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:

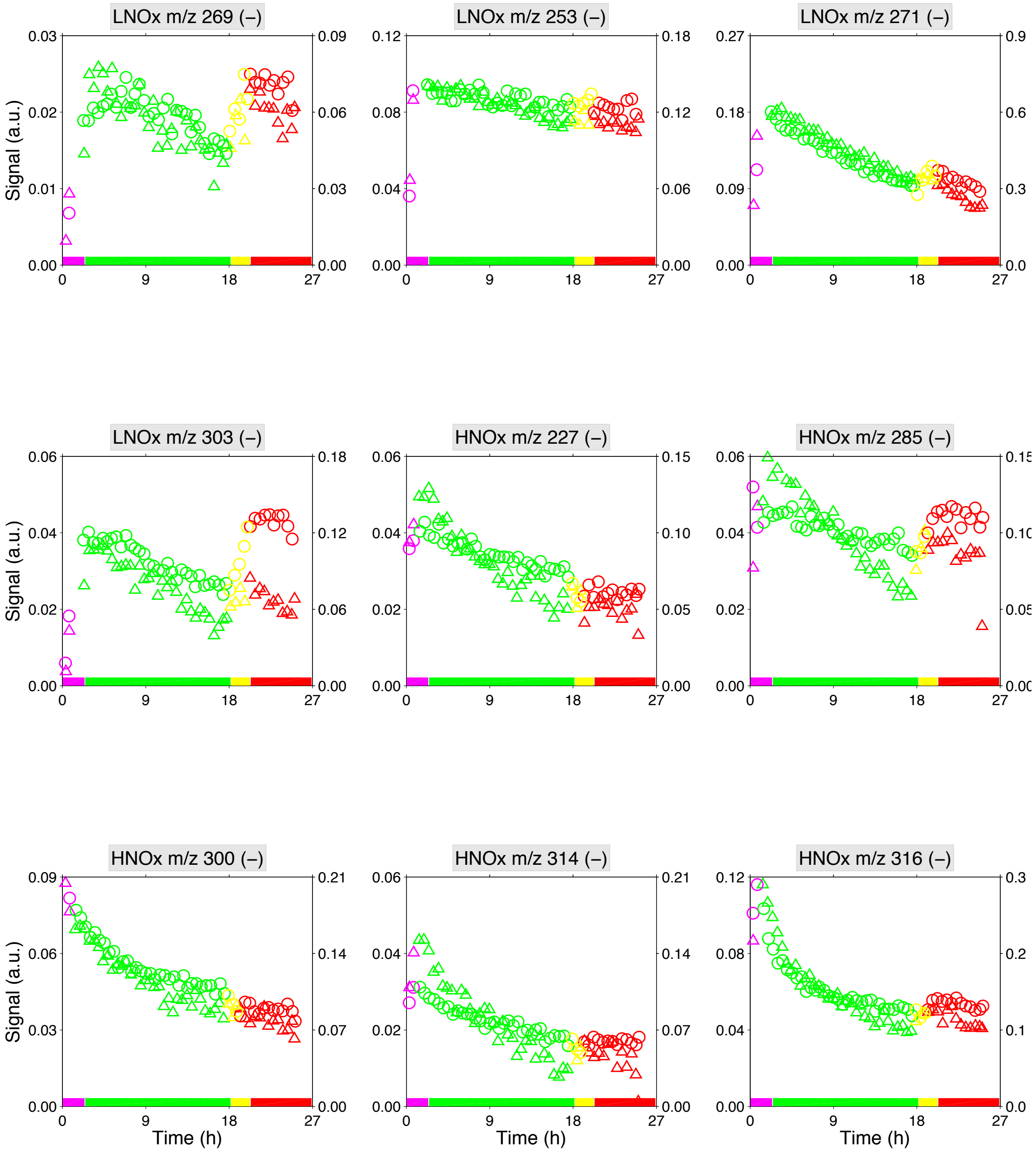
- My main concern with the current version of the paper is related to the conclusion that the vapor mass accommodation coefficient on the chamber walls is the main parameter defining the deposition rates. How can the authors distinguish this kinetic parameter from the thermodynamic properties (i.e. the 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 Cw 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 the 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?

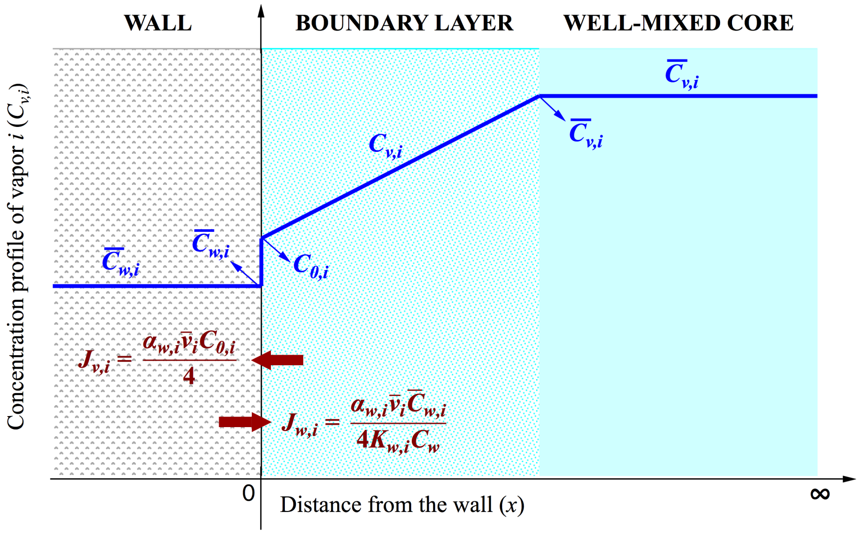
A1) The chamber wall is constructed of FEP Teflon films. Theoretically, we treat the wall as a giant homogeneous absorbing medium. The structure of this medium is discussed in Section 5 '*Vapor Sorption into FEP Teflon films*' from the perspective of its solubility behavior. Generally speaking, the FEP 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 m^3 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:

$$J_{\mathrm{v,i}} = \frac{\alpha_{\mathrm{w,i}}\overline{v}_{\mathrm{i}}C_{0,\mathrm{i}}}{4} \tag{1}$$

where $C_{0,\mathrm{i}}$ 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. $C_{0,\mathrm{i}}$ can be further expressed as:

$$C_{0,\mathrm{i}} = \frac{\overline{C}_{\mathrm{v,i}}}{\pi\alpha_{\mathrm{w,i}}\overline{v}_{\mathrm{i}}/8(D_{\mathrm{i}}K_{\mathrm{e}})^{1/2} + 1} \tag{2}$$

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

$$J_{\mathrm{v,i}} = \frac{\alpha_{\mathrm{w,i}}\bar{v}_{\mathrm{i}}\overline{C}_{\mathrm{v,i}}/4}{\pi\alpha_{\mathrm{w,i}}\bar{v}_{\mathrm{i}}/8(D_{\mathrm{i}}K_{\mathrm{e}})^{1/2}+1} \tag{3}$$

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

$$J_{\mathrm{w,i}} \propto \overline{C}_{\mathrm{w,i}} \quad \text{or} \quad J_{\mathrm{w,i}} = \lambda\overline{C}_{\mathrm{w,i}} \tag{4}$$

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

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

and

$$k_{\mathrm{w,depo,i}}\times\overline{C}_{\mathrm{v,i,\,eq}} = k_{\mathrm{w,evap,i}}\times\overline{C}_{\mathrm{w,i,\,eq}} \tag{5b}$$

Therefore,

$$\lambda = \left(\frac{\alpha_{\mathrm{w,i}}\bar{v}_{\mathrm{i}}/4}{\pi\alpha_{\mathrm{w,i}}\bar{v}_{\mathrm{i}}/8(D_{\mathrm{i}}K_{\mathrm{e}})^{1/2}+1}\right)\frac{\overline{C}_{\mathrm{v,i,\,eq}}}{\overline{C}_{\mathrm{w,i,\,eq}}} = \frac{\alpha_{\mathrm{w,i}}\bar{v}_{\mathrm{i}}/4H_{\mathrm{i}}}{\pi\alpha_{\mathrm{w,i}}\bar{v}_{\mathrm{i}}/8(D_{\mathrm{i}}K_{\mathrm{e}})^{1/2}+1} \tag{6a}$$

and

$$\frac{k_{\mathrm{w,evap,i}}}{k_{\mathrm{w,depo,i}}} = \frac{\overline{C}_{\mathrm{v,i,\,eq}}}{\overline{C}_{\mathrm{w,i,\,eq}}} = \frac{1}{H_{\mathrm{i}}} \tag{6b}$$

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

$$H_{\mathrm{i}} = \frac{\overline{C}_{\mathrm{w,i,\,eq}}}{\overline{C}_{\mathrm{v,i,\,eq}}} = K_{\mathrm{w,i}}\,C_{\mathrm{w}} \tag{7}$$

where $K_{\mathrm{w,i}}$ 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:

$$J_{\mathrm{w,i}} = \frac{\alpha_{\mathrm{w,i}}\bar{v}_{\mathrm{i}}\bar{C}_{\mathrm{w,i}}/4H_{\mathrm{i}}}{\pi\alpha_{\mathrm{w,i}}\bar{v}_{\mathrm{i}}/8(D_{\mathrm{i}}K_{\mathrm{e}})^{1/2}+1} \tag{8}$$

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 ($\alpha_{\mathrm{w,i}}$). Because of imperfect accommodation, the gas-phase concentration of vapor *i* at the surface of wall is not zero, but $C_{0,\mathrm{i}}$. We incorporated this parameter via Equation (6) to represent the flux of gas-phase molecules sticking to the wall. Thus, $\alpha_{\mathrm{w,i}}$ 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 $\alpha_{\mathrm{w,i}}$ 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 c0. 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 ($\overline{C}_{v,i}$), in the boundary layer adjacent to the wall ($C_{v,i}$), at the wall surface ($C_{0,i}$), and in the chamber wall ($\overline{C}_{w,i}$). 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 ($M_w < 300$ 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 pinanedial on the wall of a 4* m^3 *FEP Teflon chamber at equilibrium are on average 0.4 and 0.8, respectively.*'