

Response to Reviewer #1

We thank reviewer #1 for the constructive comments. Our specific responses can be found below, with reviewer comments in black and our responses in blue.

This paper presents an approach for describing the loss of organic vapors onto the walls of Teflon chambers typically used in atmospheric chemistry laboratory experiments. An experimental protocol is introduced, complemented with the equations used to interpret the data. The paper is comprehensive and generally well written. The topic is very timely and fits well the scope of ACP. I feel, however, that the issues outlined below need to be addressed before the manuscript can be considered for publication in ACP.

General / major comments:

- My main concern with the current version of the paper is related to the conclusion that the vapor mass accommodation coefficient on the chamber walls is the main parameter defining the deposition rates. How can the authors distinguish this kinetic parameter from the thermodynamic properties (i.e. the equilibrium vapor pressures) of the wall-bound molecules – particularly as the wall-bound mixture composition can be changing over the course of the experiment? It is stated that this parameter correlates with the compound volatility, which might suggest that the accommodation coefficient cannot be reliably distinguished from the equilibrium vapor pressure – in particular over the mixed population of molecules present on the wall. I would think that reliably distinguishing the two becomes particularly problematic as the authors are using an effective organic wall-bound concentration C_w to describe the evaporation rates from the chamber walls. I understand that the used formulations could be seen as an effective framework instead of something related to the exact molecular properties of the vapors. However, the accommodation coefficient and the thermodynamic equilibrium vapor pressures are fundamentally different quantities, and I am not entirely convinced that these parameters can be reliably constrained from the present complex data set. Furthermore, I suspect that the formulation of Eq. 6 causes the information about the accommodation coefficient (if defined as the evaporation and condensation coefficient, see e.g. Kolb et al., Atmos. Chem. Phys., 10, 10561) and the equilibrium vapor pressure to be intertwined (see also

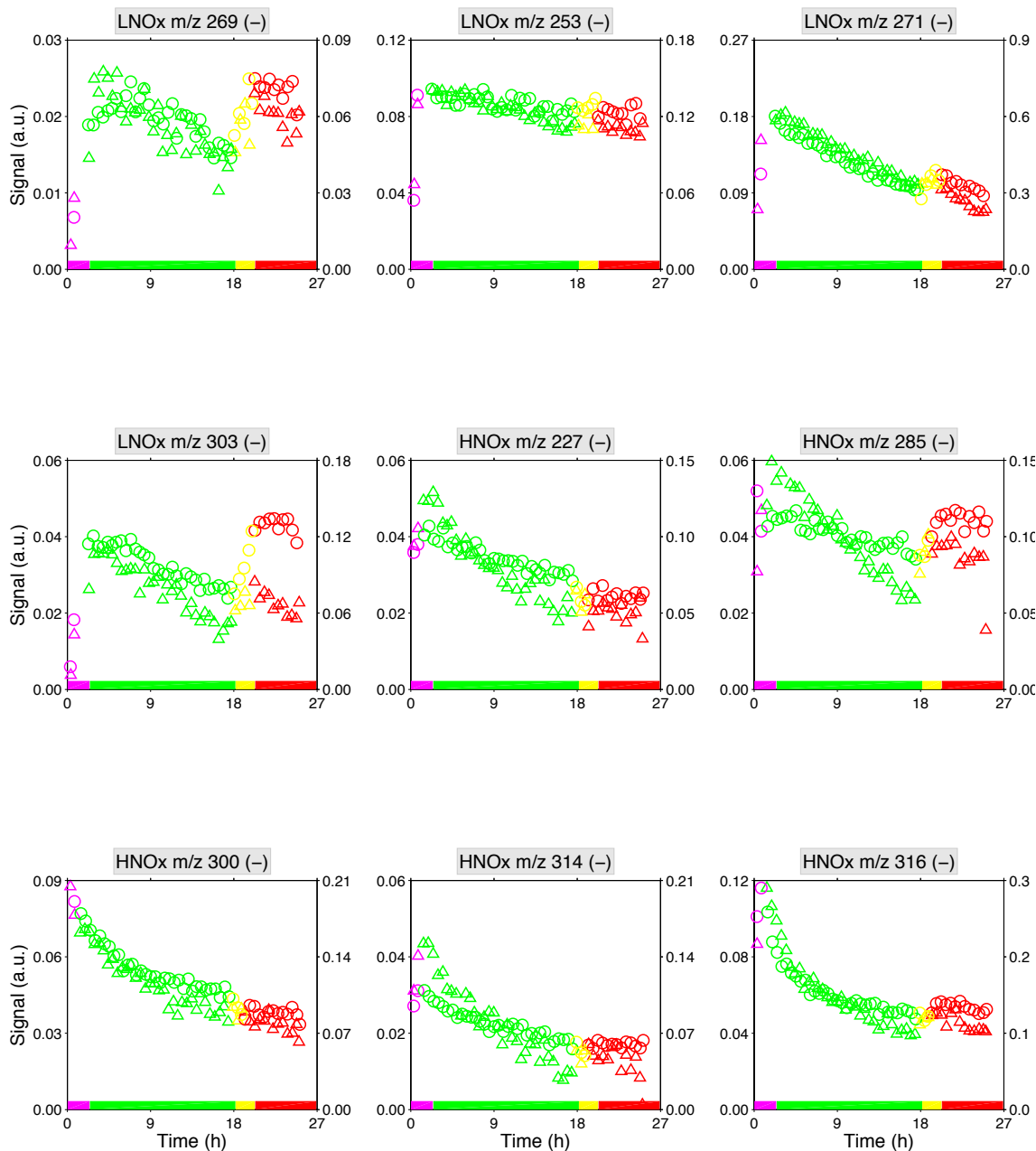
my third comment below).

Reviewer #1 brings up several important issues regarding the development of the theoretical framework that appropriately describes the vapor-wall interactions. We divide the issues into several questions and address them individually, as listed below:

Q1) What is the wall-bound mixture composition of the chamber wall?

A1) The chamber wall is constructed of FEP Teflon films. Theoretically, we treat the wall as a giant homogeneous absorbing medium. The structure of this medium is discussed in Section 5 ‘*Vapor Sorption into FEP Teflon films*’ from the perspective of its solubility behavior. Generally speaking, the FEP Teflon polymer exhibits a glassy state at room temperature (The glass transition temperature of FEP polymer is 339 K). The glassy state is considered to comprise two components: a hypothetical liquid state and a solid state, the latter containing a distribution of microvoids/holes that act to immobilize a portion of penetrant molecules. When the pressure of gas-phase vapors is sufficiently low (e.g., ppb level in the current context), the dissolution behavior of these vapors in the FEP Teflon polymer can be described by Henry’s law at room temperature (See Equations 15, 16, and 17 for more details in the revised manuscript).

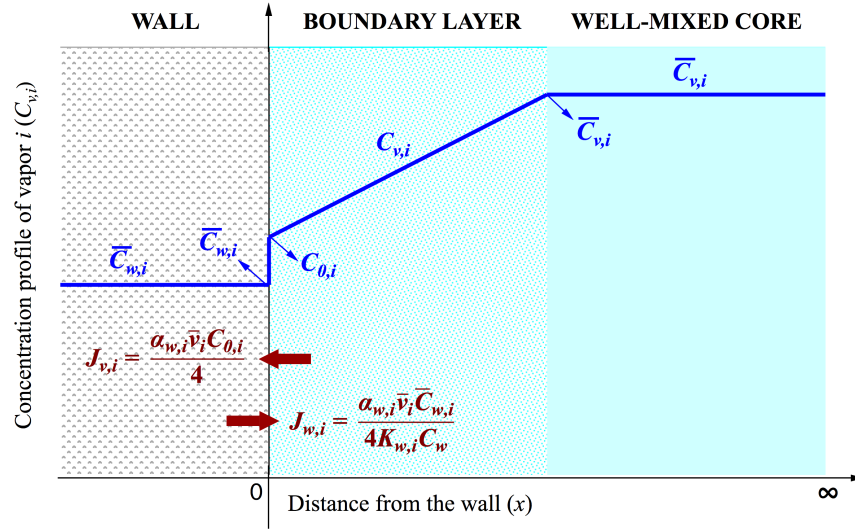
That the absorbing medium on the wall is composed primarily of SOA material can be ruled out by conducting vapor wall deposition experiments in used vs. unused Teflon chambers. As shown in the Figure below, which is now Figure 4 in the revised manuscript, the wall-induced dark decay rates of organic vapors generated from α -pinene+OH reactions under low-NO_x conditions in brand new 24 m³ FEP Teflon chambers (denoted as circles) are consistent with those measured in the chambers (denoted as triangles) that have been intensively used for ~ 2 years. This behavior, which was also observed by Matsunaga and Ziemann (2010), indicates that the primary absorbing medium on the chamber wall is the FEP Teflon film itself, consequently, the interaction of SOA material deposited on the chamber wall with suspended organic vapors seems to be weak.



Q2). Is it a problem to use the effective organic wall-bound concentration C_w to describe the evaporation rates from the chamber wall?

A2). The treatment of the gas-wall interface in the present study is by analogy with the conventional treatment of gas-particle interface (see Section 12.2.2 on Page 551-552 in Seinfeld and Pandis, 2006). Note that the gas-wall interface is a layer with infinitesimal

thickness, at which molecules arrive from the gas phase, return back to the gas phase, and diffuse into the wall. Note that this gas-wall interface differs from the boundary layer adjacent to the chamber wall. Overall, as shown in the figure below (Figure 1 in the revised manuscript), four layers are considered to exist in the gas-wall interaction processes: the well-mixed core in the chamber, a boundary layer adjacent to the chamber wall, the gas-wall interface itself, and the wall layer.



At the gas-wall interface, the flux of molecules i arriving from the gas phase is given by the kinetic theory of gases:

$$J_{v,i} = \frac{\alpha_{w,i} \bar{v}_i C_{0,i}}{4} \quad (1)$$

where $C_{0,i}$ is the gas-phase concentration of organic vapor i at the surface of the chamber wall. This flux is a result of imperfect accommodation of organic vapors by the wall. $C_{0,i}$ can be further expressed as:

$$C_{0,i} = \frac{\bar{C}_{v,i}}{\pi \alpha_{w,i} \bar{v}_i / 8 (D_i K_e)^{1/2} + 1} \quad (2)$$

The derivation of Equation (2) is given in Section 2.1 in the manuscript. Substitution of Equation (2) into Equation (1) gives:

$$J_{v,i} = \frac{\alpha_{w,i} \bar{v}_i \bar{C}_{v,i} / 4}{\pi \alpha_{w,i} \bar{v}_i / 8 (D_i K_e)^{1/2} + 1} \quad (3)$$

The flux of molecules i that evaporate from the interface back to the gas phase ($J_{w,i}$) depends on the concentration of i in the wall ($\bar{C}_{w,i}$). So we can write $J_{w,i}$ as a function of $\bar{C}_{w,i}$:

$$J_{w,i} \propto \bar{C}_{w,i} \quad \text{or} \quad J_{w,i} = \lambda \bar{C}_{w,i} \quad (4)$$

where λ is simply a quantity that reflects the positive correlation between $J_{w,i}$ and $\bar{C}_{w,i}$. If equilibrium exists between the gas phase and the wall, then

$$J_{v,i, (eq)} = J_{w,i, (eq)} \quad (5a)$$

and

$$k_{w,depo,i} \times \bar{C}_{v,i, eq} = k_{w,evap,i} \times \bar{C}_{w,i, eq} \quad (5b)$$

Therefore,

$$\lambda = \left(\frac{\alpha_{w,i} \bar{v}_i / 4}{\pi \alpha_{w,i} \bar{v}_i / 8 (D_i K_e)^{1/2} + 1} \right) \frac{\bar{C}_{v,i, eq}}{\bar{C}_{w,i, eq}} = \frac{\alpha_{w,i} \bar{v}_i / 4 H_i}{\pi \alpha_{w,i} \bar{v}_i / 8 (D_i K_e)^{1/2} + 1} \quad (6a)$$

and

$$\frac{k_{w,evap,i}}{k_{w,depo,i}} = \frac{\bar{C}_{v,i, eq}}{\bar{C}_{w,i, eq}} = \frac{1}{H_i} \quad (6b)$$

where H_i is the unitless Henry's law constant of compound i , assuming both $\bar{C}_{v,i, eq}$ and $\bar{C}_{w,i, eq}$ have units of g m^{-3} . H_i can also be expressed as:

$$H_i = \frac{\bar{C}_{w,i, eq}}{\bar{C}_{v,i, eq}} = K_{w,i} C_w \quad (7)$$

where $K_{w,i}$ is the gas-wall partition coefficient and C_w is the equivalent absorbing organic mass on the wall. This expression is obtained by analogy with equilibrium gas-particle partitioning theory.

Substitution of Equation (6a) into Equation (4) gives:

$$J_{w,i} = \frac{\alpha_{w,i} \bar{v}_i \bar{C}_{w,i} / 4H_i}{\pi \alpha_{w,i} \bar{v}_i / 8(D_i K_e)^{1/2} + 1} \quad (8)$$

So far, the vapor fluxes at the gas-wall interface are given by Equations (3) and (8). Returning to Reviewer #1's question: yes, we do use C_w to express the evaporation rate constant. However, the key parameter that governs the evaporation rate constant is the compound-specific Henry's law constant H_i . Of course, the solubility of individual compounds also depends on the nature of chamber wall. As noted earlier, the chamber wall is considered as a giant homogeneous absorbing medium, based on the evidence from vapor wall deposition experiments in used vs. new chambers. As shown in Figure 5b in the revised manuscript, H_i increases with decreasing compound volatility, indicating that larger molecules tend to dissolve more readily in the FEP polymer. As a result, the evaporation rate, which is a function of H_i , depends most strongly on the compound, rather than on the properties of the wall or the mixed SOA material on the wall. Thus, based on the experimental evidence, the expression for the evaporation rate constant expression is deemed to be appropriate.

Q3). Definition of accommodation coefficient and its meaning in this study?

A3). As a vapor molecule encounters the chamber wall, the fraction of those encounters that lead to uptake is represented by the accommodation coefficient ($\alpha_{w,i}$). Because of imperfect accommodation, the gas-phase concentration of vapor i at the surface of wall is not zero, but $C_{0,i}$. We incorporated this parameter via Equation (6) to represent the flux of gas-phase molecules sticking to the wall. Thus, $\alpha_{w,i}$ describes vapor-wall partitioning by analogy with gas-particle partitioning theory. Note that the diffusion of molecules i in the wall layer is not considered. As shown in the Figure above (Figure 1 in the revised manuscript), the value of $\alpha_{w,i}$ reflects not only the resistance to the mass transfer over the gas-wall interface, but also to the diffusion process in the chamber wall itself.

- I am also curious about what kind of phase the wall-bound molecules are assumed to be in? From the presentation of the framework I get the impression that the walls are treated as spatially homogeneous absorbing media. Can it be ruled out that the absorbing media

on the walls would instead be small droplets of the SOA material that form by heterogeneous nucleation on the chamber walls (the first steps of which could be limited by adsorption onto the walls)? If yes, how? If no, how would it change the presented theoretical framework?

This issue has been addressed in Q1) and A1).

- It is not entirely clear to me how the authors arrive at the equality expressed by Eq. 6. As far as I understand the first form of the equation is based on the Fick's law of diffusion applied over an infinitely small distance from the wall surface – implying that there is a concentration gradient over this length (and thus a sufficiently large number of molecules present), right? On the other hand, the final form on the right hand side is just the kinetic flux of molecules with the concentration c_0 . Could the authors elaborate on how they arrive to this equality? Furthermore, shouldn't the right-most kinetic form of Eq. 6 contain also the evaporation rate from the wall (multiplied with the evaporation coefficient which is equal to the accommodation coefficient) with this formulation? I think this formulation causes information on the equilibrium vapor pressure to enter the values of accommodation coefficients as defined in this study. Or have I misunderstood something? Please clarify.

The thickness of the boundary layer (δ) is small and it is traditionally assumed that a quasi-steady state condition exists in the boundary layer. This is the precondition under which Equation (6) holds. As discussed above, the evaporation rate is part of the model framework.

- Related to the three comments above, a schematic figure clearly outlining the theoretical framework and the underlying assumptions about how the vapor-wall interface is treated (including the definition of the variables and the length scales + the basic theories used in different parts of the interface) would be extremely helpful. I recommend the authors consider adding such a figure.

We have added such a schematic figure now, Fig. 1, as well as corresponding discussion in the revised manuscript.

“Figure 1 depicts the steady-state concentration profiles of an organic compound i in the well-mixed core of the chamber ($\bar{C}_{v,i}$), in the boundary layer adjacent to the wall ($C_{v,i}$), at the wall surface ($C_{0,i}$), and in the chamber wall ($\bar{C}_{w,i}$). Vapor molecules in the well-mixed core of a chamber are transported through a boundary layer adjacent to the wall by a combination of molecular and turbulent diffusion. The transport rate depends on both the molecular properties of the individual organic compound, as well as the extent of turbulent mixing in the chamber. As vapor molecules encounter the chamber wall, the fraction of those encounters that lead to uptake is represented by the accommodation coefficient ($\alpha_{w,i}$). The accommodation coefficient depends, in principle, on the nature of the wall surface as well as the compound chemical composition. Molecules deposited on the wall may re-evaporate at a rate that depends on their concentration in the wall. Overall, the net flux across the gas-wall interface is a result of the flux arriving from the gas phase ($J_{v,i}$) and the flux evaporating from the wall ($J_{w,i}$).”

Specific comments:

- P. 26766, line 5: It is not clear what is meant by ”constraining the nature” of wall deposition. Please be more specific.

We have revised this sentence to ‘We present here an experimental protocol and a model framework to constrain the vapor-wall interactions in Teflon chambers’.

- P. 26768, line 15: What do the authors mean by “physicochemical nature of the chamber walls”? Please be more specific.

The physical nature of chamber wall refers to the idealization of FEP Teflon polymer, as a high molecular weight organic liquid, in which small organic molecules ($M_w < 300 \text{ g mol}^{-1}$ in this study) dissolve. This has been discussed in Section 5 ‘Vapor Sorption into FEP Teflon films’. The chamber wall also provides a sufficiently large surface area for the occurrence of heterogeneous reactions, if present. We consider this perspective on the chemical nature of chamber wall, as discussed shortly in Section 9 ‘Conclusions’.

- Figs. 2-3: The fonts are so small that it is extremely difficult to read the axis labels and

figure titles.

We have revised these figures.

- The authors do good job discussing the older as well as more recent work on the wall deposition of organic vapors. However, to my knowledge at least the recent paper by Kokkola et al. (Atmos. Chem. Phys., 14, 1689–1700, 2014) would be a nice addition to the background with a little bit different perspective than the other mentioned studies.

Kokkola et al. (2014) is definitely a necessary addition to our short overview of recent vapor wall loss studies. We have added this reference to the second paragraph in Section 1 ‘Introduction’: ‘...Kokkola et al. (2014) measured that the fractions of nopinone and pinanediol on the wall of a 4 m³ FEP Teflon chamber at equilibrium are on average 0.4 and 0.8, respectively.’

Response to Reviewer #2

Reviewer #2 brings up several important issues that we have now addressed and clarified. Our specific responses can be found below, with reviewer comments in black and our responses in blue.

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, photooxidation 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 (C_w) and the accommodation coefficient associated with wall deposition of the vapors. The authors find a relationship between C_w 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 C_w 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?

1) Yes, we have added further discussion regarding the meaning of accommodation coefficient in Section 6, also given below:

“The significance of $\alpha_{w,i}$ is twofold: first, the accommodation coefficient for the desorption of organic molecules from the gas-wall interface equals that for the adsorption/uptake process, which together influence the time needed to establish equilibrium; and second, diffusion in the chamber wall is not considered in the theoretical framework and consequently, the best-fit $\alpha_{w,i}$ will reflect the mass transfer resistance in both the gas-wall interface and the chamber wall layer”.

2) Yes, the concentration of vapor i in the chamber walls is in the units of g m^{-3} . We have added an Appendix to the manuscript listing all the quantities and corresponding units, also shown below:

A (m^2): Total surface area of the chamber wall

$\alpha_{p,i}$ (dimensionless): Accommodation coefficient of organic vapor i on particles

$\alpha_{w,i}$ (dimensionless): Accommodation coefficient of organic vapor i on the chamber wall

$C_{0,i}$ (g m^{-3}): Concentration of organic vapor i over the gas-wall interface

C_i^* (g m^{-3}): Saturation concentration of organic vapor i

$\bar{C}_{\text{tot},i}$ (g m^{-3}): Total concentration of organic vapor i in the chamber

$\bar{C}_{v,i}$ (g m^{-3}): Concentration of organic vapor i in the well-mixed core of the chamber

$C_{v,i}$ (g m^{-3}): Local concentration of organic vapor i in the boundary layer adjacent to the wall

$\bar{C}_{w,i}$ (g m^{-3}): Concentration of organic vapor i that has accumulated on the chamber wall

C_w (g m^{-3}): Equivalent mass of absorbing organic material on the chamber wall

\bar{D}_p (m): Number mean particle diameter

\mathcal{D}_e ($\text{m}^2 \text{s}^{-1}$): Eddy diffusivity

\mathcal{D}_i ($\text{m}^2 \text{s}^{-1}$): Molecular diffusivity

δ (m): Thickness of the boundary layer adjacent to the wall

H_i (dimensionless): Henry’s law constant of organic compound i

$J_{v,i}$ ($\text{g m}^{-2} \text{s}^{-1}$): Vapor flux arriving at the gas-wall interface
 $J_{w,i}$ ($\text{g m}^{-2} \text{s}^{-1}$): Vapor flux evaporating from the wall
 K_e (s^{-1}): Eddy diffusion coefficient
 $K_{w,i}$ ($\text{m}^3 \text{g}^{-1}$): Gas-wall partitioning coefficient
 $k_{w,depo,i}$ (s^{-1}): Deposition rate coefficient to the wall
 $k_{w,evap,i}$ (s^{-1}): Evaporation rate coefficient from the wall
 $\overline{M_w}$ (g mol^{-1}): Average molecular weight of the absorbing organic material on the wall
 N_p (m^{-3}): Total number concentration of suspended particles
 $p_{L,i}^0$ (atm): Vapor pressure of organic compound i as a liquid
 γ_i (dimensionless): Activity coefficient in the wall layer on a mole fraction basis
 \bar{v}_i (m s^{-1}): Mean thermal speed
 V (m^3): Total volume of the chamber

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?

1) The time resolution of the CIMS employed in this study is ~ 9 min. The lights on time during each experiment might occur right in the middle of one CIMS measurement cycle. This is why for certain species shown in Figure 2, the starting concentration is even higher than the final concentration after ~ 15 h of dark decay. We have redrawn this figure in the revised manuscript, including 60 min of chamber air sampling period (background) before lights on.

Prior to the start of each experiment, the purified air in the chamber is sampled, and this is subtracted off as the CIMS background signal. The background signal is fairly consistent between the masses and over time. The signals are then normalized by the overall intensities of H_2O_2 and H_2O to ensure a steady supply of the reagent ion (CF_3O^-). We have added the background subtraction description in Section 3.

2) The CIMS employed in this study has unit mass resolution, which means species sharing the same molecular weight might be detected with the same m/z ($[\text{R}\cdot\text{CF}_3\text{O}]^-$ or $[\text{X}_{[\text{H}]} \cdot \text{HF}]^-$). Because of this, we are particularly careful in selecting oxidized organic vapors from each VOC+OH system. For the isoprene+OH, α -pinene+OH, and dodecane+OH systems, organic compounds selected were all identified in our previous studies with proposed mechanisms for their formation and removal pathways. The simulated temporal profiles of individual compounds match well with observations (Paulot et al., ACP, 2009; Yee et al., JPCA, 2012; Zhang et al., ACP, 2014). For the toluene+OH system, we selected only three ions and assigned structures proposed by MCMv3.2 to them. MCMv3.2 simulations of these three compounds match well with the CIMS observed time-dependent profiles. Considering that the previously proposed mechanisms for each compound can explain the CIMS observations very well, it is unlikely that the chance that several products share the same m/z in the current study. However, since we cannot absolutely rule out the possibility, we estimate uncertainties here as a result of the failure to distinguish two compounds with the same nominal m/z . Consider two organic molecules A and B, with formulas of $\text{C}_x\text{H}_y\text{O}_z$ and $\text{C}_{x+1}\text{H}_{y+4}\text{O}_{z-1}$, respectively. According to relationships between the vapor pressure and elemental composition that have been used in the literature (e.g., Donahue et al., 2011; Cappa and Wilson, 2012), addition of one O atom would lead to a decrease of the logarithm of vapor

pressure by 0.6 – 2.2 atm, depending on the actual functionality. Addition of one C atom would in general lead to a decrease of logarithm of vapor pressure by ~ 0.5 atm. As a result, the vapor pressure of molecule B can be up to \sim two orders of magnitude higher than that of molecule A, and accordingly, the wall deposition rate of molecule A would be a factor of ~ 3 -5 higher than that of molecule B.

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.

Yes, we have added a comment on this.

“When the chamber temperature was increased from 25 °C to 45 °C, with all the other experimental conditions held constant, the concentrations of most compounds in the chamber increased to a minor degree relative to the initial peak signal, reflecting modest desorption of vapors from the chamber wall”.

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 $C_{tot,i}$ 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 C_w . To the extent that the (potential) $C_{tot,i}$ underestimate correlates with vapor pressure, the C_w 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.

We did not use the the concentration (CIMS signal) at the point at which the lights are turned off as the total organic concentration ($\bar{C}_{\text{tot},i}$). As shown in Eqs (16) and (17) in the revised manuscript (also given below), $\bar{C}_{v,i@298K}$ and $\bar{C}_{v,i@318K}$ can be measured by CIMS. $K_{w,i@298K}$ and $K_{w,i@318K}$ can be calculated by Eq (14). Two unknown parameters remain, i.e., $\bar{C}_{\text{tot},i}$ and C_w . Here we combine Eqs (16) and (17) and solve them as a equation set so that the calculated $\bar{C}_{\text{tot},i}$ value is actually the total concentration of organic vapor i generated during the photooxidation period. Therefore, we believe there are no significant uncertainties in this calculation.

$$\frac{\bar{C}_{w,i@298K}}{\bar{C}_{v,i@298K}} = \frac{\bar{C}_{\text{tot},i} - \bar{C}_{v,i@298K}}{\bar{C}_{v,i@298K}} = K_{w,i@298K} C_w \quad (16)$$

$$\frac{\bar{C}_{w,i@318K}}{\bar{C}_{v,i@318K}} = \frac{\bar{C}_{\text{tot},i} - \bar{C}_{v,i@318K}}{\bar{C}_{v,i@318K}} = K_{w,i@318K} C_w \quad (17)$$

We have revised the paragraph regarding the calculation of C_w :

“Ideally, C_w can be obtained if the initial total concentration ($\bar{C}_{\text{tot},i}$) and equilibrium gas-phase concentration ($\bar{C}_{v,i}$) of vapor i can be measured by CIMS. However, since the fraction of organic compound i in the chamber walls at the onset of vapor wall deposition is unknown, we estimate C_w via the combination of equilibrium partitioning expressions at two different temperatures, e.g., 298 and 318 K...”

“...In this manner, both $\bar{C}_{\text{tot},i}$ and C_w can be calculated by solving the equation set (16) and (17)”.

Eqns. 12/13: More details are required at this point in the manuscript regarding the calculation of the species-specific and T-dependent K_w 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 K_w .

Yes. We have added these details in the revised manuscript, as shown as below:

“where $p_{L,i}^0$ is the vapor pressure of compound i as a liquid. We calculate $p_{L,i}^0$ by the average of two group contribution methods, ‘SIMPOL.1’ developed by Pankow and Asher (2008) and ‘EVAPORATION’ developed by Compernelle et al. (2011). γ_i , the activity coefficient in the wall layer on a mole fraction basis, is assumed to be unity in this study, R is the gas constant, T is temperature, and \overline{M}_w is the average molecular weight of the absorbing organic material on the wall, which is assumed to be 250 g mol⁻¹”.

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 C_w 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 C_w values from the two temperatures typically agree well? It might also be useful to add the enthalpies of vaporization (which control the T-dependence of the vapor pressure) to Table 2 for reference.

As we explained above, only one C_w value is obtained from calculation combining Eqs (16) and (17) as a equation set because there is another unknown parameter $\overline{C}_{tot,i}$. By doing this, uncertainties for the total amount of vapor i in both gas and wall phases are minimized.

Fig. 3: It 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.

Yes, they are both 30 min average data. We have changed colors and data formats for a clearer view, see Figure 4 in the revised manuscript, also given below (‘o’ for the unused chamber and ‘Δ’ for the used chamber):

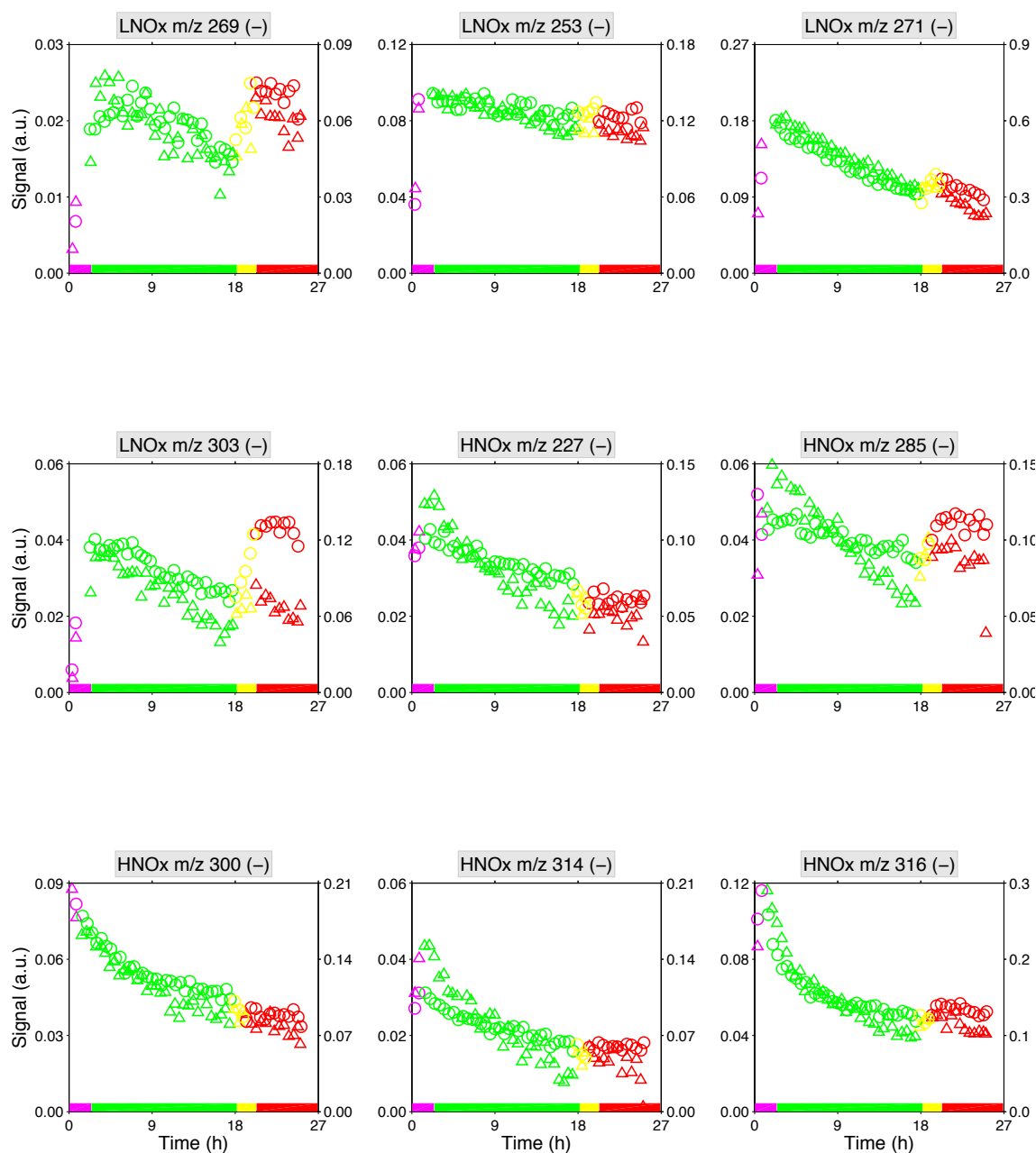


Fig. 4 and P26776: The authors note that “Their [Ziemann and Matsunaga’s] estimated C_w values are comparable with those derived from dodecane photooxidation products in the current study: : :”, and go on to mention two specific compounds. However, from Fig. 4 it is apparent that 5 compounds were considered for this system: the two explicitly mentioned but then 2 with much lower C_w values and one with a much higher C_w 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.

It is a stretch to compare these two studies since there is no overlap between organic vapors detected. Thus, we have deleted this comparison in the revised manuscript. Instead, we have added comparison between a continuous decay over a relatively long time scale observed in this study and a rapid decay followed by the establishment of equilibrium over a relatively short time scale observed by Matsunaga and Ziemann (2010).

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.

Yes, we kept the notation consistent with those in the material science literatures. It is a fair point that this notation be a bit confusing for the readers. We have revised the notation as follows:

$$C = C_H + C_L = k_H p + \frac{C_L' b p}{1 + b p} \quad (18)$$

"...where C is the total vapor concentration in the glassy polymer, C_H is the concentration based on Henry's law dissolution, C_L is the concentration based on Langmuir sorption, k_H is the Henry's law constant, p is the partial pressure in the gas phase, C_L' is the hole saturation constant, and b is the hole affinity constant."

Eqn. 15: This equation does not follow from Eqn. 14. In Eqn. 14, the k_D 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.

Thanks for pointing it out. We corrected the typo:

$$C = (k_H + C_L' b) p \quad (19)$$

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?

The vapor pressure depends ultimately on the size of the molecule, the functionalities attached, and their mutual interactions. The statement regarding "the dependence of solubility on molecular weight" is indeed too generalized. We revised this as *"This behavior suggests that organic vapor solubility in FEP films increases with decreasing volatility, i.e., increasing carbon number and functionalization."*

Eqn. 17: As with Eqns. 12/13, the authors assume here that the maximum gas phase concentration (i.e. CIMS signal) is equal to C_{tot} , and thus C_w is simply the difference between C_{tot} and the instantaneous C_v . 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 (~7 hours). The authors should consider the implications that an underestimate in C_{tot} would have for their conclusions. As with the C_w /vapor pressure relationship, I can't help but think that some part of the derived α /vapor pressure relationship is potentially driven by differences in the influence of vapor wall deposition on the assumed total (vapor + wall) concentration.

We have addressed this issue earlier.

Also related to Eqn. 17, it is not entirely clear how the unit differences have been accounted for. Specifically, the C_{tot} and C_v terms are arbitrary, but K_w and C_w aren't. That said, the product $K_w \cdot C_w$ 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.

Done.

“Note that the product $K_{w,i}@T C_w$ is dimensionless, so that the normalized CIMS signal can be directly substituted into Eqs (16) and (17) as the actual gas-phase concentration of organic vapor i ”.

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).

Done.

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.

We have rewritten Section 6 ‘Accommodation coefficient on chamber walls’ in the revised manuscript. Corresponding discussions are also shown below:

“Simulations using both reversible (SIM.1) and irreversible (SIM.2) vapor wall deposition expressions match the experimental data. Outputs from SIM.1 tend to level off, whereas those from SIM.2 exhibit a continuous decreasing trend at the end of ~ 18 h of vapor decay. The extent of agreement between observations and simulations depends on the nature of vapor wall deposition: most organic vapors in the Caltech Teflon chambers exhibit a continuous decay. The agreement between SIM.1 and SIM.2 indicates that the estimated C_w values are sufficiently large so that the wall-induced vapor deposition in the Caltech chamber can be treated as an irreversible process ($C_w \rightarrow \infty$) within a relatively long timescale (<18 h)”.

On P26781 the authors state: “The correlation of $\alpha_{w,i}$ with the average carbon

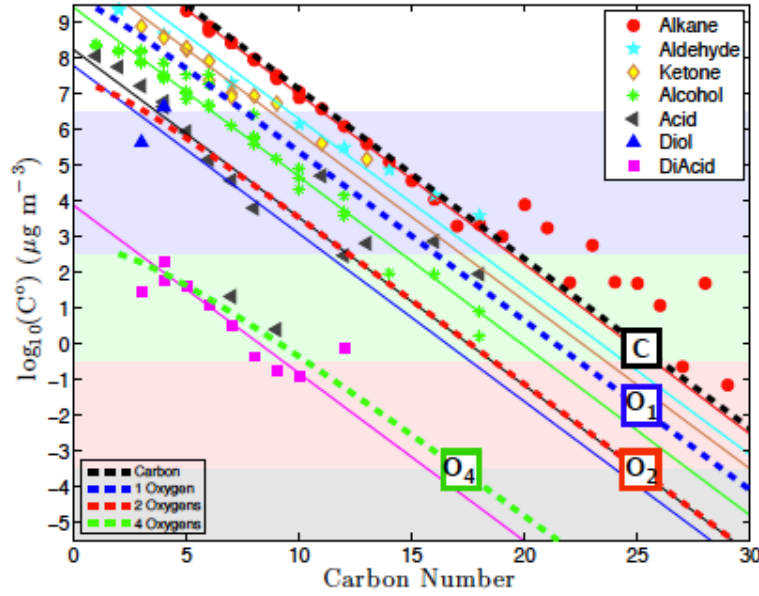
oxidation state (OSC), however, is not strong due to the fact that vapor pressures of small molecules, although highly oxidized, are not necessarily low owing to the short carbon backbone.” This statement should be considered when the authors discuss the relationship between H and molecular weight on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

We agree.

On P26781 the authors report an empirical relationship between α 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 K_w 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.

The correlation of C^* with the carbon and oxygen numbers of a molecule (n_C/n_O), as shown in below, was first developed by Donahue et al. (2011). They have used vapor pressure data from NIST as well as the literature (Koponen et al., 2007; Cappa et al., 2007) to constrain this correlation, see the figure below. This volatility estimation approach, although quite simplified, proves to be very useful considering the fact that we have quite limited knowledge of the structure of organic aerosol constituents, whereas the measurement of the O:C and H:C ratios by AMS has become a routine procedure in many laboratories. In this way, one can reasonably constrain organic aerosol composition based on only two measurable or predictable properties, volatility and the extent of oxygenation.

$$\log_{10} C_i^* = (n_C^0 - n_C^i) b_C - n_O^i b_O - n_N^i b_N - 2 \frac{n_C^i n_O^i}{n_C^i + n_O^i} b_{CO}$$



We suggest the the $\alpha_{w,i}-C^*-n_C/n_O$ relationship is very important for the following two reasons: 1) While it is almost impossible to propose corresponding chemical structures for thousands of ions detected by mass spectrometry during an experiment, the proper guess of a molecular formula, coupled with the $\alpha_{w,i} - C^* - n_C/n_O$ relationship, would be able to constrain the wall-induced decay rate of each ion, and thus provide information to better understand its formation and removal dynamics, and 2) Some semi-explicit models, such as SOM by Cappa and Wilson (2012) or 2D-VBS by Donahue et al. (2011 and 2012), use the n_C/n_O pair to represent possible SOA-forming ‘products’ formed from the photooxidation of a parent hydrocarbon. It is useful to formulate an empirical relationship between the n_C/n_O pair and vapor wall loss rate so that the impact of vapor wall loss on the SOA yield can be estimated by such models.

Reviewer #2 has a valid point that the vapor pressure predictions from the $C^* - n_C/n_O$ correlation might not be consistent with that estimated from the group contribution method. This discrepancy, however, is a result of the thermodynamic underpinning of the $C^* - n_C/n_O$ correlation. For example, addition of one OH group leads to the decrease of vapor pressure of ~ 2.2 in the log scale, whereas addition of one C=O group leads only to

the decrease of vapor pressure of ~ 1.0 in the log scale. However, the $C^* - n_C/n_O$ correlation uses a fixed value of 2.3 for the oxygen-oxygen interaction term, regardless of the structure of functional groups added. Further, volatility data were used to constrain the model performance in the development of both $C^* - n_C/n_O$ correlation and group contribution methods. Therefore, the empirical parameters obtained by optimizing the model output to the volatility measurements should represent the ‘best’ vapor pressure estimation under the current model framework. To verify this point, we have estimated the vapor pressures of 110 species, including C_5 - C_{14} *n*-alkanes, C_5 - C_{14} carbonyls, C_5 - C_{14} di-carbonyls, C_5 - C_{14} alcohols, C_5 - C_{14} diols, C_5 - C_{14} carboxylic acids, C_5 - C_{14} di-carboxylic acids, C_5 - C_{14} peroxides, C_5 - C_{14} di-peroxides, C_5 - C_{14} nitrates, and C_5 - C_{14} di-nitrates, by taking the average from ‘SIMPOL.1’ and ‘EVAPORATION’. We then fit the $C^* - n_C/n_O$ correlation to the predicted vapor pressures. The best-fit parameters are given in the table below, together with those constrained by measured vapor pressure data (Donahue et al., 2011). We can see that the estimated parameters are reasonably close.

Parameters	This study	Donahue et al. (2011)
n_C^0	28.0483	25
b_C	0.4015	0.475
b_O	2.3335	2.3
b_{CO}	-0.4709	-0.3
b_N	3.6000	2.5

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

Done.

Response to Prof. Paul Ziemann

General Comments:

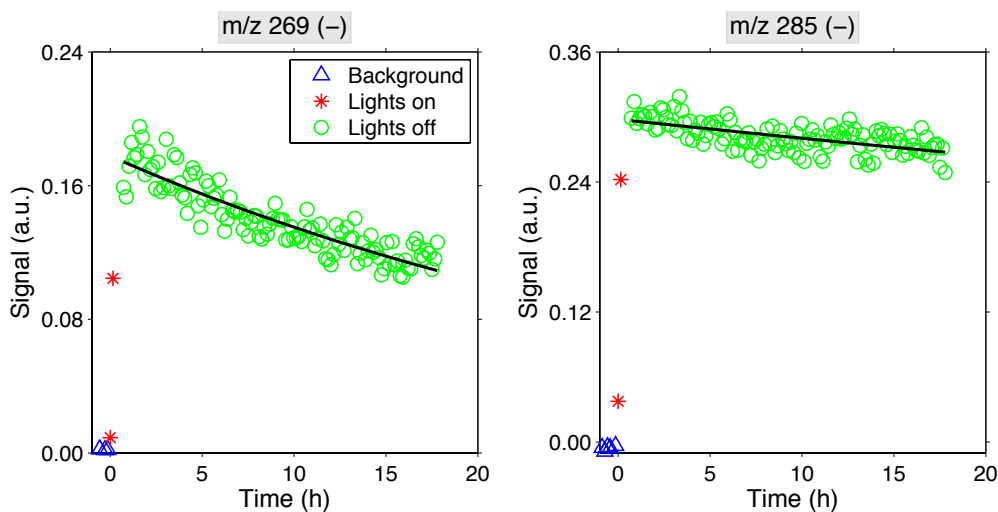
I think this paper presents a valuable approach for investigating gas-wall partitioning of organic compounds in Teflon smog chambers. The use of CIMS (or PTR-MS) to follow wall losses of reaction products seems ideal because these methods can potentially identify a large variety of compounds for which standards are not available, and also monitor in real time the wall losses of compounds that can occur over a range timescales.

Specific Comments:

My one concern with the approach used here is that because of the experimental protocol employed the measurements of wall loss were only begun following 1–7 h of reaction (at which time the lights were turned off), thus precluding the possibility of observing more rapid partitioning that may have occurred. In two previous studies (Matsunaga and Ziemann, AS&T, 2010; Yeh and Ziemann, JPCA, 2014) we observed that hydrocarbons, ketones, alcohols, and alkyl nitrates reached gas-wall partitioning equilibrium on timescales of roughly 10–100 min, and more recently observed the same behavior for acids and diols (publication in preparation). We also observed (Matsunaga and Ziemann, AS&T, 2010) that following this relatively rapid equilibration a much slower loss occurred on a timescale of ~ 100 h ($\sim 1\%$ per hour). In the present study, it is stated in the Abstract that losses can occur on timescales of minutes to hours, but for the results presented it appears that the range is ~ 10 –100 h. In a previous study by this group (Loza et al., ACP, 2014), similarly long timescales of ~ 100 –200 h were also observed using a CIMS to monitor the loss of C₁₂ ketone and alcohol standards that had been added to the chamber. There it was suggested, however, that rapid losses similar to those we have observed would probably not be detected because wall loss measurements could only begin after about an hour because of the time necessary to add the chemicals and mix them in the chamber. A similar explanation may account for the fact that only very slow wall loss was observed in the present study. It would be useful to test this by conducting some experiments similar to those described here, but with the lights turned on for only a few minutes so that rapid wall loss (if present) could be observed. Such experiments

might reconcile these measurements with ours, and also with the previous modeling study by this group (Zhang et al., PNAS, 2014) in which an optimized timescale for gas-wall partitioning equilibrium of 70 min was obtained by fitting measured time profiles of SOA formed in similar chamber reactions.

We thank Prof. Ziemann for his insightful comment. As suggested, we carried out one vapor wall deposition experiment using the α -pinene+OH low- NO_x system, with the experimental procedures identical to those in the ACPD manuscript, but with lights on for only 10 min. We also increased the initial concentrations of α -pinene and OH radical precursor H_2O_2 to 1 ppm and 4 ppm, respectively, in order to acquire sufficient organic vapor signals on CIMS during such a short irradiation period. The prompt formation of two ions, m/z 269 (-) and m/z 285 (-), was observed by the CIMS after 10 min of photochemistry. They are assigned to be two first-generation products, pinonic acid ($\text{C}_{10}\text{H}_{16}\text{O}_3$) and pinonic peroxy acid ($\text{C}_{10}\text{H}_{16}\text{O}_3$), respectively (See Table 2 for the proposed chemical structures). Owing to such a short photochemical reaction timescale, the other four products proposed in the ACPD manuscript were not found in this experiment.



The figure above shows the wall induced dark decay of m/z 269 (-) and m/z 285 (-) at 298 K. The best-fit first-order decay rates are within the same order of magnitude as those reported in the ACPD manuscript, i.e., $7.61 \times 10^{-6} \text{ s}^{-1}$ vs. $8.95 \times 10^{-6} \text{ s}^{-1}$ for m/z 269 (-) and $1.67 \times 10^{-6} \text{ s}^{-1}$ vs. $2.98 \times 10^{-6} \text{ s}^{-1}$ for m/z 285 (-). No rapid vapor wall loss was

found after lights off, and the deposition rates for both ions seem to be pretty consistent over the course of ~ 15 h dark decay. Note that m/z 285 (-), although having a higher molecular weight, decays more slowly than m/z 269 (-). We will demonstrate later that the wall-induced decay rate depends inversely on the vapor pressure, which is a function of the molecule size and functionalities. The addition of a carboxylic acid group, as in m/z 269 (-), leads to a greater decrease in volatility than that resulting from the addition of a peroxy carboxylic acid group, as in m/z 285 (-). Indeed, our observation is quite different from results reported by Matsunaga and Ziemann (2010) and Yeh and Ziemann (2014), in which organic vapors exhibit a rapid decay and then establish equilibrium within roughly 30 min. We tentatively attribute this discrepancy to the mixing status of the two chambers, i.e., static chamber (Caltech) vs. actively mixed chamber that was employed in Matsunaga and Ziemann (2010) and Yeh and Ziemann (2014).