

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 #1

General Comments

He et al. provide a good preprint in terms of scientific significance and presentation quality. However, I feel that detail is lacking, making scientific quality fair. I cannot currently recommend publication in Atmospheric Measurement Techniques until the specific points below are addressed, some of which I consider to be major revisions, though the editor may consider as minor.

We thank the reviewer for the positive comments on our scientific significance and presentation quality. Responses to the individual comments are given below.

Specific Comments

(1.1) He et al. verify that a two layer model, as detailed in Huang et al. (2018) (<https://doi.org/10.1021/acs.est.7b05575>), with parameter fitting, can reproduce chamber observations of gas-wall partitioning under varying temperatures. Furthermore, they demonstrate that the absorption and diffusion mechanisms of wall loss of uncharged organic molecules have opposite responses to temperature change under dry conditions. The finding around diffusion response to temperature is novel, and it is in the interests of the chamber community that it is published.

Their observations that wall loss of semi-volatile organics is enhanced at lower temperatures is not, to my knowledge, novel, and has been reported by Zhang et al. (2015) (<https://doi.org/10.5194/acp-15-4197-2015>) (who identify a link with pure component saturation vapour pressure, but don't conclude a direct causal relation with pure component saturation vapour pressure), and is observed in the supporting material of Huang et al. (2018) (<https://doi.org/10.1021/acs.est.7b05575>) (though they did not attribute the cause to changed pure component saturation vapour pressure). Furthermore, Matsunaga and Ziemann (2010) (<https://doi.org/10.1080/02786826.2010.501044>) show the relationship between fraction partitioned to wall and component saturation vapour pressure in their Figure 6, implying that whether the saturation vapour pressure changes because of a change of component or because of a change in temperature, the partitioning will change accordingly.

However, Huang et al. (2018) (<https://doi.org/10.1021/acs.est.7b05575>) state that the effect of temperature on gas-wall partitioning requires further study, and this paper is the first to my knowledge to fulfil this request and provide mechanistic insight. It is therefore a valuable paper.

We thank the reviewer for the positive comments. As the reviewer pointed out, Zhang et al. (2015) conducted their experiments for wall loss at 298 K and 318 K. On the other hand, we decreased the temperature for the tropospheric relevant range. Our intention for the present study was to investigate wall-loss process as a function of temperature, as Huang et al. (2018) suggested. The following sentences were added to the revised for stressing the point:

“This study investigated vapor wall loss of C₁₄-C₁₉ n-alkanes in a Teflon chamber for the temperature range of 262

to 298 K by monitoring the evolution of their gas-phase concentrations following a pulse release. *The wall-loss process was investigated as a function of temperature. The experimental results were analyzed using the two-layer kinetic model, which considers partitioning of gas phase SVOCs to the surface layer, as well as further diffusion to the inner layer. Temperature effects on the two processes were evaluated separately.*” (Lines 56-59)

(1.2) I therefore recommend that the title be changed to indicate that mechanistic insight is presented. This way readers will be directed to this article when interested in the mechanisms of gas-wall partitioning in Teflon chambers.

We thank the reviewer for this suggestion. We concur that it is better to clearly indicate the presentation of mechanistic insight in the title. As per the recommendation, we have revised the title as below:

“Wall loss of semi-volatile organic compounds in a Teflon bag chamber for the temperature range of 262-298 K: mechanistic insight on temperature dependence” (Lines 1-2)

(1.3) I recommend that units in terms of minutes be converted to seconds (e.g. k1, k-1, k2), to be consistent with the literature (e.g. Huang et al. (2018) (<https://doi.org/10.1021/acs.est.7b05575>)).

We thank the reviewer for this input. We have converted all units in terms of minutes to be seconds.

(1.4) I also recommend that the mechanistic aspect of greatest novelty – the diffusion through the Teflon interior – is expanded on in the paper. It seems quite feasible to plot k2 as a function of the effective diffusion coefficient of organics through the Teflon, along with a line/curve of best fit and its coefficients, as Huang et al. (2018) (<https://doi.org/10.1021/acs.est.7b05575>) do in their Figure 5. Additionally, then plotting diffusion coefficient (rather than k2 as currently given in Figure 7) against component saturation vapour pressure allows for a better mechanistic understanding and much easier comparison with other publications. The text of the ‘Results and discussion’ section should then be updated to reflect these new figures. If these changes around diffusivity cannot be implemented, the paper should explain why so that future research is able to improve on these experiments. In addition, if these changes around diffusivity cannot be implemented, then the abstract should be changed to discuss the Teflon inner layer interaction in broader terms, rather than inferring that diffusion is the key process in the interaction.

We thank the reviewer for this suggestion. Presenting diffusion coefficient is indeed a valuable suggestion. In our experimental protocol, however, cooling of the chamber was started 1 hour later after injection. Chamber temperature decreased from room temperature to set temperature, which meant that diffusion coefficient would change correspondingly. It is therefore difficult to estimate diffusion coefficients. We explained the reason in the main text and changed the abstract to discuss the Teflon inner layer interaction in broader terms. The text is revised as below:

“On the contrary, diffusion process of n-alkanes from the surface to inner layer slowed down at reduced temperature. Hence the relative importance of the surface and inner layers on wall loss process changes with temperature. Mechanistic studies on these processes will need to be conducted in the future to quantitatively predict the influence of temperature-dependent wall-loss processes of SVOCs on laboratory experimental results.” (Lines 23-26)

“It should be noted that fitting the experimental data using the two-layer model was challenging for the low-temperature experiments, as the chamber was cooled after the injection of n-alkanes. Since the chamber was cooled after the injection of n-alkanes, the model parameters would change correspondingly with chamber temperature.”

(Lines 167-168)

(1.5) He et al. make no mention of the effect of ageing (in their case previous experiments involving injection of alkanes), but for a paper discussing wall losses, this should be at least discussed, if not quantified, as it is in Matsunaga and Ziemann (2010) and in Huang et al. (2018).

We thank the reviewer for this input. Our chamber was newly purchased for the experiment, meaning that it was employed for no other experiments. As for the cases you mentioned, after each experiment, the chamber was heated to ~320 K and continuously flushed by purified air. The cleaning process would last for 2-3 days until the gas concentration of target alkanes decreased to the background level. We added the information of ageing in the text:

“Prior to each experiment, the chamber was heated to ~320 K and continuously flushed using purified air. The cleaning process lasted for 2~3 days until the concentration of investigated n-alkanes dropped to the background level.” (Lines 77-79)

(1.6) The area/volume ratio of a chamber is frequently described in other papers as a key determinant in gas-wall partitioning, therefore to aid readers in their interpretation, it would be useful to have this value given in units of /m in the section describing the chamber. I also find the explanation of enhanced partitioning compared to the Matsunaga results on line 175 to be too brief, and wonder whether the authors could either explain why chamber volume makes a difference, or consider an explanation in terms of area/volume rather than just volume.

We thank the reviewer for this input. We added the area/volume 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 m³. The thickness of the FEP film for the bag was 75 μm. The dimension of the bag was 260 cm × 55 cm × 70 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 m³ versus 5.9 m³) has a larger area to volume ratio (7.26 m⁻¹ versus 3.39 m⁻¹).” (Lines 175-176)

(1.7) Line 88 says that air leaked out of the bag. The authors must provide at least qualitative, and preferably quantitative, evidence that this did not significantly affect the concentration of alkanes in the bag, otherwise a leak of alkanes from the bag could cause the observed decreases in concentration with time, rather than gas-wall partitioning. On this point, have the authors considered that the removal of air from the bag for instrument sampling led to decreased pressure in the bag (rather than air leaks), which in turn led to compression of the bag volume? In this case, pressure inside the bag may have been maintained and therefore gas-phase concentration of alkanes were unaffected by changes in bag volume.

We thank the reviewer for this input. Compression of bag volume was observed during our experiments. But the pressure inside the bag would be maintained. Additionally, our measurements for phthalates ensured room air would not penetrate into the chamber. The gas-phase concentrations of alkanes were therefore unaffected by the changes in bag volume. However, compression of bag volume would lead to an increase in the area to volume ratio. Consequently, this could disrupt the gas-wall interaction, especially the relatively slow diffusion process. This could lead to an

misestimation of diffusion loss rate. We acknowledged that increase of area to volume ratio was a quite challenge. Future studies may benefit from addressing this issue. Based on some photos during the experiment, the leak-out of air could have increased the area to volume ratio by a factor of few. The point was clarified in the revised manuscript:

“Although the air in the bag leaked out during experiments due to compression of the bag by its own weight, absence of intrusion of room air to the bag was confirmed by observing no changes in contaminant signals (Table S2). The gas-phase concentrations of n-alkanes were therefore unaffected by the changes in bag volume.” (Lines 88-89)

“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. It should be noted that compression of bag volume during experiment would lead to an increase in the area to volume ratio. Consequently, this could disrupt the relatively slow diffusion process. Based on some photos during the experiment, the leak-out air could have increased the area to volume ratio by a few factors. ~~Further research, that incorporates changes in FEP film properties with temperature would be needed in the future for quantitatively interpreting the data.~~ Further study, that incorporates considering changes of chamber volume, would be needed in the future for quantitatively interpreting the data.” (Lines 223-225)

(1.8) Line 66 says fans were used, and Figure 1 shows these fans to be outside the bag but inside the chamber housing. The authors must mention how the resulting buffeting of the Teflon bag affects the rate of mixing of air in the bag and therefore the rate of gas-wall partitioning, especially when comparing to other results, such as Matsunaga and Ziemann (2010).

We thank the reviewer for pointing out this question. The fans were used to mixing the air outside the chamber, in order to make air temperature in the freezer to be uniform. As for the mixing of air in the bag, our CO₂ experiment demonstrated that it took ~30 mins for CO₂ to be well mixed in the bag (Fig. S1). No fan was installed inside of the Teflon bag. To clarify, we revised the manuscript:

“Two fans were installed in the freezer (outside the bag) to promote the mixing of the air so that air temperature in the freezer was uniform.” (Lines 66-67)

“The chamber volume was experimentally validated by employing CO₂ as a tracer (Figure S1). The timescale for CO₂ to be well mixed in the bag after a pulse injection was approximately 30 mins (Figure S1).” (Line 64)

(1.9) Given that some of these recommendations are substantial, I expect that the authors will consider making appropriate changes to text throughout the paper beyond the specific locations of text mentioned here.

We thank the reviewer for the valuable inputs. We fully revised the manuscript based on the comments.

Technical Corrections

(1.10) Line 12: consider ‘The wall-loss process’ rather than ‘Wall-loss process’

We thank the reviewer for the suggestion. The text is revised as below:

“The wall-loss process of gas-phase species in Teflon bag chambers has typically been investigated at around room temperature.” (Line 12)

(1.11) Line 23: consider ‘diffusion of n-alkanes’ rather than ‘diffusion process of n-alkanes’

We thank the reviewer for the suggestion. The text is revised as below:

“On the contrary, diffusion ~~process~~ of n-alkanes from the surface to inner layer slowed down at reduced temperature.”
(Line 23)

(1.12) Equation 7 (Line 131): should the C_{gas} term be present in the divisor on the left hand side?

We thank the reviewer for the suggestion. Left side of Equation 7 represented the apparent first-order decay loss constant (Huang et al. 2018). To clarify, we revised the description as below:

“In this case, *the apparent first-order decay loss constant* ~~the loss rate~~ of SVOC from the gas phase can asymptotically be represented as (Huang et al., 2018b).” (Lines 129-130)

(1.13) Line 143: ‘fitted’ rather than ‘fited’

We thank the reviewer for the suggestion. The text is revised as below:

“The experimental result can be well *fitted* using the two-layer model,” (Line 143)

(1.14) Line 228: consider ‘composed of FEP film’ rather than ‘composed of the FEP film’

We thank the reviewer for the suggestion. The text is revised as below:

“The present study investigated the wall loss process of C_{14} - C_{19} n-alkanes to the wall of a 1 m^3 chamber bag, which was composed of ~~the~~ FEP film.” (Line 228)