

## ***Interactive comment on “Modeling the formation and aging of secondary organic aerosols in Los Angeles during CalNex 2010” by P. L. Hayes et al.***

### **Anonymous Referee #1**

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This paper describes modeling the secondary organic aerosol (SOA) formation in Los Angeles as measured during the CalNex study in May/June 2010. The paper evaluates a variety of different models/parameterizations – WRF-CHEM, WRF-CMAQ, and a box model with several different mechanisms. None of the models are novel, but applying them to CalNex is new (EPA has been doing some evaluation of the CMAQ model, e.g. a paper is up on ACPD right now <http://www.atmos-chem-phys-discuss.net/15/157/2015/acpd-15-157-2015.html>). Given the comprehensive nature of the CalNex dataset it is valuable to use it to evaluate SOA models. The analysis is similar to previous work the authors have published for Mexico City.

The conclusions from the work appear to be largely consistent with those of previous studies. The old, traditional SOA models that only consider a relatively small number

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of volatile organic compounds cannot explain the measured SOA, even if one makes extreme corrections to yields for potential vapor wall losses to chamber walls. The paper shows that mass closure on the SOA can be achieved if one includes semivolatile and intermediate volatility precursors in a model. The paper evaluates several different schemes for doing this. The paper evaluates models against SOA mass, degree of oxygenation, and fossil/modern split. The parameterization with IVOC/SVOC all appear to work reasonably well (but not perfectly), but are not well constrained with data. The simple IVOC/SVOC schemes the authors consider appear to overpredict the amount of SOA at longer time scales (~ 3 days), presumably (as mentioned by the authors) because they do not include any fragmentation. There is reasonable agreement between fossil/modern carbon data and their apportionment. Finally, the authors show that a simple parameterization they developed in Mexico City for SOA formation appears to work in LA as well. These are basically the same set of conclusions as the Mexico City work, with the addition of fossil/modern carbon.

This is a well written paper. It is long and very comprehensive, but I found it not difficult to read and follow. It makes a contribution. Its weakness is that it does not break much new ground. There is value to show that they largely reach the same conclusions as they did with Mexico City. I would recommend the paper for publication after the authors address the following comments:

“The work presented here quantitatively demonstrates that PAHs are relatively unimportant compared to other precursors such as methylbenzenes” This statement is too strong. The model only included a few PAH (naphthalenes, methylnaphthalene). It seems clear that these PAHs do not appear to be major precursors, but large amounts of unspciated IVOCs include a fair number of more alkylated or functionalized PAHs. The authors claim that unspciated IVOC are mainly alkanes, but that has not really been established. If a reasonable fraction (10s of %) were PAHs then PAHs could play an important role.

The authors should report the effective yields of the SI-SOA precursors. How do they

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compare of the recent work of Jathar (PNAS, 2014), which derived yields from chambers? How do they compare to the yields proposed by Zhao (EST, 2014) who performed this sort of model with more extensive set IVOC data? How do they compare to smog chamber data for traditional precursors (alkanes, aromatics, etc.)?

The paper uses the results to apportion SOA to different sources. Since the SVOC and IVOC concentrations are scaled with primary organic aerosol; this apportionment is presumably the same as the primary organic aerosol. The authors should clarify this point in the manuscript. I suspect it is high uncertain. For example, gasoline vehicles emit relative little POA but likely contribute significant SOA (Jathar et al. 2014).

Zhao (EST, 2014) recently reported measurements of more IVOCs, including an estimate of the unspciated IVOC. It appears that the naphthalene data came from the same dataset? How do the authors estimates of unspciated IVOC inferred from primary organic aerosol compare to the measured data of Zhao et al.? How do the predictions of the authors compare to Zhao et al.?

“Indeed, decreases in SOA concentration at high photochemical ages have been observed in flow-tube studies, although typically at photochemical ages much longer than 3 days (George and Abbatt, 2010).” More recent flow tube studies (Lambe et al. EST 2013; Tkacik et al. EST 2014) suggest that the fall off may occur at shorter photochemical ages (between 2 and 3 days).

SIMPLE parameterization is interesting. It is not clear how much fitting versus predicting is being done. This needs to be clarified in the manuscript. It appears that it has been retuned for CalNex. If so then that is not as impressive – it is just a curve fit. If it is using previous parameters then that would be good. It would be interesting to better characterize the atmospheric conditions under which it may be applicable / influence SOA formation (VOC/NO<sub>x</sub>, etc.). Presumably LA and Mexico City are pretty consistent

The importance cooking emissions to SOA formation is interesting. I am not aware of data to support this. I believe that the 1.5 factor of Robinson et al. (Science 2007) is

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based on data for combustion sources. Is there evidence from source test data that it might also apply to cooking? What evidence is there for SOA from cooking.

References.

Jathar, S. H.; Gordon, T. D.; Hennigan, C. J.; Pye, H. O. T.; Pouliot, G.; Adams, P. J.; Donahue, N. M.; Robinson, A. L., Unspciated organic emissions from combustion sources and their influence on the secondary organic aerosol budget in the United States. *Proceedings of the National Academy of Sciences* 2014, 111, (29), 10473-10478.

Tkacik, D. S.; Lambe, A. T.; Jathar, S.; Li, X.; Presto, A. A.; Zhao, Y.; Blake, D.; Meinardi, S.; Jayne, J. T.; Croteau, P. L.; Robinson, A. L., Secondary Organic Aerosol Formation from in-Use Motor Vehicle Emissions Using a Potential Aerosol Mass Reactor. *Environ. Sci. Technol.* 2014, 48, (19), 11235-11242.

Lambe, A. T.; Onasch, T. B.; Croasdale, D. R.; Wright, J. P.; Martin, A. T.; Franklin, J. P.; Massoli, P.; Kroll, J. H.; Canagaratna, M. R.; Brune, W. H.; Worsnop, D. R.; Davidovits, P., Transitions from Functionalization to Fragmentation Reactions of Laboratory Secondary Organic Aerosol (SOA) Generated from the OH Oxidation of Alkane Precursors. *Environ. Sci. Technol.* 2012, 46, (10), 5430-5437.

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