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

**Anonymous Referee #1**

Received and published: 23 December 2014

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-

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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).

- 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?

- 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

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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.

- 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.

Specific comments:

- P. 26766, line 5: It is not clear what is meant by "constraining the nature" of wall deposition. Please be more specific. - P. 26768, line 15: What do the authors mean by "physicochemical nature of the chamber walls"? Please be more specific. - Figs. 2-3: The fonts are so small that it is extremely difficult to read the axis labels and figure titles.  
- 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.

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

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