

We appreciate the reviewer for providing us useful comments. In the following, original reviewer comments, author's responses, and corresponding updates on the main text are shown as purple, black, and *italic*. Line numbers in the responses correspond to those in the originally submitted version.

Reviewer #2

(2.1) This manuscript investigates the wall loss of organic gases in FEP Teflon chambers at temperatures below 298 K. This is a previously identified gap in our understanding of vapor wall loss in chamber simulations of atmospheric chemistry, and the importance of this question makes studies such as this one essential. The manuscript provides good, useful information about the effects of lower temperature on wall loss, but the study design leaves some significant gaps in understanding that could be improved with revision and potentially some additional experiments.

We thank the reviewer for providing us insightful comments. Responses to the individual comments are given below.

(2.2) Critically, the authors first inject n-alkanes at room temperature and then spend several hours cooling the chamber. Given prior literature on the effect of partitioning to Teflon polymer at temperatures above 298 K, our knowledge of how diffusion coefficients of organic compounds in polymers vary with temperature, and the other conclusions drawn by the authors from this data, I am concerned that the partitioning observed at $t = 3$ hours may be highly path-dependent, and might differ from the partitioning that would occur if the alkanes had been injected into a pre-cooled chamber.

We thank the reviewer for the insightful comment. We compared the results in pre-cooled chamber (at 270 K) with the post-cooled experiment (at 270.2 K) which chamber was cooled down 1 hour after injection. The comparison was presented in the revised manuscript and Figure S2. Generally, the experimental results for pre- and post-cooled experiment provided similar outputs. Results in post-cooled experiments (solid points in Figure S2) align well with the two-layer kinetic model fitting results of pre-cooled experiment (black lines in Figure S2). Specifically, the values of C_{gas}/C_0 at 206 min (measurement timepoint in post-cooled experiment) were 0.26, 0.14, 0.05, and 0.02. While the corresponding values calculated by the fitted model for pre-cooled experiment were 0.20, 0.13, 0.06, and 0.03. The consistency between pre- and post-cooled experiment demonstrated the validity of employing post-cooled operation procedure. It should be noted that in the pre-cooled chamber, particles were detected by OPC to be $0.9 \mu\text{g m}^{-3}$. As a precaution, in the following experiments, cooling was conducted 1 hour after injection to avoid particle formation. We added this discussion in the main text and Figure S2 in supporting information:

In main text:

“For experiments below room temperature, the cooling system of the freezer was turned on one hour after the completion of the injection. The operation procedure was employed to avoid homogeneous nucleation and subsequent condensational growth of aerosol particles. The validity of employing this post-cooled operation procedure was demonstrated by comparison with a pre-cooled chamber result at 270 K (Figure S2).” (Lines 83-85)

Added in supporting information:

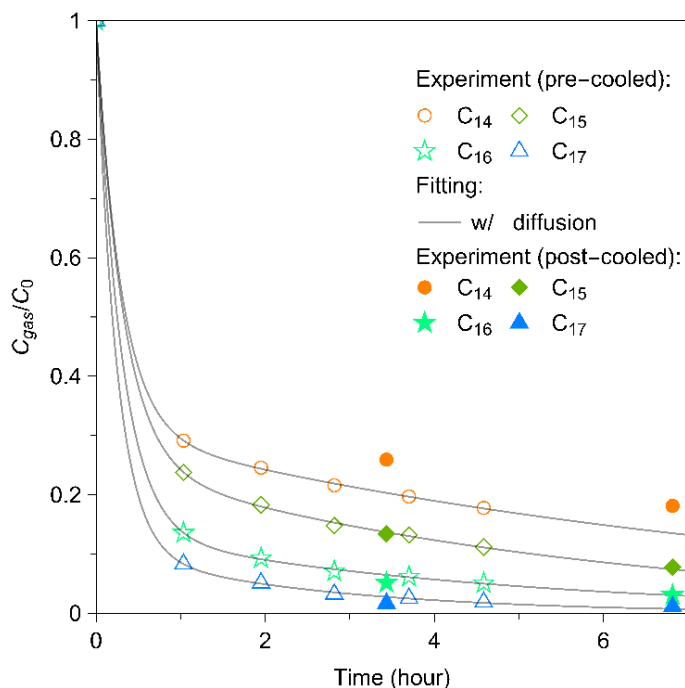


Figure S2. Comparison of C_{gas}/C_0 between pre-cooled experiment at 270 K (hollow points) and post-cooled experiment at 270.2 K (solid points). The two-layer kinetic sorption model was employed to fit the pre-cooled chamber data (black solid lines). Results in post-cooled experiments (solid points) aligns well with the two-layer kinetic model fitting results of pre-cooled experiment (black lines). The consistency between pre- and post-cooled experiment demonstrated the validity of employing post-cooled operation procedure.

(2.3) Investigation of gas-wall partitioning in Teflon tubing at 120 °C (Mattila et al. <https://doi.org/10.1080/10962247.2023.2174612>) has shown that partitioning delays did not vary with temperature. This indicated that the increase in vapor pressure of analytes was largely compensated by an increase in C_w (or $C_{FEP_Surface}$ in the authors' notation). This result suggests that at lower temperatures, one might observe that the decrease in vapor pressure would be offset by a *decrease* in C_w . However, the authors here observe consistent slopes in Figure 5, indicating that the $C_{FEP_surface}/\gamma$ ratio is remaining constant with temperature. And following the authors literature review, the lack of temperature dependence in γ suggests that $C_{FEP_Surface}$ is constant below 298 K.

We Thank the reviewer for introducing us the very interesting paper. Mattila et al. (2023) investigated the sampling delay in measuring per- and polyfluoroalkyl substances (PFAS) by PFA tubing at 30 and 120 °C. The major differences from our present study include the temperature range and differences in chemical characteristics between *n*-alkanes and PFAS. Our conclusion about the constant $C_{FEP_surface}$ was derived solely based on the experimental result for *n*-alkanes. We admit that further studies that employs chemical species that have different characteristics would be needed in the future for understanding the phenomenon in more detail. The following statement was provided in the revised manuscript for addressing the point:

*“The result suggests that equation (8) can be applied to a wide range of temperatures without considering the temperature dependence of $C_{FEP_surface}/(M_{wall}\gamma_{FEP_surface})$ to account for partitioning of ~~a chemical specie~~ *n-alkanes* to the surface layer.”* (Lines 197-199)

“The values of activity coefficients change by 10~20% for a temperature change of 100 K. Further studies, that

employ different chemical species, would be needed in the future for validating and applying the relation to a wide range.” (Line 203)

(2.4) The authors’ retrieval of k_2 (the first-order rate constant representing diffusion in to the bulk polymer) in Figure 7 indicates that at lower temperatures the rate of diffusion into the polymer is slowed. This is consistent with the results of Matilla et al: where at high temperatures there is more polymer available for partitioning, and then here at lower temperatures there is a restriction in the movement of analyte through the Teflon.

We thank the reviewer for the valuable input. Our results about diffusion rate constants are consistent with the results of Mattila et al. (2023). We cited Mattila et al. (2023) in our revised text for supporting the discussion:

“The decrease in k_2 at lower temperature could be induced by reduced viscosity in the inner layer or weakened thermal motion of n-alkane molecules (Mattila et al., 2023).” (Lines 223-224)

(2.5) The potential mechanism that concerns me is that $C_{FEP_Surface}$ may be lower at colder temperatures (less polymer available for sorption), but since the authors’ experimental design first establishes equilibrium at higher temperatures, there is ‘extra’ alkane locked up in the polymer at depths that would not be accessible within 3 h if the injection had been done in a pre-cooled freezer. Given the long timescales for evaporation from FEP, it seems plausible that as the chamber is cooled, the diffusion coefficients drop, and the surface layer potentially shrinks there could be significant mass transfer limitations keeping sorbed alkane at a given depth. In a two-layer model, this would be equivalent to transfer into the bulk polymer due to a shift in the dividing point between the two layers. This would significantly overstate the amount of wall loss compared to a case where the chamber was already cooled at the time an S/IVOC was introduced.

To support the authors’ conclusion that $C_{FEP_Surface}$ is constant with temperature, authors need to demonstrate that the amount of alkane sorbed in the walls at 3 hours is not a path-dependent process. Ideally this would be done through injection of analyte into a pre-cooled chamber. This could be done with just the most volatile alkanes to avoid any issues with nucleation. If this is not an option, another approach would be showing that the partitioning equilibrium at 3 hours is not dependent on cooling rate. In the methods, the authors wait an hour after injecting before cooling the freezer. Alternate approaches could be eliminating this one hour wait; and conversely slowing the cooling rate by gradually lowering the setpoint of the freezer. If the authors observe that the partitioning at 3 hours is consistent across these cases, it would be strong evidence in support of their result that $C_{FEP_Surface}$ does not vary with temperature. If faster cooling (or pre-cooling) gives a significant decrease in the amount of alkane sorbed, that would indicate that there is a strong temperature dependence in C_w , consistent with prior literature.

We thank the reviewer for the constructive comment and suggestion. As previously mentioned in response to comment (2.2), we have conducted the pre-cooled chamber experiment at 270 K for comparison. The experimental result was comparable to that of the post-cooled experiment, demonstrating the validity of employing the post-cooled experiment. We revised the main text and supporting information as mentioned in our responses to comments (2.2) and (2.3).

(2.6) Line 171: Prior literature has established that $C_{FEP_Surface}$ does in fact scale directly with chamber surface area to volume (SAV) ratio. Authors should directly compare the SAV ratio of the Matsunaga & Ziemann chamber to their own, and report if the $C_{FEP_Surface}$ results are consistent.

We thank the reviewer for this input. As described in the response to comment (1.6), We added the SAV ratio in

the Method section and in the comparison with previous results to better explain the enhanced partitioning. The text is revised as below:

“Figure 1 shows the experimental setup. The experiment was conducted using a fluorinated ethylene propylene (FEP) bag with the volume of 1 m^3 . The thickness of the FEP film for the bag was $75\text{ }\mu\text{m}$. The dimension of the bag was $260\text{ cm} \times 55\text{ cm} \times 70\text{ cm}$. The area to volume ratio of the chamber was 7.26 m^{-1} .” (Lines 62-64)

“The enhanced partitioning to the surface layer in our study is likely due to that the chamber for the present study we used is smaller (~~1 m^3 versus 5.9 m^3~~) has a larger area to volume ratio (7.26 m^{-1} versus 3.39 m^{-1}).” (Lines 175-176)

(2.7) Line 207: How does the $C_{\text{FEP_Surface}}$ value compare to the Huang et al recommendation of $C_w = 10.8 * A / V$?

We thank the reviewer for pointing out this question. We assumed thickness of the surface layer ($\sim 5\text{ nm}$) and the density of FEP film (2150 kg m^{-3}), following Huang et al. 2018. Therefore, our $C_{\text{FEP_Surface}}$ value was the same as recommendation of C_w . To clarify, we revised the text as below:

“For the chamber in this experiment, $C_{\text{FEP_surface}}$ =was assumed as 78.2 mg m^{-3} , following the recommendation by Huang et al. (2018b).” (Line 207)

(2.8) Line 211: Literature values for γ_{inf} are all calculated within Huang et al. 2018, who assume a fixed $C_{\text{FEP_Surface}}$ (C_w). References and phrasing here should be updated to reflect the source of the calculated γ_{inf} values and also mention the assumed C_w value.

We thank the reviewer for this suggestion. We cited Huang et al. 2018 and revised the description in manuscript to reflect the source of the calculated γ_{inf} values and to mention the assumed C_w value. The text is revised as below:

“The figure also shows the corresponding parameters obtained from previous experimental studies (compiled by Huang et al. (2018b), including Matsunaga and Ziemann (2010), Yeh and Ziemann (2014, 2015), and Krechmer et al. (2016)). It should be noted the literature results were analyzed with fixed area to volume ratio of 3 m^{-1} and fixed $C_{\text{FEP_surface}}$ of 32.2 mg m^{-3} (Huang et al., 2018b).” (Line 211)

“Figure 6. Activity coefficient ($\gamma_{\text{FEP_surface}}$) of organic compounds in FEP film. The sources of data include this work and the literature (compiled by Huang et al. (2018b), including Matsunaga and Ziemann (2010), Yeh and Ziemann (2014, 2015), and Krechmer et al. (2016))-(Matsunaga and Ziemann, 2010; Yeh and Ziemann, 2014, 2015; Krechmer et al., 2016).” (Lines 411-412)