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Interactive comment on "Modeling of Gas-Wall Partitioning of Organic Compounds Using a Quantitative Structure–Activity Relationship" *by* Sanghee Han et al.

Anonymous Referee #1

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General comments:

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.

Specific comments: 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 (Zhang et al. 2015, Ye et al. 2016, Krechmer et al. 2016, 2018. Huang et al. 2018) report tau_GWP 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 tau_GWP values determined in this work (21 to 144 minutes on L 239; Table 2) are $\sim$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, 2018. Huang et al. 2018). All report tau_GWP time scales from 10 to 20 minutes. In Krechmer et al. 2016 (Figure 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 $\sim$10. Because that is what the authors do in this work, it is likely they could expect tau_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 CO2 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.

L. 99 and L312: The authors attribute their much longer tau_GWP value than other literature values to the small SA/V ratio (1.65) of the UF_APHOR chamber (vs. 3.0 in Yeh and Ziemann). According to the parameterization provided in McMurray and Grosjean [1985], the wall loss rate should actually be slightly faster than the one reported by Yeh and Ziemann. What is the reason for the wide discrepancy in modelled tau_GWP of this work?

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 and Matsunaga and Ziemann experments, 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 is larger due to the high RH) without additional experimental evidence.

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. (2014) 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.

Technical corrections: N/A

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