our comments are in black, and modifications to the manuscript are in red. Other edits and corrections not instigated by the reviewers are summarized at the end.

Reviewer # 2

This manuscript investigated the oxidation of D5 siloxane in an oxidation flow reactor (OFR) and the formation of volatile oxidation products, such as formaldehyde (HCHO) and formic acid (HCOOH), and secondary organic aerosol (SOSiA). It was found that there was substantial formation of HCHO, HCOOH and SOSiA, highlighting their environmental importance. To reconcile the discrepant SOSiA yields reported in the literature, the study employed a volatility-based multi-generation aging model (VBS) to fit the observed SOSiA in all experiments simultaneously, by tuning the volatility and aging parameters. It was found that the model was able to better capture SOSiA formation from the literature with aging accounted for. This suggested that multi-generational aging may be very important for D5 siloxane oxidation, more so than other systems like monoterpene oxidation, where SOA forms early on. This study is generally well designed, and acceptance is recommended if the comments can be addressed.

We thank the anonymous reviewer for highlighting areas where the manuscript can be improved prior to publication. We updated the manuscript as outlined below.

1. When simulating the OFR experiments, were the OH concentrations corrected for suppression by external reactivity?

We use the D_5 measurements from the PTR-MS to derive the OH_{exp} (Eq. 2) during the experiments instead of relying on offline OH_{exp} calibrations. Since the model uses a constant [OH] derived from the empirical OH_{exp} , suppression effects are accounted for empirically. While designing the experiments, we mitigated the risk of OH suppression by keeping the OHR_{ext} low. For instance, the highest experimental $[D_5]_0$ was 167 ppb, which corresponds to an OHR_{ext} of 8.3 s^{-1} , which is within the recommended PAM-OFR conditions by Peng and Jimenez (2020).

Added lines 158-159:

“With these target $[D_5]_0$, we get external OH reactivities (OHR_{ext}) of $2.5 - 9.8 \text{ s}^{-1}$ at 298.15 K and 1 atm (Peng and Jimenez, 2020), where OHR_{ext} is the reactivity caused by the injection of D_5 into

the PAM-OFR. With these OHR_{ext} , we reduce the risk of OH suppression and VOC photolysis (Peng and Jimenez, 2020).”

2. Since HCHO and HCOOH are continuously formed with aging, why quantify their molar yield at zero OH exposure? The yield would change significantly with aging, is that right? Please clarify.

The reviewer is correct that HCHO and HCOOH are likely formed continuously throughout the course of the experiment. We explain in Sect. 3.1.2 that HCHO itself is reactive with OH, while HCOOH is not reactive enough to be appreciably lost by OH within the PAM-OFR residence times. Thus, we expect Y_{HCHO} to decrease with higher OH_{exp} , while Y_{HCOOH} is less affected, which is consistent with the measurements.

We fit γ_{HCHO} in the limit of $\text{OH}_{\text{exp}} \rightarrow 0$ to estimate the cumulative yield of HCHO; this value is often used to estimate VOC emissions using satellite retrievals of HCHO (Millet et al., 2006). Mao et al. (2009) also suggest that there are unaccounted for HCHO sources, and we wish to report a rough estimation of the ozone formation potential of D_5 through its production of HCHO. We have added the following:

Added lines 334-335:

“This γ_{HCHO} is also used to correlate satellite column retrievals of HCHO with VOC emissions (Millet et al., 2006), where an empirical value can be used to constrain uncertainty.”

3. In the all the OFR experiments simulated, were seed particles added to promote SOSiA condensation? If not, how would new particle formation and kinetically limited particle growth affect the model predictions? Please include this in the discussion.

We appreciate the reviewer for catching these experimental limitations. We did not use seed aerosol in these experiments and do not have time-series measurements of new particle formation from which we can derive nucleation and growth rates. Instead, we have calculated the condensational sink based on the particle size distribution (Palm et al., 2016) measured out of the PAM-OFR in Sect. S1.3. Based on those calculations, we expect the condensation of LVOC to particles to have been rapid compared to loss to the wall. However, this calculation assumes unity mass accommodation, and particle growth may have been slower if the assumption is incorrect. We have made the following additions to the main text:

Added lines 268-269:

“We also report the condensational sink and condensation lifetimes (Palm et al., 2016) calculated using the particle size distributions in Sect. S1.3.”

Added lines 493-496:

“The condensation timescale calculations suggest that the loss of low-volatile species to the wall is small (Sect. S1.3), however, these calculations assume a high mass accommodation coefficient for SOSiA and do not account for particle nucleation. Should particle nucleation be delayed or happen slowly, the gas wall loss may be higher than expected, leading to under quantification of SOSiA.”

4. This may be related to 3. I think the authors should make clear in the discussion that this study is focused on reconciling the SOSiA yields by accounting for multi-generational aging only, but aging may be not the only factor affecting the yields, especially in OFR experiments where particle kinetics, phase state etc. can play important roles. Limitations should be acknowledged and if possible, sensitivities should be probed.

We thank the reviewer for pointing out these limitations of the current aging-VBS model. In addition to the model limitations discussed in the supplementary, we have edited this section in the conclusion:

Revised lines 492-506:

“We also find that the aging-VBS model is sensitive to $k_{\text{age,particle}}$ (Fig. S11) and not sensitive to $k_{\text{age,gas}}$ (Fig. S12), suggesting that heterogeneous aging should be considered in these models. The condensation timescale calculations suggest that the loss of low-volatile species to the wall is small (Sect. S1.3), however, these calculations assume a high mass accommodation coefficient for SOSiA and do not account for particle nucleation. Should particle nucleation be delayed or happen slowly, the gas wall loss may be higher than expected, leading to under quantification of SOSiA. Furthermore, the aging-VBS model assumes that $k_{\text{age,gas}}$ is uniform across products or that chemical aging results in a ten-fold decrease in volatility.

While the proposed model assumes that the particles are internally well mixed, the high [OH] used in OFRs may induce faster radical reactions and dimerization near the particle surface (Zhao et al., 2019), which affects particle composition and equilibrium timescales. While dimers and oligomers have been found in SOSiA (Wu and Johnston, 2017; Avery et al., 2023; Chen et al., 2023), the model currently does not account for particle-phase oligomer formation. How oligomerization in the $D_5 + OH$ SOSiA system evolves the volatility distribution and particle properties is currently not considered in the aging-VBS model. Moreover, high degrees of oxidation should lead to fragmentation and increasing volatility (Isaacman-VanWertz et al. 2018), which is also not considered in the aging-VBS model. Hence, multiphase modeling to evaluate SOSiA chemistry and translate experimental findings to atmospheric conditions remains a direction for future research.”

5. The use of “pseudo persistent” in line 68 is somewhat unclear. Please add that D_5 siloxane has temporary reservoirs in the atmosphere, if that is right.

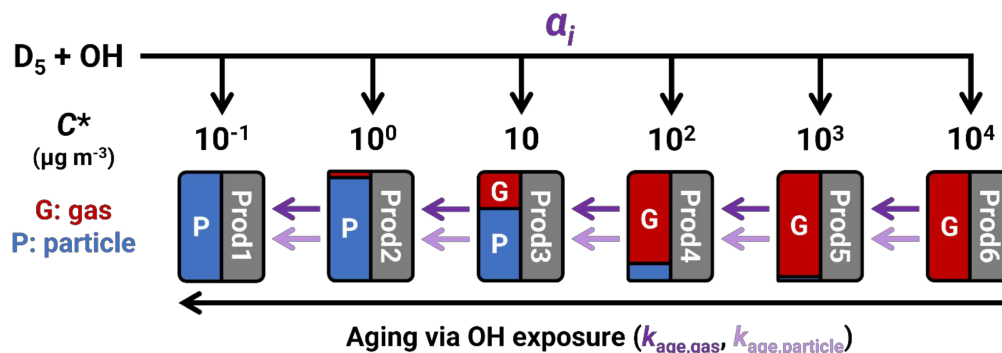
We agree with the reviewer that the phrase “pseudo persistent” can be misinterpreted. The phrase comes from Xiang et al. (2021), who used it to mean that the constant emissions of D_5 make it persist in the atmosphere. We have corrected the text to prevent misinterpretation:

Revised lines 69-71:

“Siloxanes have been classified as environmentally persistent or emitted continuously to appear as such (Howard and Muir, 2010; Xiang et al., 2021), while other studies have found that methyl siloxanes are removed on timescales of days to weeks (Graiver et al., 2003; Whelan and Kim, 2021).”

Additional Manuscript Changes

Graphical Abstract: We have replaced the original figure to the one below, which removes the reference to RO₂, whose pathways are not considered in the proposed aging-VBS model.



Correction to “D” and “T” in the molecular formulas. Previously, we stated that “D” and “T” refer to units of (CH₃)₂SiO and CH₃SiO respectively. We have corrected explanations of this nomenclature throughout the manuscript for consistency with the literature: “D” and “T” refer to silicon center atoms being bonded with two and three oxygens respectively.

Changed the title of Sect. 3.2.2 from “Reconciling Literature Y_{SOSiA}” to “Consolidating Literature Y_{SOSiA}” to prevent misinterpretation. While the reported SOSiA mass yields vary between papers, they can be consolidated with a single aging-VBS model.

Added model explanation on how experiment temperature variation was accounted for. We add the below model detail for replicability.

Added lines 226-228:

“Since the experiments had slight variations in temperature, we correct for temperature impacts on C* between experiments using the Clausius-Clapeyron equation and an enthalpy of vaporization of 60 kJ mol⁻¹, which is that of D₅ siloxane (Lei et al., 2010).”

Corrected condensational sink values in Table S3: We previously misstated the CS to be in units of m⁻², while it should be in units of s⁻¹ and miscalculated the τ_{CS} to be too fast. Eqs. S1 and S2 have been corrected, and the values in Table S3 have been revised.

Revised Table S3:

“Table S3. Summary of experiment condensational sinks, LVOC condensation lifetimes, and growth factors calculated with the particle size distribution exiting the PAM-OFr as described in Section S1.3.”

Parameters	SOA, LVOC κ = 0.13, M = 0.200 kg mol ⁻¹			SOSiA, D ₅ κ = 0.01, M = 0.370 kg mol ⁻¹		
	CS (s ⁻¹)	τ _{CS} (s)	Growth Factor	CS (s ⁻¹)	τ _{CS} (s)	Growth Factor
Experiment 1	2.57 × 10 ⁻²	38.8	1.02	1.88 × 10 ⁻²	53.3	1.00

2	3.99×10^{-2}	25.1	1.02	2.92×10^{-2}	34.3	1.00
3	3.88×10^{-2}	25.76	1.02	2.84×10^{-2}	35.2	1.00
4	0.173	5.77	1.17	0.101	9.85	1.02
5	0.303	3.30	1.17	0.182	5.50	1.02
6	0.394	2.54	1.17	0.239	4.19	1.02
7	6.68×10^{-2}	15.0	1.02	4.95×10^{-2}	20.2	1.00
8	0.138	7.27	1.02	0.104	9.63	1.00
9	0.250	3.99	1.02	0.192	5.20	1.00
10	0.338	2.95	1.12	0.217	4.61	1.01
11	0.522	1.92	1.12	0.342	2.93	1.01
12	0.913	1.09	1.12	0.605	1.65	1.01
13	1.25×10^{-2}	80.1	1.02	9.06×10^{-3}	110	1.00
14	1.23×10^{-2}	81.3	1.02	8.96×10^{-3}	112	1.00
15	1.01×10^{-2}	99.3	1.02	7.35×10^{-3}	136	1.00

Corrected Y_{HCHO} error values in Table S8. An error in the error propagation calculation resulted in the errors being overstated.

Revised Table S8''

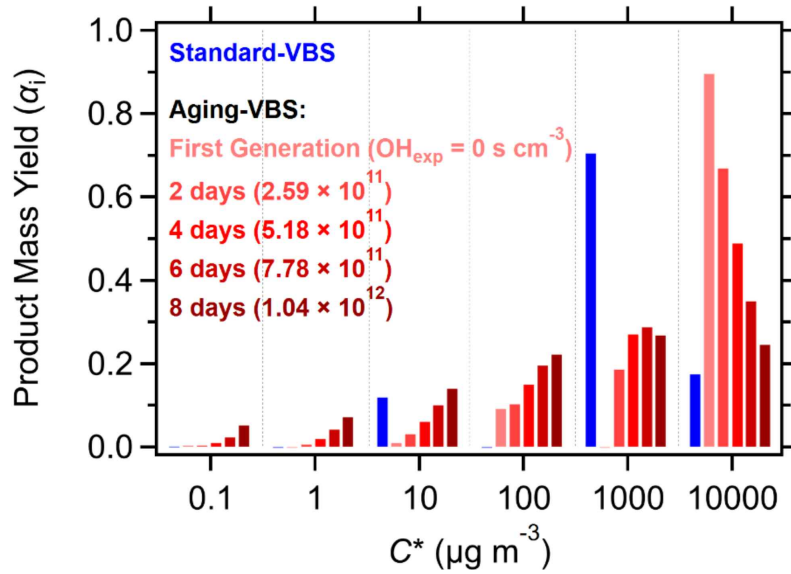
“Table S8. Experimental molar yields of HCHO and HCOOH. As these species are formed in the OFR at an unknown point, there may be some loss through oxidation with OH. Consequently, the OH_{exp} determined with D5 may not represent the OH_{exp} these VOP experienced.”

Experiment	$\Delta\text{HCHO}/\Delta\text{D}_5$ (ppb/ppb)	$\Delta\text{HCOOH}/\Delta\text{D}_5$ (ppb/ppb)
1	1.79 ± 0.25	0.94 ± 0.15
2	1.35 ± 0.15	0.69 ± 0.09
3	1.21 ± 0.21	0.52 ± 0.09
4	1.52 ± 0.11	0.90 ± 0.09
5	1.28 ± 0.11	0.83 ± 0.09
6	0.96 ± 0.06	0.62 ± 0.05
7	1.06 ± 0.06	0.68 ± 0.05
8	1.18 ± 0.09	0.80 ± 0.07
9	0.88 ± 0.04	0.60 ± 0.04
10	0.69 ± 0.03	1.27 ± 0.11
11	0.55 ± 0.02	0.84 ± 0.06
12	0.52 ± 0.02	0.68 ± 0.04

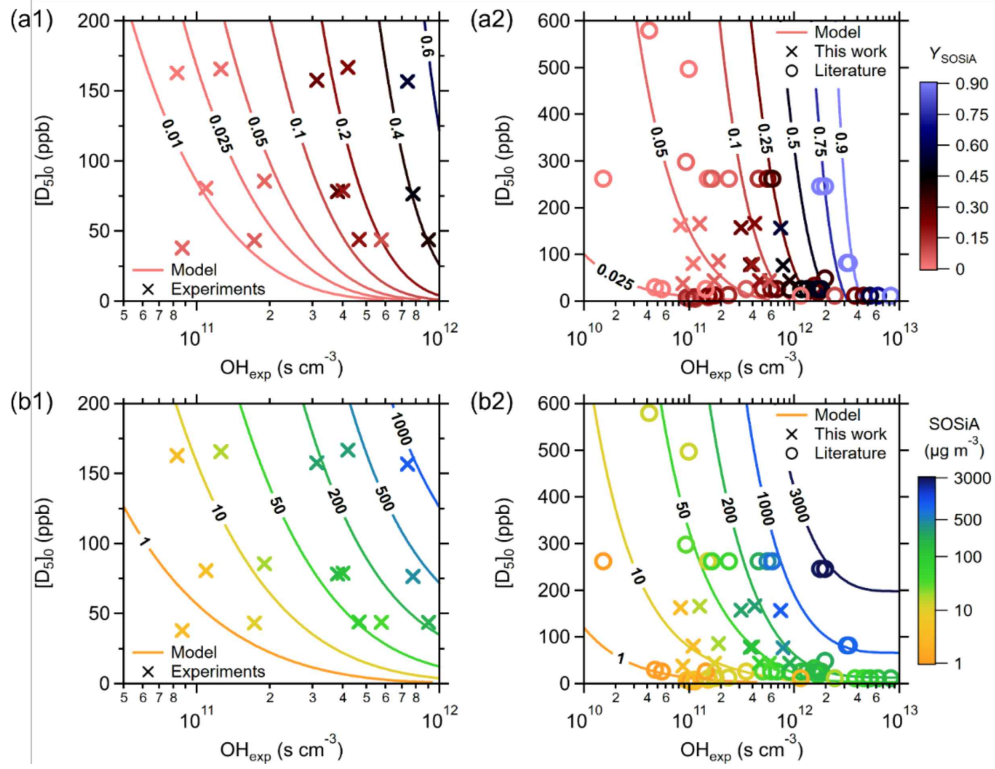
13	2.11 ± 0.76	0.98 ± 0.37
14	1.11 ± 0.24	0.49 ± 0.12
15	1.15 ± 0.29	0.45 ± 0.12

Updates to Figures. Aside from the figures discussed above, we regenerate all the model figures with the revised aging-VBS model.

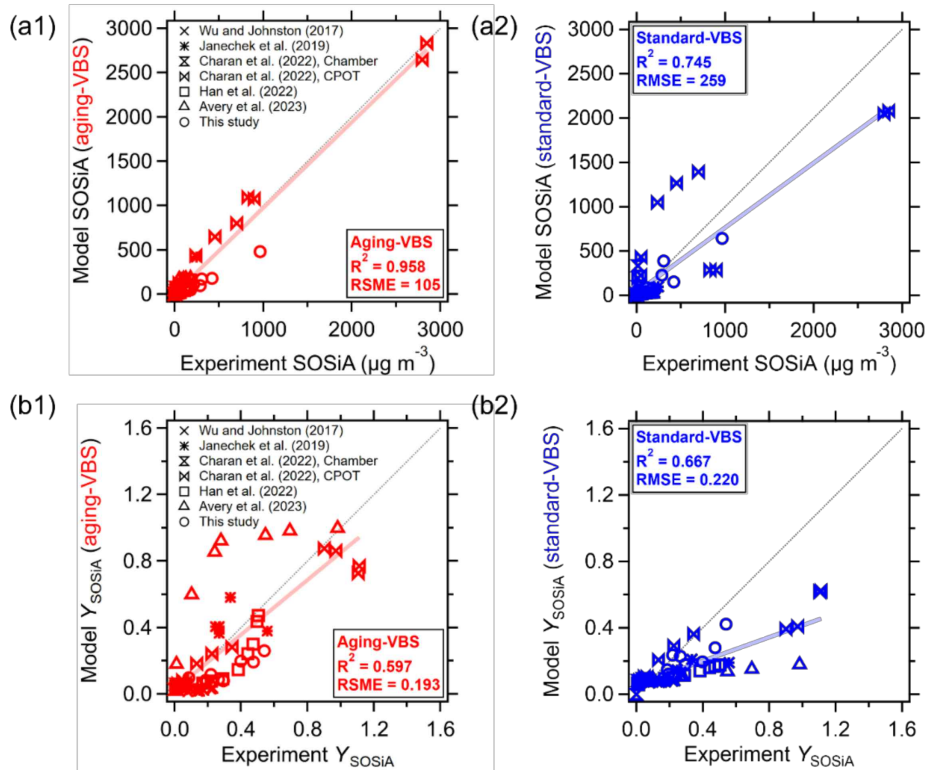
Revised Fig. 5:



Revised Fig. 6:



Revised Fig. S8:



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