

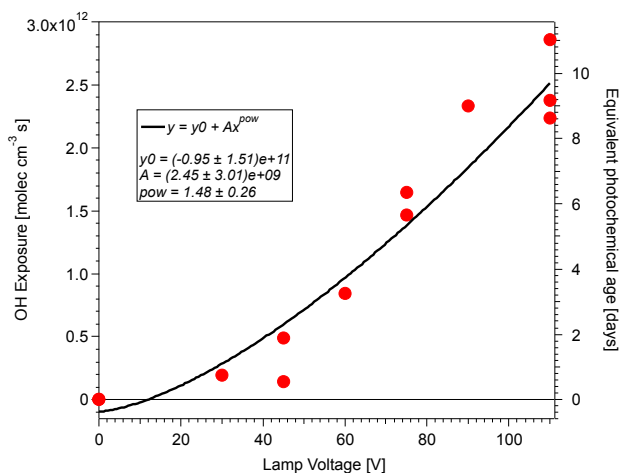
Peng et al. extends previous work by Li et al. (2015) in presenting a modeling analysis that is used to characterize radical chemistry in oxidation flow reactors (OFRs) using OH radicals produced from photolysis of radical precursors ( $O_2$ ,  $H_2O$ ,  $O_3$ ) at  $\lambda = 185$  and/or  $254$  nm. The radical chemistry is systematically characterized as a function of UV irradiance and mixing ratios of  $O_3$  and  $H_2O$  that are input to the OFR. Perturbations in the radical chemistry are additionally examined in the presence of added  $HO_x$  sinks such as  $NO_x$  and VOCs. These results are used to interpret previous OFR measurements and also to derive empirical OH exposure estimation equations.

Peng et al. addresses the need for improved characterization of OFRs as an emerging atmospheric measurement technique for providing inputs to chemistry and climate models. However, the analysis of VOC- and  $NO_x$ - induced perturbations to OFR radical chemistry is incomplete and is not supported by available measurements. Excluding this model/measurement comparison provides no context within which to evaluate the accuracy of the modeled OH suppression. The manuscript would be significantly improved after consideration of specific comments discussed below:

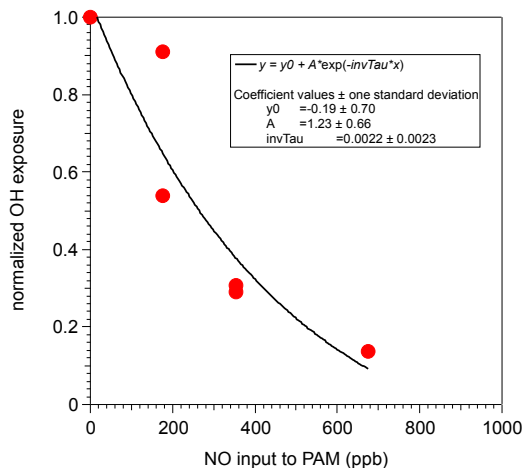
1. The modeling results in Figure 8 of Peng et al. show that up to 90% of the OH in Lambe et al. (2011) is consumed following VOC addition. This result is not consistent with measured OH suppressions conducted by Lambe et al (2012, 2015) that were also discussed in response to an online comment posted by Day et al. (2015) during the open discussion of Lambe et al. (2015). They conducted OH exposure calibrations in the presence of known amounts of added JP-10 and isoprene. Neither of these publications are cited or discussed in Peng et al., nor are they used to evaluate the accuracy of the model that is presented in this manuscript. Lambe et al. (2012) and (2015) specifically state:
  - a. Following addition of  $\sim 55$  ppbv JP-10 ( $'OHR_{ext}' \sim 31 \text{ s}^{-1}$ ), OH suppressions were measured that range from  $\sim 10\%$  to  $\sim 50\%$  at corresponding OH exposures ranging from  $2.2 \cdot 10^{12} \text{ molec cm}^{-3} \text{ sec}$  to  $1.6 \cdot 10^{11} \text{ molec cm}^{-3} \text{ sec}$  at zero  $OHR_{ext}$  respectively.
  - b. Following addition of  $\sim 462$  ppbv isoprene ( $'OHR_{ext}' \sim 1136 \text{ s}^{-1}$ ), no OH suppression was measured relative to the zero  $OHR_{ext}$  case over a similar range of OH exposures as in (a).
2. Another incorrect representation of data is in Figure 8 of Peng et al., which shows that  $\sim 92\text{-}97\%$  of the OH is suppressed in tunnel measurements conducted by Tkacik et al (2014). OH suppression calibration data is reported in Figures S3 - S6 of the Supporting Information in Tkacik et al. (2014). Following the addition of  $\sim 460$  ppbv  $NO$ , which was the median  $NO$  mixing ratio measured by Tkacik et al. (2014), OH suppression ranged from approximately  $5\%$  to  $80\%$  at corresponding OH exposures ranging from  $2.5 \cdot 10^{12} \text{ molec cm}^{-3} \text{ sec}$  to  $5.8 \cdot 10^{11} \text{ molec cm}^{-3} \text{ sec}$  in the absence of added  $NO$ , respectively, and is used to adjusted OH exposure data presented in that paper. As with the data of Lambe et al. (2012, 2015), the OH suppression measurements conducted by Tkacik et al. (2014) are also not discussed or compared with the model results of Peng et al.
3. The following consideration should have been included in the manuscript of Peng et al.: the plug flow assumption does not represent the PAM conditions (e.g. Fig. 3 in Lambe et al., 2011). In non-pulsed experiments, as are used in OH exposure calibrations, the gas phase concentration includes molecules that have spent a short time in the flow reactor (no recirculation) and molecules that have spent a long time in the flow reactor (recirculated). The majority of the molecules ( $\sim 85\%$ ) spend a shorter time in the reactor than assumed by plug flow and the other  $\sim 15\%$  spend a longer time than assumed by plug

flow (as estimated from integrating under the CO<sub>2</sub> curve in Fig. 3 of Lambe et al. (2011)). This suggests measured OH suppression values would actually be lower than OH suppression values that are modeled assuming plug flow— a trend that is qualitatively consistent with the measurement/model discrepancies outlined above.

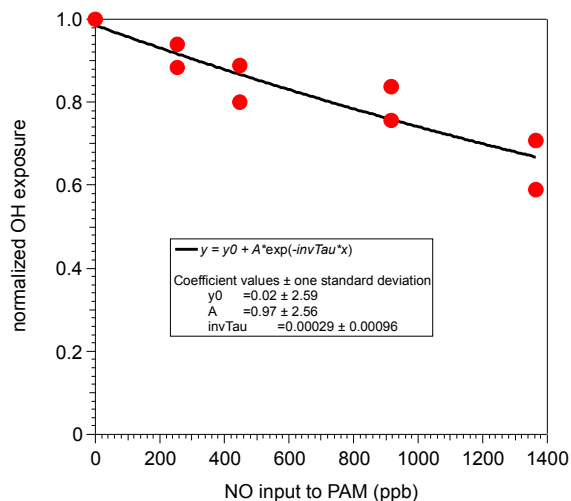
4. The above comment #2 relating to Tkacik et al. (2014) is supported by Figures S3 – S6 from the Supporting Information of that manuscript. These figures are reproduced below for reference.



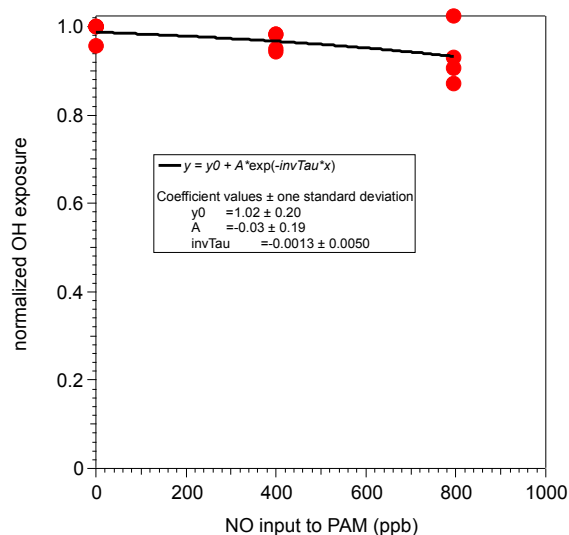
**Figure S3. OH exposure calibration data for the PAM reactor in the absence of NO<sub>x</sub>. Relative humidity was maintained between 49%-51% RH.**



**Figure S4. Reduction in OH exposure as a function of NO added to the PAM reactor with UV lamp voltages set to 45V.**



**Figure S5. Reduction in OH exposure as a function of NO added to the PAM reactor with UV lamp voltages set to 75V.**



**Figure S6. Reduction in OH exposure as a function of NO added to the PAM reactor with UV lamp voltages set to 110V.**

This comment was prepared by Andrew Lambe, Lindsay Renbaum-Wolff and Paul Davidovits.

### References

Day, D. A., B. B. Palm, A. M. Ortega, Z. Peng, W. Hu, and J. L. Jimenez. Interactive comment on “Comparison of secondary organic aerosol formed with an aerosol flow reactor and environmental reaction chambers: effect of oxidant concentration, exposure time and seed particles on chemical composition and yield” by A. T. Lambe et al. Atmos. Chem. Phys. Discuss., 14, C11295, 2015.

Lambe, A. T., A. T. Ahern, L. R. Williams, J. G. Slowik, J. P. S. Wong, J. P. D. Abbatt, W. H. Brune, N. L. Ng, J. P. Wright, D. R. Croasdale, D. R. Worsnop, P. Davidovits, and T. B. Onasch, Characterization of aerosol photooxidation flow reactors: heterogeneous oxidation, secondary organic aerosol formation and cloud condensation nuclei activity measurements, *Atmos. Meas. Tech.*, 4, 445–461, 2011.

Lambe, A. T., T. B. Onasch, D. R. Croasdale, J. P. Wright, A. T. Martin, J. P. Franklin, P. Massoli, J. H. Kroll, M. R. Canagaratna, W. H. Brune, D. R. Worsnop, and P. Davidovits. Transitions from functionalization to fragmentation reactions of secondary organic aerosol (SOA) generated from the laboratory OH oxidation of alkane precursors. *Environmental Science and Technology*, 46,5430-5437, 2012.

Lambe, A. T., P. S. Chhabra, T. B. Onasch, W. H. Brune, J. F. Hunter, J. H. Kroll, M. J. Cummings, J. F. Brogan, Y. Parmar, D. R. Worsnop, C. E. Kolb, and P. Davidovits. Effect of oxidant concentration, exposure time and seed particles on secondary organic aerosol chemical composition and yield. *Atmos. Chem. Phys.*,15, 3063-3075, 2015.

Li, R., B.B. Palm, A.M. Ortega, J. Hlywiak, W. Hu, Z. Peng, D.A. Day, C. Knote, W.H. Brune, J. de Gouw, and J. L. Jimenez. Modeling the radical chemistry in an Oxidation Flow Reactor: radical formation and recycling, sensitivities, and OH exposure estimation equation. *Journal of Physical Chemistry A*, 119, 4418–4432, doi:10.1021/jp509534k, 2015.

Tkacik, D. S., A. T. Lambe, S. Jathar, X. Li, A. A. Presto, Y. Zhao, D. R. Blake, S. Meinardi, J. T. Jayne, P. L. Croteau, and A. L. Robinson, Secondary organic aerosol formation from in-use motor vehicle emissions using a Potential Aerosol Mass reactor. *Environ. Sci. Technol.*, 48, 11235-11242, 2014.