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.

The authors have done a very thorough job of responding to the reviewer comments, as well as the comments by Paul Ziemann, including performing a new experiment. This paper should be published once the authors address the minor issues below.

The addition of the CIMS measurements prior to when the lights were turned on in Fig. 3 is very useful. However, it seems as if Fig. 3 is showing the non-background subtracted signals. The authors should note this in the caption.

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. However, this background subtraction does not guarantee that the background for every m/z signal is absolutely zero, as noted in Fig. 3 that the CIMS background for certain ions is hovering around zero.

Regarding the comparison between the current study and the work from Ziemann and co-workers, there remains an unfortunate discrepancy. It is very difficult to reconcile the results from the two studies, and there is overlap in the vapor pressure ranges considered, even if the functional group types here are more diverse. Certainly, this issue is not going to be worked out from this single study. Nonetheless, in the authors response they note that they tentatively attribute the discrepancy to differences in mixing between the two chambers. I think that there are two main arguments against this being the predominant aspect.

1. The theoretical loss rate of gases, absent accommodation limitations, is governed by mixing and diffusion. This has not been measured here for the gases, but this group has previously reported wall loss rates for particles as a function of size. These particle wall loss rates provide constraints on the potential for differences in mixing to be responsible

for the differences. Although the Caltech chamber may operate in a static mode (no active mixing), the loss rates of particles are nonetheless substantial, even for the smallest particles for which sedimentation is not an issue. I believe the consideration of these particle wall loss rates places bounds, at least approximate ones, on mixing effects. The particle loss rates reported in Loza et al. (2012) for the smallest particles sampled (~10 nm) were on the order of 10 4 s 1. This is much larger than many of the values observed in the current study, suggesting that diffusion (i.e. mixing) is not a limiting factor.

The accommodation coefficient for particles on the wall was assumed to be unity in previous theoretical studies (e.g., Crump and Seinfeld, 1981; McMurry and Grosjean, 1985), meaning that particles that encounter the wall will lead to 100% uptake. This assumption is reasonable considering that particles are in a liquid state. In this case, one can expect that as along as particles are transported onto the wall, they are accommodated immediately. In other words, the gas-phase transport (molecular diffusion and turbulent mixing) is the limiting step that governs the overall loss rate of small particles. Note that the diffusion coefficients of particles > 2 nm are at least an order of magnitude lower than that for gases.

On the other hand, the derived accommodation coefficients for the organic vapors investigated in the current study are very low, in the range of 10^{-8} to 10^{-6}. In this case, the wall accommodation is definitely the limiting process that governs the wall loss rate of organic vapors.

One can determine which process is the limiting step by referring to Eqs (25) and (26) in the manuscript. The threshold value of $\alpha_{w,i}$, at which the gas phase transport (molecular diffusion and turbulence mixing) and wall accommodation contribute equally to the vapor wall deposition rate, is 6.8×10^{-6} in the Caltech chamber.

2. Although the authors rightly note that Ziemann and co-workers use “active” mixing, the action is very limited in scope. Specifically, it appears that after injection into the Ziemann chamber, a small fan is turned on for a few 10’s of seconds before it is turned off for the remainder of the experiment. Thus, the “active” mixing is only at the very, very beginning of the experiment. In the current study, the authors fill the bag and allow the system to sit for ~1hr prior to turning on the lights. Mixing, i.e. homogenization, will

occur during this period thus that at the point when the lights are turned on the system may, in fact, be reasonably well mixed. As such, the differences in the experiments may not be as large as one might think.

My point is not that one of the studies is right or wrong, but simply that I don't think that differences in mixing will ultimately prove to be the final answer to the disparity between these studies. The authors have obviously done their due diligence in that they performed an additional experiment as recommended by Ziemann and this certainly provides further confidence in the results from the current study. In any case, I would suggest that the authors update their "tentative attribution" statement. Hopefully this discrepancy will be fully resolved through future studies, as this is an important topic.

We agree with the reviewer that turbulent mixing is not the limiting step of the vapor wall loss process in the Caltech chamber, and theoretically, should not be the limiting step in the chambers employed in Ziemann's work either.

We have done similar vapor wall deposition experiments during the past few years in both Caltech 28 m^3 and 24 m^3 chambers by different experimentalists (Christine Loza, Xuan Zhang, Alex Teng, and John Crounse). We have always observed the first-order decay trend, instead of the rapid establishment of gas-wall equilibrium. We recently investigated the vapor wall losses of isoprene oxidation products under different RHs (5%, 50%, and 90%). The experimental protocols were identical to the current study and lights-on time was controlled within 4-6 min. Rapid loss was only observed for isoprene-derived epoxide at 90% RH. Otherwise, first-order and slow decay was universally observed for all the other isoprene oxidation products (including nitrates, alcohols and carbonyls) at all RHs.

For now, it is not possible to reconcile the differences between our studies and Ziemann's work. However, there are three differences regarding equipment setup and experimental protocols:

(1) The chamber size and depletion rate: In our study, the chamber volume is 24 m^3 and sampling flow rate is ~ 2.6 L/min (2.5 L/min for CIMS and 0.087 L/min for AMS). After 20 h of vapor wall deposition, the overall bag volume lost due to sampling is 3.1 m^3 (12.9 % of the total bag volume). Two Teflon chambers, with sizes of 1.7 and 5.9 m^3,

respectively, were employed in Ziemann's work. The sampling flow rate is 0.6 L/min (0.3 L/min for GC-FID and 0.3 L/min for TSI SMPS). The overall volume lost after 400 min of sampling in the 5.9 m^3 chamber is 0.24 m^3 (4.1 % of the bag volume). The overall volume lost after 160 min of sampling in the 1.7 m^3 chamber is 0.096 m^3 (5.7 % of the bag volume).

(2) Mixing status of the chamber: We agree with the reviewer that theoretically, the turbulent mixing should not be the limiting step in the overall vapor wall loss process. It is not clear to what extent the mixing fan inside of the chamber affects the initial wall loss rate of organic vapors.

(3) The definition of starting point of the gas-phase vapor concentration. The initial concentration of gas-phase vapors at the onset of vapor wall loss experiment was measured by CIMS in our studies, whereas in Ziemann's work, the initial concentrations were stated as 300 ppb for all the vapors investigated, see notations in Figure 1 in Matsunaga and Ziemann, (2010). This suggests, perhaps that the initial vapor concentration was calculated based on the total liquid organic standard volume injected into the chamber, as quoted in their paper "It is worth emphasizing that in this study the values of $[OC]_T$ are accurately known because of the precautions (described above) that were taken to guarantee that measured amounts of OC were quantitatively transferred into the chamber…". We are not sure if this estimation is a source of any uncertainties.

Response to Reviewer #2

We thank reviewer #2 for the constructive comments. Our specific responses can be found below, with reviewer comments in black and our responses in blue.

The manuscript addresses an important topic of vapor wall losses and presents a protocol for constraining vapor wall interactions in Teflon chamber. In general the manuscript is well written, presents quality research and the topic suits well for ACP. Therefore publication in ACP can be recommended. Several parts of the manuscript had been improved in the revised version making the manuscript more clear. However, I find that couple of issues in the modeling framework still require clarification before publication of the manuscript. Below are my specific comments.

P6 eq. 6: I agree with reviewer #1 in that the it is not clear how Eq. 6 is obtained and this was not clarified by the reply of the authors' or the revised manuscript. The first part of Eq. 6 is based on diffusion and concentration gradient and describes the net molecular flux towards wall (difference between those coming from gas phase and those evaporating from the wall). The right hand side of the Eq. 6 is the kinetic flux of molecules to the wall with non-perfect accommodation accounted for. However, as it is written in Eq. 6 that these two expressions are equal, it seems that evaporation from the wall was included in the alpha_w. This means that alpha_w is not the actual accommodation coefficient defined in the similar way as for particles (=fraction of molecules that accommodate on the surface from those colliding it) but an "effective" accommodation coefficient including the evaporation. In order for alpha_w in Eq. 6 to represent the actual accommodation coefficient the right hand side of the equation should include evaporation term as noted already by reviewer #1. If alpha_w includes evaporation then it should indeed depend on the concentration of i in the wall and the volatility of the compounds. In that case it is not clear if the derivation of Eq. 12 for the evaporation flux of i is consistent as Eq. 10b assumes that k_w,depo,i does not include evaporation (which it seems to include in alpha_w). Therefore, I am wondering if the Eq.

6, 8 and 12 are inconsistent or if there was some additional assumptions incorporated in the deriving of them which are not stated in the text. Could the authors clarify their definition of alpha_w in the text?

The definition of $\alpha_{w,i}$ is shown below:

"As vapor molecules encounter the chamber wall, the fraction of those encounters that lead to uptake is represented by the accommodation coefficient ($\alpha_{w,i}$), and molecules rebound with a probability of $1 - \alpha_{w,i}$. The accommodation coefficient depends, in principle, on the nature of the wall surface as well as the compound chemical composition. It is worth emphasizing that $\alpha_{w,i}$ characterizes imperfect wall accommodation of the gas-wall interface"

We have reorganized the overall structure of 'Section 2. Vapor wall deposition — theory'.

Yes, in Eq (6) both deposition and evaporation processes should be accounted for in deriving the molecular flux balance across the gas-wall interface, as what we actually did in the derivation of the final mass conservation equation. In the updated manuscript, Eq (6) is expressed as Eq (13), also shown below:

$$\mathcal{D}_{\mathrm{i}} \frac{dC_{\mathrm{v,i}}}{dx}\bigg|_{x=0} = J_{\mathrm{v,i}} - J_{\mathrm{w,i}} = \frac{\alpha_{\mathrm{w,i}} \bar{v}_{\mathrm{i}} C_{0,\mathrm{i}}}{4} - \frac{\alpha_{\mathrm{w,i}} \bar{v}_{\mathrm{i}} \bar{C}_{\mathrm{w,i}}}{4 K_{\mathrm{w,i}} C_{\mathrm{w}}} \tag{13}$$

P7 L265-283: It is not clear from the text which values of the gas phase concentration were used from the measurements in solving Eq. 16 and 17. Was the concentration @298K taken just before the temperature was increased and concentration @318K taken at the end of the experiment? The Eq. 16 and 17 are valid only for equilibrium situation. In Supplementary Material it is stated based on model results that gas-wall equilibrium is reach in 20-25 hours. However, based on Fig. 3 it seems like gas-wall equilibrium was not reached during the experiment as the concentrations do not reach constant value for most compounds. In some cases equilibrium was almost reached at 298K but none of the cases show clear equilibration at 318K. Could this cause error or uncertainty in the C_w and alpha_w values and could the effect be dependent on the volatility of the compound?

We have added explanations in the revised manuscript, also as shown below:

"*In the actual calculation,* $\overline{C}_{v,i@298K}$ *and* $\overline{C}_{v,i@318K}$ *were obtained by taking a 30-min average of the first-order extrapolation of the normalized CIMS signals at 298 K and 318 K, respectively, during the temperature ramping period.*"

As shown in Fig. 2, for most species, simulations from SIM.1 (reversible gas-wall partitioning; C_w was calculated via Eqs 16 and 17) and SIM.2 (irreversible gas-wall partitioning; C_w was assumed to be infinite) match the experimental data, indicating 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 within a relatively long timescale (<18 h). For certain species, e.g., m/z 287, outputs from SIM.2 exhibit a better agreement with the observations than those from SIM.1, indicating that C_w values were underestimated.

Overall, since the wall-induced decay of most organic vapors in the Caltech Teflon chambers is well represented by first-order kinetics, we conclude that the vapor wall deposition of individual compounds can be adequately parameterized through the accommodation coefficient $\alpha_{w,i}$ as the single dominant variable. In this case, there should be no uncertainties arising from the estimation of C_w.

Minor comments:

Table 2: The equation numbers in the footnotes seem to refer to wrong equations.

We have revised this.

P35, Second last line of figure caption of Fig. 3: It says that red circles represent 're-evaporation'. Maybe the 're-evaporation' is a typo as the concentrations are going down.

We meant the re-evaporation of molecules from the wall at the moment when the temperature was increased from 298 K to 318 K.

Figure 1: The figure shows different expression for J_w,i compared to the text (Eq. 12). It seems that the equation given in the Fig. 1 was not used in the calculations and therefore I suggest removing that expression from the Fig. 1.

We have given a simpler definition of $J_{\mathrm{w,i}}$ in Fig. 1.

The expression of $J_{\mathrm{w,i}}$ and $J_{\mathrm{w,i}}$ are crucial because we applied the accommodation coefficient to characterize the wall accommodation in both deposition and evaporation processes via the equation $J_{\mathrm{v,i,\,(eq)}} = J_{\mathrm{w,i,\,(eq)}}$.