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Interactive comment on "Vapor wall deposition in Teflon chambers" *by* X. Zhang et al.

Anonymous Referee #2

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The authors present measurements of loss rates of oxidized vapors within Teflon chambers. These vapors are produced from photooxidation of high volatility volatile organic compounds on timescales ranging from 1 hr to 7 hrs. After formation, photoxidation was stopped, and the decay of different compounds was monitored using CIMS. After ~12 hrs the temperature of the chamber was increased to induced evaporation of the vapors from the walls. These observations were interpreted to deduce values for the effective absorbing wall mass concentration (Cw) and the accommodation coefficient associated with wall deposition of the vapors. The authors find a relationship between Cw and the compound vapor pressure. They also find a relationship between the accommodation coefficient and the compound vapor pressure. They conclude that loss of vapors to chamber walls may be compound specific and more important for lower volatility compounds that apparently are transferred more rapidly to the walls due to their larger accommodation coefficients. Overall, this is a very interesting and important study. Since I can see this serving as the basis of many future studies and playing a key role in the interpretation of future chamber SOA studies, I think that it is critical that it be as clear as possible, and also fully consider any potential artifacts. My comments are made with this in mind. There are certainly times where more information could be provided to help the reader fully understand what was done. Most importantly, the authors need to consider the implications of vapor deposition during the photooxidation stage, the potential influence of interferences in the CIMS, and the potential influence of (or corrections for) "background" signals in the CIMS. How might any of these influence the results, especially the relationships between Cw and accommodation coefficients with vapor pressure? Specific comments and suggestions are provided below.

P26768/9: The authors might note that microscopic reversibility would suggest that the accommodation coefficient for uptake will be equal to that for desorption, which together influence the time it takes to establish equilibrium.

Regarding Eqn. 1 and 2, does this formulation imply that the concentration of “vapor i that has accumulated on the chamber wall” is in units of per volume of air?

Figure 2 and P26775: One aspect unclear from this figure is whether the signals were corrected for “background.” For some of the compounds, the first point in the time series is close to zero, while for many others it is well above zero. Related to this, for some of the compounds the signal at the end of the experiment is lower than that in the very first data point. It is unclear, as presented, what this means or how it can be interpreted. Is this a decrease below the initial background? One example where this really stands out is in the bottom left-hand panel of the first page of Fig. 2 (26795). The signal of this species (m/z = 241) is relatively constant for a while before shooting up during the photooxidation phase. But by the end of the study the signal has decreased below that initial stable period. Clarification of exactly how the data are being presented with respect to whether a background subtraction has been performed or not is needed.

The authors make no mention of the potential for interferences in the CIMS measurements. More specifically, of detection of two different compounds with the same m/z but different vapor pressures. What is the resolution of the CIMS? Can different compounds with the same nominal m/z be distinguished? What would be the implications if there were two compounds at one m/z, one that decays fast and one that decays slow? Can this be ruled out?

P26755: Where the authors note: “When the chamber temperature was increased from 25 to 45 C, with all the other experimental conditions held constant, the concentrations of most compounds in the chamber increased. . .” they might consider noting that the increase in many cases was relatively minor relative to the initial peak signal.

Eqns. 12 and 13, and subsequent discussion: Here the authors assume that the total amount of species i can be estimated from the “initial” concentration of vapor, which (although not explicitly stated) I assume to be the concentration (CIMS signal) at the point where the lights are turned off. One point raised by Paul Ziemann in his comment is the extent to which vapor wall deposition during the photooxidation/product generation stage might influence the results. Vapor wall deposition during the formation stage would tend to decrease the Ctot,i values, as estimated from the CIMS vapor measurements. This would have the effect of decreasing the numerators, which would in turn decrease the estimate of Cw. To the extent that the (potential) Ctot,i underestimate correlates with vapor pressure, the Cw estimates might then evidence an apparent vapor pressure dependence, as was observed. I think that this possibility needs to be considered, as well as the subsequent consequences for the Henry’s Law interpretation. Additionally, as it is unclear whether the data have been “background” corrected or not, this also needs to be addressed, as offsets due to different species (potentially) having different backgrounds would lead to disparate results. This latter point can be easily dealt with by clarifying the data presentation.

Eqns. 12/13: More details are required at this point in the manuscript regarding the calculation of the species-specific and T-dependent Kw values. The figure caption indicates that the EVAPORATION model is used to estimate compound vapor pressures, but this information should be in the main text. Further, it is not clear what assumption was made regarding the value for gamma, the activity coefficient, or for the assumed molecular weight of the absorbing material, both of which seem to be required in Eqn. 9 to allow for calculation of Kw.

It is also not clear exactly how the information at the two temperatures is used? Are the reported values averages from the two temperatures? Are both reported? Only in the Table 2 caption is it stated that Cw is calculated from the "combination" of the two equations. Is this an average? Are the reported uncertainties from a standard deviation of the two measurements, or some other uncertainty estimate? Do the Cw values from the two temperatures typically agree well? It might also be useful to add the enthalpies of vaporization (which control the T-depedence of the vapor pressure) to Table 2 for reference.

Fig. 3: I appears that 30 min average data are only used for one of the data sets. The caption makes it seem as if both are averaged to 30 minutes. I also recommend the same use of colors as in Fig. 2, for consistency. Overall, however, it is a bit difficult to distinguish between the different experiments. Perhaps if both really are averaged to 30 minutes this will become clearer.

Fig. 4 and P26776: The authors note that "Their [Ziemann and Matsunaga's] estimated Cw values are comparable with those derived from dodecane photooxidation products in the current study. . .", and go on to mention two specific compounds. However, from Fig. 4 it is apparent that 5 compounds were considered for this system: the two explicitly mentioned but then 2 with much lower Cw values and one with a much higher Cw value. Thus, this statement seems overly general. Additionally, the authors might consider adding lines to Fig. 4 to indicate the range determined by Ziemann and Matsunaga.

Eqn. 14: I'm sure the authors are simply being consistent with the literature, but it is a bit confusing when the subscript "H"s do not mean "Henry's Law". Why is "D" used? "Dissolution". The definitions are clearly stated, so this is not a problem per say, but simply a little confusing to the reader.

Eqn. 15: This equation does not follow from Eqn. 14. In Eqn. 14, the kD term is not multiplied by p, but in Eqn. 15 it is. There is a typo in one or the other. This has implications for Eqn. 16, if Eqn. 14 is correct.

P26778: The authors conclude that the dependence of H on the saturation concentration implies a molecular weight dependence to solubility. It would be much more straightforward to simply graph H vs. MW to demonstrate this, as the figure (as currently presented) does not compellingly make the case, especially since there is only a loose relationship between molecular weight and vapor pressure since not all functional groups are created equally.

Additionally, the authors focus their discussion here on molecular weight. But shouldn't the nature of the functional groups also play an important role on solubility? Can this be commented upon?

Eqn. 17: As with Eqns. 12/13, the authors assume here that the maximum gas phase concentration (i.e. CIMS signal) is equal to Ctot, and thus Cw is simply the difference between Ctot and the instantaneous Cv. This does not take into account the possibility (or even likelihood) that vapors can be deposited to the walls during the photooxidation phase of the experiment, especially for the experiment with the longest photooxidation time ($\sim$7 hours). The authors should consider the implications that an underestimate in Ctot would have for their conclusions. As with the Cw/vapor pressure relationship, I can't help but think that some part of the derived alpha/vapor pressure relationship is potentially driven by differences in the influence of vapor wall deposition on the assumed total (vapor + wall) concentration.

Also related to Eqn. 17, it is not entirely clear how the unit differences have been accounted for. Specifically, the Ctot and Cv terms are arbitrary, but Kw and Cw are not. That said, the product Kw*Cw is dimensionless so it may not matter. But I suggest that the authors add some explicit statement here that indicates that they are using the CIMS signals with arbitrary units in their calculations.

The results from SIM.1 should be included in Fig. 2 in addition to the simulation results from SIM.3 (which is equivalent to SIM.2, apparently).

I do not necessarily agree with the conclusion on P26780 that the “outputs from SIM.3 [irreversible uptake] match the experimental data better than those from SIM.1 [reversible uptake] in general.” Certainly there are a few compounds for which SIM.3 does a clearly better job: these tend to be the cases where the decay is visually linear with time and also the extent of loss (decrease from the max signal) is relatively small. But, there are also many cases where I think one could make an argument that the SIM.1 results do a better job. For example, the case shown in Fig. 2S, top left on the first page of Fig. 2S (m/z = 175). It is partly for this reason that I suggest the authors move the SIM.1 results to the main paper; this way the reader can more easily see the differences and decide for themselves which does a better overall job.

On P26781 the authors state: “The correlation of alphaw,i with the average carbon oxidation state (OSC), however, is not strong due to the fact that vapor pressures of small molecules, although highly oxidized, are not necessarily low owing to the short carbon backbone.” This statement should be considered when the authors discuss the relationship between H and molecular weight on P26778 (and mentioned above).

On P26781 the authors report an empirical relationship between alpha and C*. Given everything up to this point, I would have to assume that the C* values in Fig. 5 (as in Figs. 3 and 4), and used to deduce this relationship, were estimated from the EVAPORATION model. The authors then go on to report a relationship between C* and the number of carbon and oxygens in a molecule (Eqn. 21). It is not clear how well this expression reproduces the C*s from EVAPORATION. It seems to me that a critical aspect of allowing for combination of Eqn. 20 and 21 is that the C*’s are internally consistent.

My concern here is that they are not. The authors need to clarify where the C* values in Fig. 5 (and Eqn. 20) come from (EVAPORATION or Eqn. 21). If they come from Eqn. 21, then this is inconsistent with what is shown in Fig. 3 and Fig. 4 (and presumably used the equations up to this point when estimating Kw values). If the C* values in Fig. 5 come from EVAPORATION, then the authors must demonstrate that Eqn. 21 and their derived vapor pressures from EVAPORATION are in good agreement. Alternatively, I suggest that the authors simply remove Eqn. 21 as it is unnecessary. The point being made in Fig. 6 can be made more generally just with words, without Eqn. 21.

Minor: Page 26769: “an species” should be “a species”

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 26765, 2014.