

Response to Prof. Paul Ziemann

General Comments:

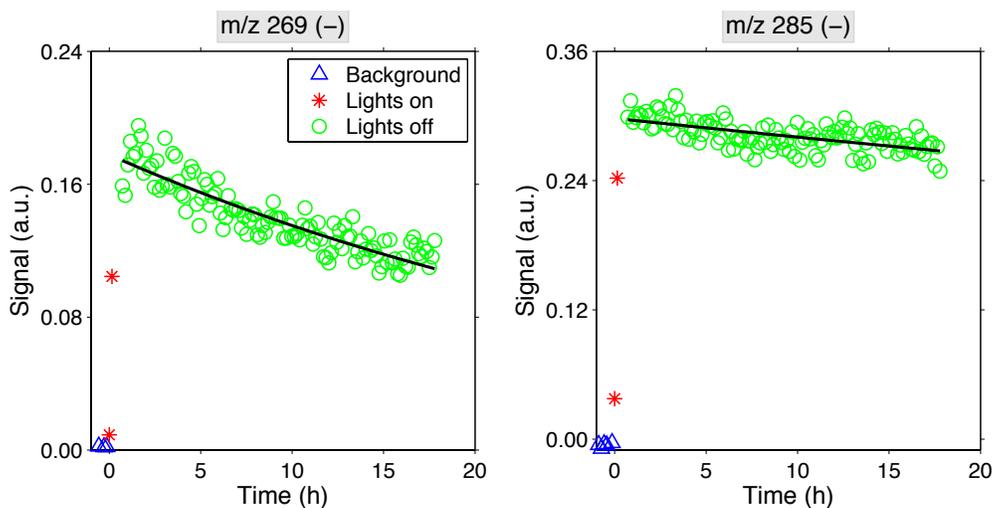
I think this paper presents a valuable approach for investigating gas-wall partitioning of organic compounds in Teflon smog chambers. The use of CIMS (or PTR-MS) to follow wall losses of reaction products seems ideal because these methods can potentially identify a large variety of compounds for which 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 H₂O₂ 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 (C₁₀H₁₆O₃) and pinonic peroxy acid (C₁₀H₁₆O₃), 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).