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Atmospheric Chemistry and Physics
Discussions

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

Anonymous Referee #3

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The authors report on a study that aims to allow for prediction of the loss of organic vapors to the walls of Teflon chambers based on the compound identity. This is an interesting framing of a complex problem. However, I unfortunately find that there are fundamental flaws with this study that I do not think can be addressed through revision. The two of these that I think are most important are: (i) the fundamental assumption that vapors partition only to organic matter that is bound to the walls of the teflon chamber, rather than to the chamber itself, and (ii) the quality of the data shown does not appear sufficiently high to allow for robust determination of the desired properties, and there are issues with the overall experimental design. A third issue, although one that could be addressed through revision, is that I too often found the study details

and the description of the procedures to be lacking in terms of clarity. After writing my review, I read that of Reviewer #1 and we seem to come to similar conclusions. I unfortunately do not see a path forward for this manuscript.

My specific comments follow below:

L47: I am concerned that this statement, which discusses partitioning into "absorbing organic matter on the Teflon film," demonstrates a misunderstanding of how others have been thinking about the partitioning process. There is clear evidence that the partitioning occurs into the Teflon material directly, without need for any "organic matter." Unless, of course, the authors are referring to the Teflon as "absorbing organic matter." However, by stating that the issue is partitioning into OM that is "on" the Teflon film, it makes it seem as if the authors believe the key issue to be bound OM and not the Teflon material. Adsorbed OM can contribute to the partitioning, but is not necessary. Given the discussion in Section 2.3, where the authors sample OM from the Teflon walls, it seems clear that they are considering only partitioning into wall-bound OM. But this is a small fraction of the apparent wall mass, as used by Matsunaga and Ziemann (2010), that is important to consider. This issue is also raised by Reviewer #1 and is a core limitation of the current study.

L58: it is unclear why this should be the mean molecular weight of the organic material on the Teflon. The MW term is needed to convert from vapor pressure to saturation concentration, and thus should be the MW of the SVOC under consideration.

L62: Differences in O:C ratios does not provide support for there being "diverse functionalities." If the focus is on functionalities, then I suggest the authors focus on functionalities and not generic properties such as O:C.

L68: The definition of alpha_w does not seem correct to me. It is the mass accommodation coefficient to the wall, not "the fraction that reversible uptake of a gas-phase species will occur upon collision with the chamber wall."

L96: It is not clear how the procedure the authors use “reduce[s] the delay attributable to inject chemicals.” Reduces how and from what? The mixing time reported is still 10 minutes, which Krechmer et al. (2017), among others, has shown to be a very long time compared to the time to partition to walls, especially in a highly turbulent chamber as would be the case here based on the procedure described.

L104: The authors state “to ensure particle formation…”. Was there particle formation and was this desired? This does not seem correct.

L102&108: How long were samples collected on the denuders?

L109: Based on the data presented, the measurement uncertainties are undoubtedly underestimated here. It would be useful to have a more accurate representation of the true uncertainty.

Section 2.1: The authors never directly state what chemicals they actually use. This would seem the place to give this detail.

Section 2.3: there is no mention of the RH at which the measurements are made. Are they really made at 10% and 80% RH? How was the RH controlled, if this is the case? How long were samples allowed to equilibrate? This is critical information if the statements regarding the wall-bound OM hygroscopicity are to be believed on L140.

L166: it is unclear to me how this statement is true. If the k_on increases the k_off will increase the balance and give the same Kw, which is an equilibrium property.

L176: is unclear why the Alpha would depend on the chamber area to volume ratio. Alpha is simply a property of the species condensing and material onto which it is condensing.

Eqn 13: It is unclear how equation 13 derives from equation 15. This needs to be shown more explicitly.

L187: I disagree with the authors Monday contend that the change in the functional

group distribution is small year around. They show a total of 2 spectra. The spectra actually show substantial differences. Further, the authors have not quantified any of the differences, taking only a very qualitative approach period if they wish to make this type of statement they need to support their conclusions more with their measurements.

Fig. 3: The data, to me, do not appear of sufficiently high quality to allow for robust determination of the model parameters derived by the authors. In many, or even most, cases the fits to the observations appear poor. I strongly suggest that a rigorous discussion of the measurement uncertainties and data quality, along with the fit quality, is required for this work to be publishable.

Section 4.3: A discussion of uncertainties is lacking entirely. The authors give no sense of whether the (for example) difference of a factor of 7 in Kw for 1-decanoic acid and n-nonadecane is statistically justified.

Overall, I find that the details provided regarding determination of the model parameters are insufficient to truly allow for this study to be reproduced. I think the authors need to do a more thorough job explaining how the calculations work and what assumptions go into them.

I do not find it clear how the authors determined the Kw values. They give a bunch of equations, but how this is determined experimentally is not clear to me. The “polynomial equation” (L179) that is used is not clear, and it is also not clear that this is really an observed value, versus a calculated value, given that the determination relies on calculated values of a variety of parameters. This, to me, makes it circular to compare the Kw to the 1/Ci* values (L249). Perhaps I am simply missing the distinction, but I do not find that the authors have presented their analysis in a sufficiently clear way to understand the details.

Other Comments:

L20: I suggest that the first sentence be rewritten. As currently written, it is not a fully formed sentence. What does “atmospheric process of reactive hydrocarbons” mean? I find this ambiguous and difficult to parse.

L23: SOA can constitute much more than 40% of the OA budget in a region. “Up to 40%” is not correct.

L26: technically, many SOA models are not mass-conserving, and thus do not take a “mass balance” approach.

L38: To what, more specifically, does “the gas-wall process” refer? Conventionally, people have used GWP (in this context) to mean gas-wall partitioning, not process.

L42: “underrated” should be “underestimated” or “under-predicted”.

L44: I suggest these two sentences need be rewritten. They are very difficult to understand, yet I am also not certain that they are correct. What “database?” “Burdensome” how?

L52: The citation of Im et al. (2014) here seems unnecessary and arbitrary.

References: Krechmer, J. E., Day, D. A., Ziemann, P. J., and Jimenez, J. L.: Direct Measurements of Gas/Particle Partitioning and Mass Accommodation Coefficients in Environmental Chambers, Environmental Science & Technology, 51, 11867-11875, https://doi.org/10.1021/acs.est.7b02144, 2017.

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

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