Reviewer 1

Interactive comment on "Modeling of Gas-Wall Partitioning of Organic Compounds Using a Quantitative Structure-Activity Relationship" by Sanghee Han, Myoseon Jang*, and Huanhuan Jiang

Department of Environmental Engineering Science, University of Florida, Gainesville, Florida, USA

mjang@ufl.edu

We thank reviewer 1 for the valuable comments on the manuscript.

Overall comment:

This manuscript details a modeling framework for estimating the effects of wall losses in environmental chamber experiments using a structure-activity modelling framework. The idea for this paper is creative and addresses a useful topic. Environmental chambers are a critical tool of atmospheric chemistry research and there are many chambers around the world. Not every chamber user has the equipment to accurately measure gas-phase wall losses, and such a formulation would assist in modelling of both past and future chamber experiments. Particularly, investigating the effect of humidity on GWP is useful and needed. There are, however, serious flaws in the quality of the chamber experiments and the interpretation of those results. This work presents major discrepancies with state-of-the-art literature that are not sufficiently explained. Recently, wall loss literature has largely agreed on the principles of the phenomenon. If the authors want to disprove much of this consensus, much more rigorous examination and additional experimentation is needed.

Summary of response to the reviewer 1:

Based on the valuable comments from the reviewer, this manuscript was significantly improved. In summary,

1) The chamber operation procedures (Table R1) are summarized.
2) Additional experiments
    - To verify the significance of the mixing fan on the GWP (Fig. R1).
    - To evaluate the impact of the injection and sampling time on the prediction of GWP (Fig. R2 shows the feasibility of the GWP predictive model for experiment with reduced injection and sampling time).
    - To compare the chemical composition of the organic layer (OM_{wall}) on the Teflon surface of the chamber wall and that of unused Teflon film by using FTIR spectra (Fig. R3)
3) Updating the coefficients in the GWP predictive polynomial equation to include the initial time (17.5 minutes) required for organic vapor transfer and organic vapor

sampling.

4) Discussion about utilizing other chamber data and GWP prediction for other chambers.

The detail responses to the comments from Reviewer 1 are following:

Specific comments:

Comment 1) There is a problem with the SVOC wall loss experiments as they are conducted in the UF-APHOR chamber. The authors inject their SVOC tracers, open the door between two chambers, mix the two chambers vigorously with a fan, and then close the door between them. This process is described as taking 10 minutes (L98 and Section S1), after which the authors start collecting SVOC on their absorbent tube at that point. Recent wall loss measurements (Huang et al., 2018) report characteristic time for GWP ($\tau_{GWP,i}$) time scales from 10 to 20 minutes. Thus, the gas-wall partitioning process in the UF-APHOR chamber in this work has likely finished by the time they start measuring. The measured τ_{GWP} values determined in this work (21 to 144 minutes on L 239; Table. 2) are ~1 order of magnitude longer than those reported by measurements in recent literature (Zhang et al., 2015; Ye et al., 2016; Krechmer et al., 2016; Huang et al., 2018). All report τ_{GWP} time scales from 10 to 20 minutes. In Krechmer et al. (2016) (Fig. S1), the authors demonstrate that using a fan for active mixing significantly increases the diffusion of compounds to the walls, increasing the mixing by a factor of ~10. Because that is what the authors do in this work, it is likely they could expect τ_{GWP} to be on the order of 1 minute, depending on the size of their fan. By starting measurements at 10-15 minutes after turning the fan on, the authors here have missed the bulk of the SVOC decay to the walls. Determining this mixing time scale with a trace gas such as ozone or CO_2 would have been relatively simple and important for understanding these results. If the mixing time scale is < 10 minutes as expected, then starting the experiment after 10 minutes of mixing means that the vast bulk of gas-wall partitioning has occurred before measurement. The authors claim with no experimental evidence that the UF-APHOR chamber has a longer mixing time scale. This is a major experimental weakness of this work and should be rectified before publication.

Response:

In order to clarify the injection of organic vapor to the chamber, we summarized the chamber operation procedure. Table R1 is added to the supporting information.

Table R1. Chamber operation procedures.

	Duration	Low RPM gear motor Fan	Middle door	East chamber	West chamber
Vaporization of organics to the East chamber (low RPM mixing fan on)	30 minutes	East only	Closed	Organic vapors	Clean
Transfer of organic vapor from the East chamber to the West chamber	10 minutes	Both chambers	Open	Organic vapors	Organic vapors

Sampling from the West chamber	Sampling began immediately after closing the door. Using the two sampling lines, the time gasp between sampling is short.	Off	Closed	No use	Use

a. Chemical injection time: UF-APHOR, a duel outdoor chamber (East chamber and West chamber), benefits the reduction of the time to vaporize organic species to the chamber. To avoid the chemical reaction between organic compound groups (i.e., alcohol and acid) at high temperature, the vaporization of organic compounds was performed through several batches. Generally, heating of the chemical injector under clean air streams requires at least 30 minutes for the vaporization of several batches of organic compounds. During the vaporization of organic compounds into the East chamber, the middle door (1 m x 1 m) between the two chambers was closed. After the completion of the chemical vaporization and mixing, the middle door between the two chambers was opened for 10 minutes to transfer organic vapor from the East chamber to the West chamber (see Table R1). Thus, the actual chemical injection time to the West chamber is 10 minutes. Organic vapor sampling from the West chamber began, immediately after closing the middle door,

b. Impact of a mixing fan: In order to evaluate the impact of the mixing fan on chamber gas mixing time, we conducted the separated experiments. CCl_4 was introduced into the East chamber. The CCl_4 concentration in the East chamber monitored using GC/FID over the course of time with and without the mixing fan to observe the impact of mixing fan on the mixing time. We found that the impact of the low-RPM gear motor fan on the air mixing is negligible. As seen in the Figure R1, no difference appeared in the mixing time between mixing with the fan and that without the fan. The chamber air mixing almost completes within a time shorter than 2 minutes via the Eddie flux. The chamber is too large to be impacted by such a small fan (with a low RPM gear motor). Additionally, we measured the CCl_4 concentration during the transferring chemicals from the East chamber to the West chamber for 15 minutes. As shown in Fig. R1 (b), CCl_4 is immediately dispersed into the chamber. The mixing time is almost synchronized with the time amount for exchanging the chamber air between two chambers. Repeatedly, we found that the small mixing fan was inefficient. Thus, we conclude that the diffusion of compounds to the walls might not be affected by our mixing fan.

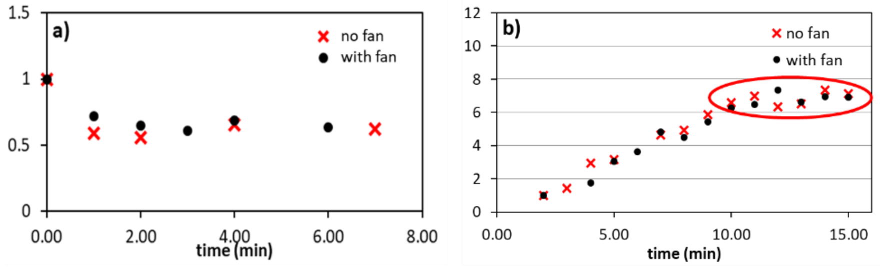

Figure R1. Impact of the low-RPM mixing fan on the relative concentration of CCl_4

(conc./initial conc.) in the chamber. The relative concentration of CCl_4 in the west chamber with and without mixing fan. (a) Relative concentrations of CCl_4 with no fan and with the mixing fan. (a) Relative concentrations of CCl_4 during transferring CCl_4 vapor from the East chamber to the West chamber with no fan and with the mixing fan in the West chamber.

c. Impact of mixing time and the initial sampling time: There is an uncertainty in the calculation of the characteristic time of GWP (k_{on} and k_{off}) associated with the time requirement for chemical injection (10 minutes) and the collection of the first sample at 7.5 minutes (mid-point of 15 minutes sampling). By considering those delays, the actual time for the first sample is 17.5 minutes. Based on this time, we updated the polynomial equations to predict $k_{on,i}$ and $K_{w,i}$. To evaluate the impact of mixing time and the sampling time on the GWP prediction, we conducted the additional experiment with the reduced air transferring time from the East to the West chamber: the first sampling time at 11.5 minutes with 8 minutes organic vapor transferring time and sampling at 3.5 minutes (7 minute sampling) after closing the door between two chambers. These data set was evaluated using the updated polynomial equations as seen in Figure R2.

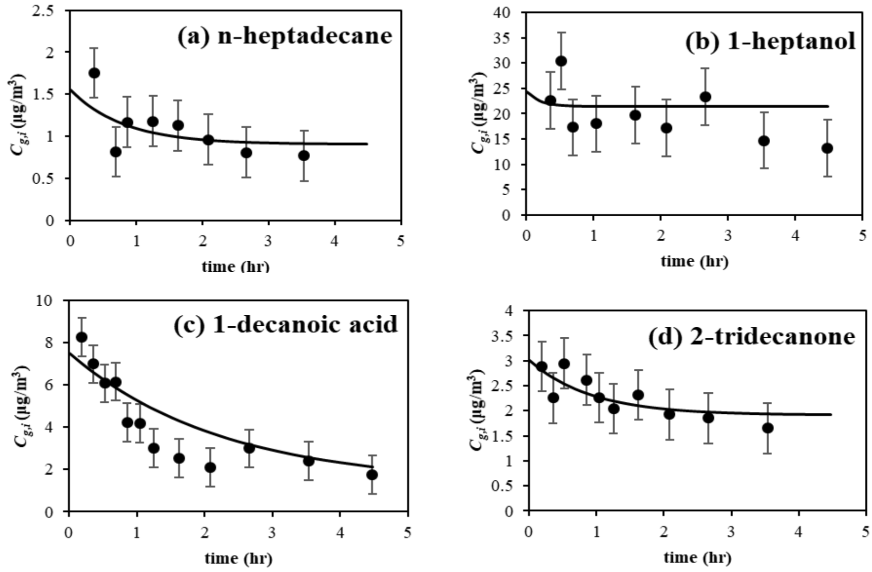

Figure R2. The evaluation of the suitability of the updated polynomial equation against the measurement from additional chamber data (09/30/2019) with the first sampling time at 11.5 minutes (8 minutes organic vapor transferring time + sampling time at 3.5 minutes (7 minute sampling) immediately after closing the middle door between the two chambers)

Comment 2) L. 99 and L312: The authors attribute their much longer characteristic time for GWP ($\tau_{GWP,i}$) value than other literature values to the small surface area/volume (A/V) ratio (1.65) of the UF-APHOR chamber (vs. 3.0 in Yeh and Ziemann). According to the parameterization provided in McMurry and Grosjean (1985), the wall loss rate should actually be slightly faster than the one reported by Yeh and Ziemann (2015). What is the reason for the wide discrepancy in modelled $\tau_{GWP,i}$ of this work?

Response:

It seems that the reviewer misunderstood the impact of surface/volume ratio (A/V). The smaller number means the less wall loss of organic vapor with a slower wall loss rate. Based on the Eq. 5 of McMurry and Grosjean (1985), the smaller A/V ratio leads the slower gas deposition rate (β_g).

$$-\frac{1}{C_1}\frac{dC_1}{dt} = \beta_g = \left(\frac{A}{V}\right)\frac{\alpha\bar{v}/4}{1.0 + (\pi/2)[\alpha\bar{v}/[4(k_e D)^{1/2}]]} \quad (5)$$

The characteristic time of the GWP is calculated by Eq. 13 in the manuscript.

$$\tau_{GWP} = \frac{1}{k_{on,i} + k_{off,i}}$$

The $k_{off,i}$ is related to $k_{on,i}$ and $K_{w,i}$ as follows (Eq. 7)

$$K_{w,i} = K_{OM,i} OM_{wall} = \frac{k_{on,i}}{k_{off,i}}$$

Thus, the characteristic time can be rewritten as

$$\tau_{GWP,i} = \frac{K_{W,i}}{k_{on,i}(K_{W,i} + 1)}$$

The $\tau_{GWP,i}$ is generally greater with the smaller $k_{on,i}$. Thus, the $\tau_{GWP,i}$ in this study should be larger than that reported by Yeh and Ziemann (2015).

Comment 3) L244: The authors also attribute the discrepancy to the high RH of the chamber. While this is possible and would be an interesting and useful result, they do not perform any experiments at the University of Florida under dry conditions. While it is useful to compare their own experiments against the Yeh and Ziemann (2015) and Matsunaga and Ziemann (2010) experiments, the UC Riverside and UF chambers are different. Indeed, in other sections (L49-50), the author group here claim that the age of the chamber makes a difference in the GWP. If that were the case, then how can they use the Ziemann group results in the same model with the UF chamber results without controlling for these effects? Thus, they cannot suitably make this claim (that $\tau_{GWP,i}$ is larger due to the high RH) without additional experimental evidence.

Response:

a. Limitation in the reduction of RH in the outdoor chamber: To avoid the photochemical reaction of organic vapor, all experiments were performed at night. The outdoor chamber is limited to reduce humidity at nighttime. During the daytime, humidity can reach to below 10 percent by addition of the dry tank air. However, the chamber humidity increases at nighttime when temperature drops. We waited for the stable temperature and humidity. It is difficult to reduce chamber humidity at night to the extremely dry condition (less than 0.3) because of the large volume of chamber. Prior to each experiment, the chamber air was dehumidified for three days and used two dry air tanks during the daytime at the experimental day. Then, we can reach to 0.4 RH at night under relatively constant temperature as seen in Table 1 in the manuscript.

b. Feasibility of the QSAR approach to the data sets from different chamber: Ultimately, our predictive model aims to predict GWP of organic vapor originating from any chamber with the chamber specific parameters (OM_{wall} and A/V ratio). Although the chamber specific parameters in the chamber data reported by Yeh and Ziemann (2015) and Matsunaga and Ziemann (2010) are different, we was able to use their chamber data with their chamber characteristic parameters. Additionally, the predictive GWP model was tested for two different experimental sets that were not used to the model development. Those data were different in the RH range (Figure S7 for revised SI) or the initial sampling time (Figure R2, Figure S3 was newly added to the revised manuscript).

Comment 4) L49-50: The model in this work assumes that gas-wall partitioning of vapors occurs by absorption into organic material (OM) deposited on the Teflon walls. This assumption has been shown previously by Matsunaga and Ziemann (2010) and Zhang et al. (2015) to be incorrect. Matsunaga and Ziemann clearly show that gas-phase compounds are lost at equal rates and amounts to new and old chambers. Further, Matsunaga and Ziemann provide additional evidence and a mechanism based on Eyring hole theory. If the authors here want to overturn this precedent, then they need to perform experiments, such as those like Matsunaga and Ziemann with clean and dirty chamber walls and show a difference.

Response:

In this study, we assume that gaseous SVOCs partition onto OM_{wall} of the Teflon film. OM_{wall} consists of the low volatile organic mass ($M_{wall-OM}$) and the water content ($M_{wall-water}$) that is modulated by the chemical composition of $M_{wall-OM}$ and humidity. In order to characterize the chemical compositions of OM_{wall}, FTIR spectra of OM_{wall} were measured. OM_{wall} was obtained by extracting the surface of the fresh Teflon film or the aged Teflon film (the chamber used for SOA experiments) as seen in Fig. R3. The curve fitting analysis of the FTIR spectrum indicates that the aliphatic functionality (C-H stretching bend) is dominant and a small quantity of oxygenated functionalities, such as carbonyl, alcohols, and carboxylic acid, is minor in samples collected at different time and film spots. The FTIR spectrum of OM_{wall} originating from the fresh Teflon film and that of the aged chamber wall shown similar spectra as seen in Fig. R3 (Fig. S4 in the revised SI).

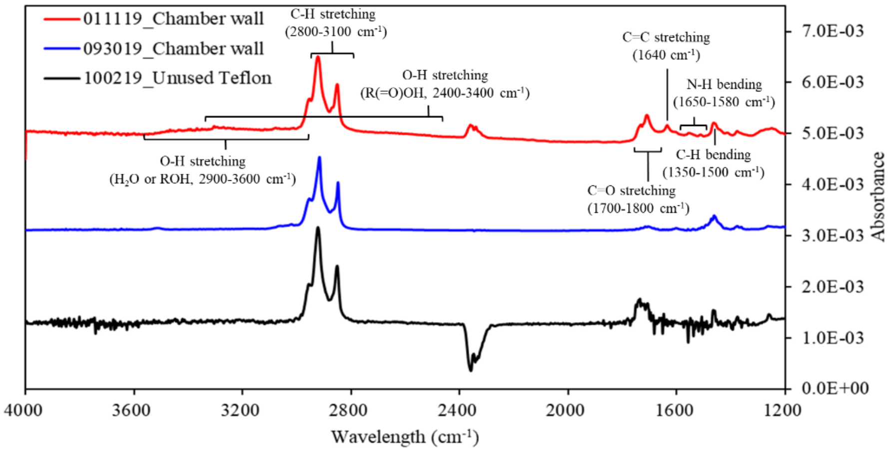

Figure R3. FTIR spectra of the OM_{wall} for the Teflon film chamber wall (measured on 09.30.2019 and 01.11.2019) and the unused Teflon film (measured on 10.03.2019).

The aliphatic hydrocarbons (C-H stretching bend) is major components in extracted organic matter while a small quantity of oxygenated functionality (carbonyl, alcohols, carboxylic acid, nitrate) varied in samples collected at different time. Interestingly, the adsorption of organics on the glass window has been reported in studies of indoor air (Eichler et al., 2019; Weschler and Nazaroff, 2017). Based on the study by Liu et al. (2003), the major compounds found on the glass window includes long chain alkanes and long chain-alkanoic acids, which are hydrophobic.

In particular, the fresh Teflon film has wax-like film layers. After the Teflon film is produced in industries and the film will be shipped to research institutes or chamber manufacturing companies. Most cases, the Teflon film is exposed to the ambient air and absorb wax-like materials. Furthermore, the wax-like materials slowly decay and stay on the film for many days. The Teflon film is very hydrophobic based on the Hansen's solubility parameters of Teflon (12.7) and can adsorb hydrophobic organics. Our OM_{wall} composition obtained from FTIR results supports the deposition of long-chain alkanes on the chamber wall. Thus, we conclude that Teflon wall of the chamber can adsorb the organic matter from the ambient air and assume GWP as an absorption-desorption of vapor on the OM_{wall}. This wax-like layer would also be very viscous and may affect diffusion of SVOCs. In our model, $K_{w,i}$ can greater for the larger molecule (α_i) suggesting that GWP is influenced by viscosity of OM_{wall}.

References:

Eichler, C., Cao, J., Isaacman-VanWertz, G., and Little, J.: Modeling the formation and growth of organic films on indoor surfaces, Indoor Air, 29, 17-29, 10.1111/ina.12518, 2019.
Huang, Y., Zhao, R., Charan, S., Kenseth, C., Zhang, X., and Seinfeld, J.: Unified Theory of Vapor-Wall Mass Transport in Teflon-Walled Environmental Chambers, Environmental Science & Technology, 52, 2134-2142, 10.1021/acs.est.7b05575, 2018.
Liu, Q., Chen, R., McCarry, B., Diamond, M., and Bahavar, B.: Characterization of polar organic compounds in the organic film on indoor and outdoor glass windows, Environmental

Science & Technology, 37, 2340-2349, 10.1021/es020848i, 2003.

Matsunaga, A., and Ziemann, P.: Gas-Wall Partitioning of Organic Compounds in a Teflon Film Chamber and Potential Effects on Reaction Product and Aerosol Yield Measurements, Aerosol Science and Technology, 44, 881-892, 10.1080/02786826.2010.501044, 2010.

McMurry, P., and Grosjean, D.: Gas and aerosol wall losses in Teflon film smog chambers, Environmental Science & Technology, 19, 1176-1182, 10.1021/es00142a006, 1985.

Weschler, C., and Nazaroff, W.: Growth of organic films on indoor surfaces, Indoor Air, 27, 1101-1112, 10.1111/ina.12396, 2017.

Yeh, G., and Ziemann, P.: Gas-Wall Partitioning of Oxygenated Organic Compounds: Measurements, Structure-Activity Relationships, and Correlation with Gas Chromatographic Retention Factor, Aerosol Science and Technology, 49, 726-737, 10.1080/02786826.2015.1068427, 2015.