Manuscript entitled "Rethinking the global secondary organic aerosol (SOA) budget: stronger production, faster removal, shorter lifetime" by Hodzic et al.

Comment by N. Hewitt:
The authors of this interesting manuscript may wish to refer to a paper we published in ACP in 2014 in which we studied the formation of aerosol particles in a reaction chamber into which gas-phase emissions from trees where fed:
Emissions of biogenic volatile organic compounds and subsequent photochemical production of secondary organic aerosol in mesocosm studies of temperate and tropical plant species (2014) K.P. Wyche, A.C. Ryan, C. N. Hewitt, M. R. Alfarra, G. McFiggans, T. Carr, P.S. Monks, K.L. Smallbone, G. Capes, J.F. Hamilton, T.A.M. Pugh, and A. R. MacKenzie, Atmospheric Chemistry and Physics, 14, 12781 – 12801

We thank Dr. Hewitt for pointing us to this interesting laboratory study on the VOC emissions from three Southeast Asian tropical plant species and their potential to form SOA. However, we did not find the way to make reference to this study as we were not able to make a connection between the importance of these plants and their global emissions relative to the biogenic emissions present in our model.

Comment by M. O. Andreae:
Congratulations to an excellent paper, which represents important progress in our understanding of the global atmospheric cycle of secondary organic aerosols! I have a minor, but important, technical comment, which should be addressed in the revised version. In presenting concentrations at altitude, it is essential to state clearly whether these represent concentrations at ambient temperature and pressure, or whether they have been normalized to a standard temperature and pressure. Since standard conditions vary depending on different conventions, their value should be given explicitly. To help the reader, I recommend including this specification in the captions of Figures and Tables, in addition to giving it in the methods section. This has been done in commendable fashion in Figure 6, although the unit "smˆ3" for "cubic meter at standard conditions" is in conflict with SI recommendations and probably should be replaced by "mˆ3 (STP)". Unfortunately, however, Figure 2 is missing any information about whether the concentrations shown here represent ambient or standard conditions. I request that the authors provide this information in the revised paper.

We thank Dr. Andreae for contributing his suggestions. In the caption of Figure 2, we have clarified that SOA concentration profiles are shown at ambient temperature and pressure:

"*Figure 2: Vertical profiles of average SOA concentrations (at ambient temperature and pressure) integrated globally and regionally over the continental U.S. between 2005 and 2008. The ratios between SOA predictions by the NY_DPH and REF runs are also shown for each region.*"

We have also clarified our notations to be conform with SI units, and replaced "sm^3" to "m^3(STP)" as in: "Figure 6: Comparison of mean OA vertical profiles (μg m^{-3}(STP) at 288.15K and 1013.25 hPa).." or ". larger than 16 μg m^{-3}(STP) (where 'STP' stands for standard conditions of 273 K and 1 atm)".

Reviewer #1 (Comments to Author):

RI.0) This manuscript presents another 'rethink' concerning global secondary organic aerosol, and although 'rethinking' has already been done and will certainly be required many times more in the SOA world, I like both the title and intention of this paper. The manuscript presents a number of new ideas and points the way to the use of new constraints (namely vertical profiles) for the evaluation of proposed SOA mechanisms. The general approach is generally sound I think, but there are some confusing aspects which I think the authors could address.

Response RI.0) We thank the reviewer for recognizing that our manuscripts present new ideas and that our approach is sound. We respond to reviewer's specific comments below (in blue). The updated text in the manuscript is indicated in red. For the revised version of the manuscript we redid all model simulations to account for reviewer's suggestions (e.g. updates to the enthalpy of vaporization, isoprene treatment). The text and figures have been updated accordingly. The conclusions of the paper have not changed.

My main concerns are:

RI.1) Discrepancies between observed and modelled OA are explained or discussed through the lens of problems with SOA-production and loss mechanisms, but we are not told how well the model performs for simpler species such as sulphate or nitrate (for vertical profiles), or for example NO2 or CO. Maybe the under or over predictions seen for OA simply reflect dispersion issues and can be diagnosed through other pollutants? (As an extreme example, the authors worry about factor of two changes in OA over urban areas. I wonder how appropriate GEOS-Chem is for NO2 in urban areas for example.

Response RI.1) We agree with the reviewer that it would be useful to diagnose whether factors such as dispersion errors might contribute to discrepancies between observed and modeled OA. While tracers such as NO2 and CO are useful in principle, in practice their use to diagnose dispersion errors is limited by the fact that there are other uncertainties related to the emissions and chemistry of these individual tracers that precludes from isolating dispersion errors that may be similar across tracers (Arellano et al. 2006; Miyazaki et a.l 2012). We have therefore chosen to compare model simulations with a broad suite of OA surface and vertical profile measurements to assess the extent to which they provide support for our alternative hypotheses of SOA sources and sinks. We also note that model performance with regards to inorganic aerosol components is documented in Jo et al. (2013).

To address this comment, we have added the following text (in red) to section 3.2:
"3.2 Evaluation of the modeled organic aerosol concentration
The results presented above confirm that the modeled SOA distribution is quite sensitive to the treatment of removal processes. Here, we evaluate the extent to which simulated OA fields using various configurations of the model are consistent with observations. We note that dispersion errors might contribute to discrepancies between observed and modeled OA, but isolating the impact of these errors is difficult (Arellano et al. 2006). We therefore compare model simulations with a broad suite of OA surface and vertical profile measurements to assess the extent to which they provide support for our alternative hypotheses of SOA sources and sinks. We also note that performance with regards to inorganic aerosol components is documented in Jo et al. (2013), who find that the simulation results are in general agreement with surface observations of sulfate and ammonium, but that nitrate is overestimated."

Arellano, A. F., Jr., P. S. Kasibhatla, L. Giglio, G. R. van der Werf, J. T. Randerson, and G. J. Collatz (2006), Time- dependent inversion estimates of global biomass-burning CO emissions using Measurement of Pollution in the Troposphere (MOPITT) measurements, J. Geophys. Res., 111, D09303, doi:10.1029/2005JD006613.

Miyazaki, K., Eskes, H. J., and Sudo, K.: Global NOx emission estimates derived from an assimilation of OMI tropospheric NO2 columns, Atmos. Chem. Phys., 12, 2263-2288, doi:10.5194/acp-12-2263-2012, 2012.

RI.2) In fact, I don't understand why a model with such a coarse resolution (2x2.5 degrees!) is compared with urban data or used to evaluate population-weighted SOA concentrations. This model is only suitable for consideration of large-scale concentration fields. Although I know that previous GEOS-Chem papers have also made use of urban data, I don't see the point and think that the paper would be stronger if it stuck to scales where one would expect GEOS-Chem to have some validity. I would remove the sections dealing with urban concentrations and health effects. (The authors were not really consistent with this anyway. In Sect. 2.5.2 they exclude data from heavily polluted regions because of the coarse resolution, but elsewhere they make use of urban data.)

Response RI.2) We agree with the reviewer that a 2x2.5 degree resolution model should not be compared with urban measurements. Following the reviewer's comment we have removed comparison points corresponding to urban locations. Manuscript, figure 4 and its caption have been updated accordingly (see below):

Figure 4c also compares the predicted monthly mean SOA concentrations (averaged over 2005-2008) with the AMS measurements made at 20 locations worldwide [Zhang et al., 2007]. Only background and rural sites were considered given the model coarse horizontal resolution. Figure 4c suggest that the REF simulation is underpredicting SOA concentrations by on average ~40% over all sites. Increased production in the NY simulation leads to a 38% average overprediction of surface SOA. The best agreement *is obtained for simulations that accounted for both updated production yields and removal processes (NY_DPH) with a small negative model average bias of 5%. Given the coarse model resolution, the most meaningful comparison with the measurements is expected to be with the background sites (blue triangles) at which the NY_DPH simulations is capturing reasonably the observed SOA levels. Again the correlation coefficients for all simulations are low (R2~0.1) due to differences in time periods.*

The updated figure below displays the results for the new simulations.

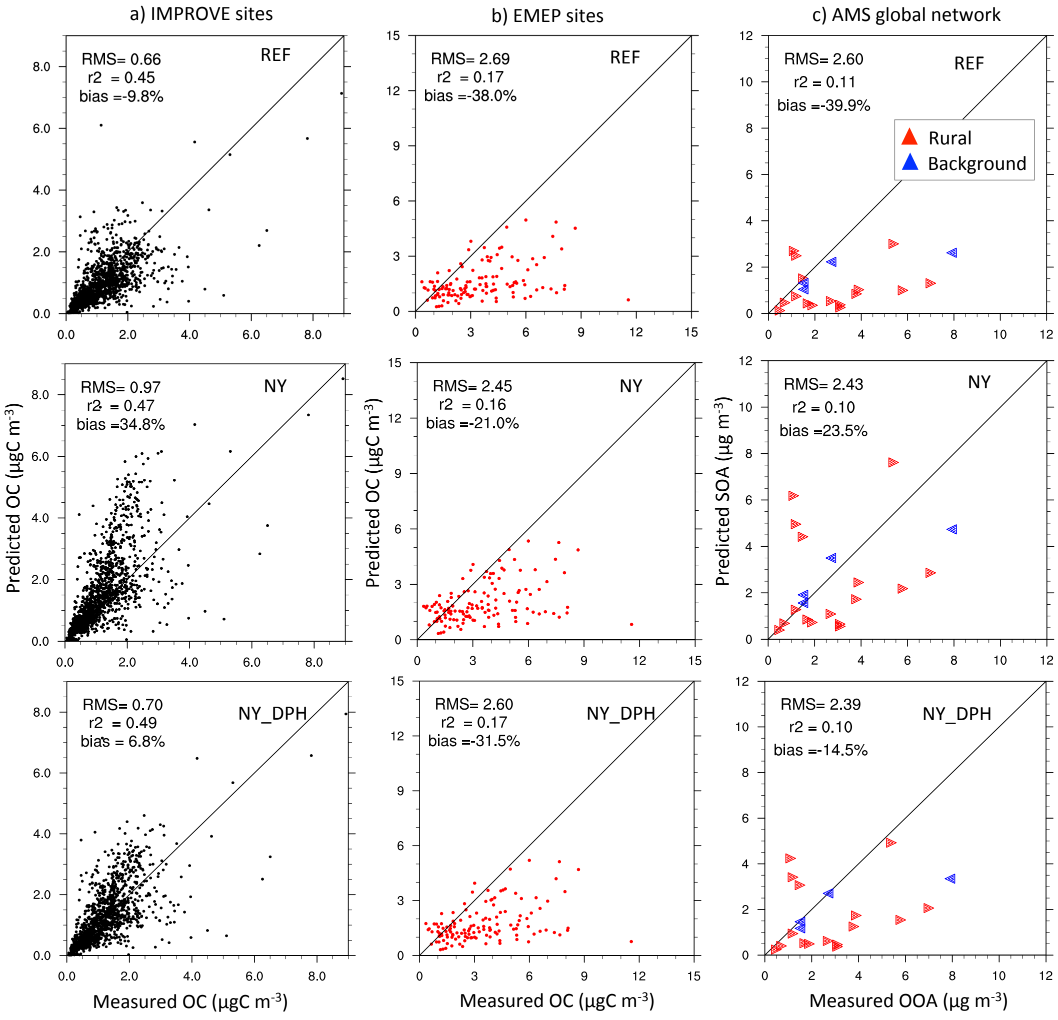

Figure 4: Scatter plots of predicted vs. measured monthly mean OC (µgC m^{-3}) and SOA (µg m^{-3}) at the surface sites of the U.S. IMPROVE network, the European EMEP network and the global AMS network. AMS data are divided into rural sites (red) and background sites (blue). Given model coarse horizontal resolution, urban sites were not considered. Modeled monthly mean values are representative of years 2005 to 2008 and are compared with monthly mean observations averaged over 2005-2008 for IMPROVE, and 2002-2003 for EMEP sites.

The reviewer also suggested removing the section on the "effect on health exposure" due to the model coarse resolution. We would like to clarify that we are not trying to quantify the health effects, but rather are identifying broad regions where this could be significant. We have modified the text to acknowledge that we need a higher resolution model to look at the health effects:

A detailed analysis of health impacts is beyond the scope of this paper, and would require higher resolution model predictions. Here, we focus on a simple metric to characterize human-health relevant changes in surface SOA concentrations, and identify broad regions where these changes could have an impact.

RI.3) I missed more use of supporting data, e.g. O/C ratios, 14C, etc.

Response RI.3) We agree with the reviewer that comparing with O/C and 14C data would be of interest, however we are not able to perform this type of comparison in the present study due to the lack of information available in the model outputs, and we focus on the evaluation of the predicted OA mass which is important for the radiative forcing that global models mostly care about. The difficulties of using those data are described below:

To compute O/C ratios, one needs to keep track separately of SOA from various sources (biogenic, anthropogenic, biomass, etc), make the assumption in the model of what the OM/OC fraction is typically for each source, and account for the gain in oxygen due to ageing reaction (Hodzic et al, 2010a). Recent studies have reported values of 1.6 and 2.1 for mixed OA at urban and rural sites (Turpin and Lim, 2001, Aiken et al., 2008). Canagaratna et al. (2015) reported source-specific OM/OC ratios for ambient aerosols including POA (1.96), biomass burning POA (1.64), and total SOA (1.54), whereas Shilling et al. (2009) suggested OM/OC of 1.6 for biogenic SOA. The value of OM/OC for ambient particles depends not only on the source but also on the degree of oxidation of the aerosol, and can be increased in outflow regions due to atmospheric ageing (Lee-Taylor et al., 2015). In our GEOS-Chem runs, we do not keep track of source-specific SOA (biomass burning and anthropogenic SOA are lumped together), and of the oxygen gain with ageing. The mechanism is very simple, and these ageing reactions are embedded in the yield. To estimate O/C in GEOS-Chem, one would need to keep track of oxygenated-SOC for each volatility bin and for each source e.g. fire, biog., fossil fuels, and assume ageing reactions and the corresponding oxygen gain (which are currently unknown). This type of analysis would be more suitable for shorter runs, and is beyond the scope of this paper.

To compare with 14C data, one needs to keep track of source specific OC in the model which are currently not available in our runs. For instance in our earlier study (Hodzic et al., 2010b), we have shown that the fraction of non-fossil carbon can be derived according to the following equation:

$$fC_{NF}^{OC} = \frac{SOC_{BSOA} + POC_{BB} + SOC_{BB} + POC_{PBAP} + 0.2 \times (POC_{urb} + SOC_{urb})}{\sum_i OC_i}$$

where one needs to keep track separately of organic carbon in primary and secondary organic aerosols from biogenic, biomass burning (BB), and urban sources, as well as the amount of primary organic particles (PBAP). Currently GEOS-Chem does not have this type of distinction, and in particular it does not allow separating the non-fossil carbon emissions from urban sources (e.g. food cooking, tire and brake wear, resuspended road dust, trash burning, biofuel use, cigarette smoke, etc.). In addition, although 14C measurements are available at several locations (see Table 1, Hodzic et al., 2010b), these data are much influenced by hypothesis used for their retrievals, and can lead to a range of values even for the same location (e.g. Mexico City, Hodzic et al., 2010b). Therefore, using this type of measurements in the present study would not provide robust constraints on model results.

Aiken, A.C., P.F. DeCarlo, J.H. Kroll, et al. O/C and OM/OC Ratios of primary, secondary, and ambient organic aerosols with high resolution time-of-flight aerosol mass spectrometry, Environmental Science and Technology, 42, 4478–4485, doi: 10.1021/es703009q, 2008.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys., 15, 253-272, doi:10.5194/acp-15-253-2015, 2015.

Hodzic, A., J. L. Jimenez, S. Madronich, M. R. Canagaratna, P. F. DeCarlo, L. Kleinman, and J. Fast, Modeling organic aerosols in a megacity: Potential contribution of semi-volatile and intermediate volatility primary organic compounds to secondary organic aerosol formation, Atmos. Chem. Phys., 10, 5491-5514, 2010a.

Hodzic A., Jimenez J.L., Prevot A.S.H., Szidat. S., Fast J.D., Madronich S., 2010. Can 3D Models Explain the Observed Fractions of Fossil and non-Fossil Carbon In and Near Mexico City? Atmos. Chem. Phys., 10, 10997-11016, doi:10.5194/acp-10-10997-2010b.

Lee-Taylor J., Hodzic A., Madronich S., Aumont B., Camredon M., Valorso R., Multiday growth of condensing organic aerosol mass in urban and forest outflow, Atmos. Chem. Phys., 15, 595-615, 2015.

Shilling, J. E., Chen, Q., King, S. M., Rosenoern, T., Kroll, J. H., Worsnop, D. R., DeCarlo, P. F., Aiken, A. C., Sueper, D., Jimenez, J. L., and Martin, S. T.: Loading-dependent elemental composition of α-pinene SOA particles, Atmos. Chem. Phys., 9, 771-782, 2009.

Turpin BJ, Lim HJ, Species contributions to PM2.5 mass concentrations: Revisiting common assumptions for estimating organic mass, Aerosol Sci. Technol., 35, 1, pp. 602-610, 2001.

RI.4) P32423, L24 The authors should explain why their estimate of J-SOA differs from that of Henry and Donahue (2012) by an order of magnitude, and why their's is to be preferred. Presumably, if the much higher rates of H& D were used the vertical profiles and budgets would look very different.

Response RI.4) A detailed analysis of various aspects related to SOA photolysis, including the comparability to photolysis rates derived from laboratory experiments of Henry and Donahue (2012), as well as the impact of higher photolysis rates on modeled SOA distribution, is presented in Hodzic et al., 2105 (Hodzic, A., Madronich, S., Kasibhatla, P. S., Tyndall, G., Aumont, B., Jimenez, J. L., Lee- Taylor, J., and Orlando, J.: Organic photolysis reactions in tropospheric aerosols: effect on secondary organic aerosol formation and lifetime, Atmos. Chem. Phys., 15, 9253–9269, doi:10.5194/acp-15-9253-2015, 2015). We have chosen not to repeat the discussion here.

We have added the following text (in red) to Section 2.3.2 to address this comment:

The resulting value for JSOA is 0.04 % of JNO2 (JSOA = 4 x 10^{-4} x JNO2) which is more than an order of magnitude lower than the photolysis loss coefficients reported by Henry and Donahue (2012) who estimated the photolytic loss of SOA as 2 % of JNO2 (average value of the net effect of both particle and gas-phase photolysis). It should be noted that the implicit assumption in this formulation is that only one carbon atom is lost upon SOA photolysis reaction and not the entire SOA molecule. For more details on the parameterization we refer readers to a previous study by Hodzic et al. [2015] that presents a detailed discussion of the comparability of the photolysis rate estimates used in his study with the laboratory-derived estimates of Henry and Donahue [2012] and also discussed impact of faster photolysis rates on modeled SOA distributions.

We have also added the following text (in red) to section 4:

While initial comparisons with the limited available measurements are encouraging, uncertainties remain in the proposed source and sink parameterizations. One important uncertainty pertains to SOA photolysis rates. To the extent that atmospheric SOA photolysis rates seem to be in the lower range of estimates reported from limited laboratory studies, SOA production rates may need to be higher to explain the observed SOA distribution. An important next step therefore is to reconcile laboratory and theoretical estimates of SOA photolysis rates. More field measurements are also needed to better characterize and evaluate boundary layer vs. free troposphere gradients in various source regions and in the remote atmosphere to validate our hypothesis.

RI.5) I missed a sensitivity test to illustrate the importance of the enthalpy assumptions. Would a different set of dH change the vertical profiles in a significant way?

Response RI.5) We agree with the reviewer that SOA predictions can be sensitive to the assumptions made on dH. In the updated simulations we have used experimentally derived values from Epstein et al. 2010.

This is now explained in the new manuscript:

The enthalpy of vaporization was updated to the experimentally derived values starting at 151 kJ mol^{-1} at C = 0.01 µg m^{-3} and decreasing by 11 kJ mol^{-1} for each increase in order of magnitude of C* [Epstein et al., 2010].*

Epstein S.A., Riipinen I., and Donahue N.M., A Semiempirical Correlation between Enthalpy of Vaporization and Saturation Concentration for Organic Aerosol Environmental Science & Technology, 44 (2), 743-748 DOI: 10.1021/es902497z, 2010.

RI.6) I found Sections 2.1 and especially 2.2 to be rather confusing.
Sect. 2.1: Explain why you have no oxygen gain after OH oxidation. This sounds unrealistic, and has implications for the O/C ratios of your system I would have thought. The sentence "we do not support in any case ad hoc aging of oxidation products", begs the question: why not? Although the phrase 'ad hoc' sounds bad, ageing should be expected for SOA and SVOC in the atmosphere, and is usually assumed to add oxygen.

Response RI.6) In the default formulation (REF) used by Jo et al., 2013, the ageing is applied artificially to chamber derived yields (i.e. yields that have been determined by fitting to chamber data). However, experimentally "ageing" is a continuous process, and thus the reference model parameterization already inherently accounts for "ageing" to some unknown extent that occurred in the chamber experiment. The importance of "ageing" to the chamber SOA formation is VOC specific, as certain VOC precursors have to go through a greater number of reactions before forming condensable products than do others. Given that the chamber data already include the influence of ageing (to some extent), it is not experimentally justified to include ad hoc ageing again when using parameterizations derived from chamber experiments when the parameterization does not account for ageing in the first place. Instead, a self-consistent approach should be taken in which "ageing" reactions (i.e. multi-generational chemistry) should be accounted for explicitly during the data fitting exercise and parameterization development. This is the approach taken here, both for SOM and for GECKO-A. That is why we say in the paper "we do not support in any case ad hoc aging of oxidation products". In the SOM derived yields we account for ageing and the oxygen gain. The chemistry that is happening in reality during the initial 36h of continuous reaction (so effectively 3 days) is parameterized using the yields. This is now better explained in the manuscript as described in RI.7.

RI.7) Sec. 2.2: There were several parts of this section which confused me, since the methods mix SOM, VBS and ageing approaches in a complex way.

Response RI.7) We have clarified how the VBS parameterization was derived (see responses below). We have also reformulated the reported VBS in Table 1 to provide both gas-phase and particle material in each volatility bin. In the original manuscript the gas-phase mass was missing from the total reported mass in each bin, which lead to underestimated mass in C* bins of 10, 100 and 1000. This correction is expected to increase SOA production in regions where OA is greater than 10ug/m^3. We have also updated isoprene yields as discussed in RI.7a. The new yield table is shown below, and has been updated in the manuscript. To account for this change we have redone model simulations for NY, NY_D, NY_DP, NY_DPH runs.

Table 1: Parameters used in the new volatility basis set (VBS_NEW). Wall corrected mass yields are based on the Statistical Oxidation Model (SOM) fit to the chamber data from Zhang et al. [2014]. For isoprene, an isoprene-specific version of SOM was used (see Supplementary Material for details). IVOC yields are derived from the explicit model GECKO-A simulations performed for n-alkanes mixtures at low (0.1 ppb) and high (10 ppb) NO_X levels. For SOM and GECKO-A fits, yields were derived assuming background OA concentrations of 10 $\mu g\ m^{-3}$.

Precursor	**IVOC**	**TERP**	**ISOP**	**BENZ**	**TOL**	**XYL**	**SESQ**
Mw g mol^{-1}	189	136	68	78	92	106	204
$k_{OH@298K}$ (s^{-1})	1.34×10^{-11}	5.3×10^{-11}	10^{-10}	1.22×10^{-12}	5.63×10^{-12}	2.31×10^{-11}	5.3×10^{-11}
Log[C*]	Mass yields at low NO_X						
< -2	0.315	0.093	0.012	0.007	0.371	0.395	0.270
-1	0.173	0.211	0.013	0.003	0.028	0.041	0.253
0	0.046	0.064	0.001	0.270	0.207	0.203	0.080
1	0.010	0.102	0.100	0.142	0.586	0.121	0.157
2	0.007	0.110	0.078	0.400	0.063	0.232	0.068
3	0.008	0.125	0.097	0.120	0.138	0.145	0.072
	Mass yields at high NO_X						
< -2	0.140	0.045	0.001	0.031	0.042	0.015	0.157
-1	0.136	0.015	0.000	0.011	0.123	0.056	0.220
0	0.069	0.142	0.027	0.507	0.263	0.006	0.083
1	0.019	0.061	0.021	0.019	0.020	0.026	0.097
2	0.010	0.074	0.044	0.030	0.319	0.087	0.054
3	0.012	0.165	0.185	0142	0.329	0.193	0.100

RI.7a) P32419, L7, The SOM method is said to provide yield curves. However, Cappa and Wilson stated that the SOM framework is not well suited for species with multiple double bonds, such as sesquiterpenes or isoprene. In this case, how were yield curves made for these species?

Response RI.7a) The parameters for the SOM are determined by fitting to chamber data. Based on these fits, yield curves are generated and the VBS then fit to these yield curves to determine VBS parameters. The reviewer is correct that the SOM is not especially well-suited to the simulation of compounds with double bonds. This is because the current SOM framework assumes that all product species react with rate coefficients that only depend on the number of carbons and oxygens in the molecule. (The k_{rxn}/"structure" relationship for SOM was determined by explicit comparison with GECKO-A. See the supplemental material of Zhang et al. (2014) for further details.) Given this framework, this means that the 1st generation products that retain a double bond, such as produced from parent species containing two double bonds, may react more slowly than expected. As suggested by the reviewer we have taken into account a more realistic reaction rate for isoprene products, and we have created a new isoprene-specific VBS fit for isoprene. Table 1 was updated accordingly, and all the model simulations have been redone to account for the new isoprene-specific fit. As explained in the supplementary material section (see below), the resulting isoprene-specific SOM yields for isoprene at low-NOx range from ~3.4% at 1μg/m^3 ambient OA to ~8.3% at 10μg/m^3 of ambient OA; whereas at high-NOx they range from ~1.7% at 1μg/m^3 OA to ~4.2% at 10μg/m^3 OA. These values are comparable to the mean isoprene SOA mass yield of 3.3% reported by Marais et al., 2016 for the Southeast US.

In the case of sesquiterpenes, the large size of the molecule (C15) means that a very large fraction of the condensable products are actually "first generation" products, and thus subsequent reactions are of generally less importance. This helps to minimize any issues that come from not considering the higher reactivity of these first generation products more explicitly for this system. Additionally, the yields from sesquiterpenes are large (close to unity). Thus, compared to other SOA types, the SOA concentrations simulated from sesquiterpenes are much more sensitive to emissions than to uncertainties in the yields. Ultimately, although the use of SOM for precursor species containing multiple double-bonds is not perfect, the model framework still allows for a reasonably robust parameterization to be developed. The discussion associated with how the SOM simulations were run has been updated (see Response RI.7b below).

Marais, E. A., Jacob, D. J., Jimenez, J. L., Campuzano-Jost, P., Day, D. A., Hu, W., Krechmer, J., Zhu, L., Kim, P. S., Miller, C. C., Fisher, J. A., Travis, K., Yu, K., Hanisco, T. F., Wolfe, G. M., Arkinson, H. L., Pye, H. O. T., Froyd, K. D., Liao, J., and McNeill, V. F.: Aqueous-phase mechanism for secondary organic aerosol formation from isoprene: application to the southeast United States and co-benefit of SO2 emission controls, Atmos. Chem. Phys., 16, 1603-1618, doi:10.5194/acp-16-1603-2016, 2016.

The following text was included in the supplementary material to explain the isoprene-specific treatment in SOM:

Annex 1: Isoprene-specific SOM scheme

The statistical oxidation model [Cappa and Wilson, 2012] was developed to simulate the multi-generational reactions associated with oxidation (functionalization and fragmentation) of volatile organic compounds (VOCs) within a medium-complexity framework (when compared to models that don't treat ageing explicitly, such as the 2-product model, or to fully-explicit models, such as GECKO-A or MCM). The original [Cappa and Wilson, 2012] and updated [Zhang et al., 2014] SOM framework assumes that the reactivity of all "product" species can be described based only on the number of carbon (n_C) and oxygen (n_O) atoms making up that SOM species. The dependence of the SOM rate coefficients on n_C and n_O was determined based on an assessment of the output from the GECKO-A model for multi-component simulations run based on mixture of organic compounds that is representative of Mexico City [Zhang et al., 2014]. For species containing multiple double bonds, such as isoprene, the original SOM framework may not properly reflect the enhanced reactivity of some of the early-

generation product species due to the presence of a residual double bond. Here, we focus on isoprene.

The products formed from isoprene photooxidation depend importantly on whether the intermediate peroxy radicals react with NO or with HO_2 or RO_2 or whether the molecule isomerizes. Generally speaking, one can distinguish between "low-NO_x" conditions (where reactions with HO_2 dominate) or "high-NO_x" conditions (where reactions with NO dominate). Considering first low-NO_x conditions, as an example, one key product from oxidation of isoprene by OH radicals conditions is the double-bond containing isoprene hydroxy hydroperoxide (ISOPOOH, $C_5H_{10}O_3$) [Surratt et al., 2010]. ISOPOOH reacts rapidly with OH radicals, with room-temperature rate coefficients of k_{OH} = 7.5 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for the (1,2)-isomer and k_{OH} = 11.8 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for the (4,3)-isomer [St. Clair et al., 2015]. These are comparable with the isoprene rate coefficient for reaction with OH, which is k_{OH} = 10 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, but much larger than the original SOM k_{OH} for the C_5O_3 species ($k_{OH,SOM}$ = 0.72 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}). Other key product species formed from multi-generational isoprene photooxidation, such as isoprene epoxydiols (IEPOX), react with rate coefficients more similar to those used with the original SOM. For example, estimates of the k_{OH} for IEPOX range from 0.84 x 10^{-11} to 3.5 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} [Jacobs et al., 2013; Bates et al., 2014], which can be compared with the SOM prediction for C_5O_3 ($k_{OH,SOM}$ = 0.72 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}). Altogether, this suggests that for VOC precursors such as isoprene the original SOM can substantially underestimate the reactivity of some of the early-generation product species in particular, when low-NO_x conditions prevail. Turning to high-NO_x conditions, key first-generation product species are methacrolein (MVK, C_4O_1) and methyl vinyl ketone (MVK, C_4O_1). Both of these react with OH with rate coefficients around 2-3 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} [Paulot et al., 2009], which can be compared to the SOM rate coefficient for C_4O_1 of 0.96 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. This suggests that although the SOM rate coefficient may be too low for these species, the discrepancy is not nearly as large as is possible for low-NO_x conditions, and further these key first generation products react much more slowly with OH than does isoprene.

Although the above discussion demonstrates that the chemistry governing isoprene oxidation is highly complex, it seems nonetheless useful to consider as an alternative method an isoprene-specific SOM scheme that attempts to account for this enhanced reactivity of some product species compared to the original SOM. The development of such a scheme in the SOM framework is complicated by isoprene product compounds (such as ISOPOOH and IEPOX) having the same n_C and n_O but very different rate coefficients for reaction with OH (and in SOM, all species with the same n_C and n_O are assumed to behave identically). Nevertheless, as a first effort towards an isoprene-specific SOM mechanism, an alternate SOM has been developed in which the original SOM k_{OH} relationship with (n_C,n_O) has been modified for the subset of species with n_C = 5 and 1 ≤ n_O ≤ 4. Specifically, it is assumed that k_{OH} for all of these species (C_5O_1, C_5O_2, C_5O_3 and C_5O_4) are all the same as isoprene (C_5O_0), namely k_{OH} = 10 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Although certainly not a perfect representation of the complexity of isoprene oxidation, this modification nonetheless allows for faster reaction of a subset of products that correspond reasonably to "first generation." This alternate SOM formulation is likely to be most applicable to reactions occurring under low-NO_x

conditions, since this is when the largest product k_{OH} values are obtained. The alternate SOM model has been fit to laboratory chamber data on isoprene SOA formation for experiments conducted under either low-NO_x or high-NO_x conditions [Chhabra et al., 2011; Zhang et al., 2014] to determine an alternative set of SOM parameters. The fits were conducted assuming that vapor wall losses influenced the experiment with a first-order loss coefficient of $k_{wall} = 1 \times 10^{-4}\ s^{-1}$ (as was done for all other species, discussed in the main text). The resulting fits using alternate SOM are shown in Figure S1, along with the fits that resulted from the original SOM.

The SOM parameters for this alternate fit are shown in Tables S1 and S2 along with the original SOM fits. It is evident that both model formulations (original or alternate SOM) fit the observations well. Using the fit parameters determined from this fitting exercise, simulations were then run where all conditions were the same as the experimental conditions but now where the vapor wall loss rate coefficient was set to zero. This is meant to reflect what might happen in the atmosphere when the loss rate of vapors is decreased substantially relative to that in the chamber. For both the original and alternate SOM formulations, the amount of SOA simulated when $k_{wall} = 0$ is substantially increased relative to when $k_{wall} = 1 \times 10^{-4}\ s^{-1}$, indicating the importance of accounting for vapor wall losses when fitting chamber observations. There are, however, notable differences between the two formulations that depend on the NO_x condition. For the low-NO_x case, the alternate formulation leads to less SOA than does the original formulation. For the high-NO_x case, the alternate formulation leads to more SOA than does the original formulation.

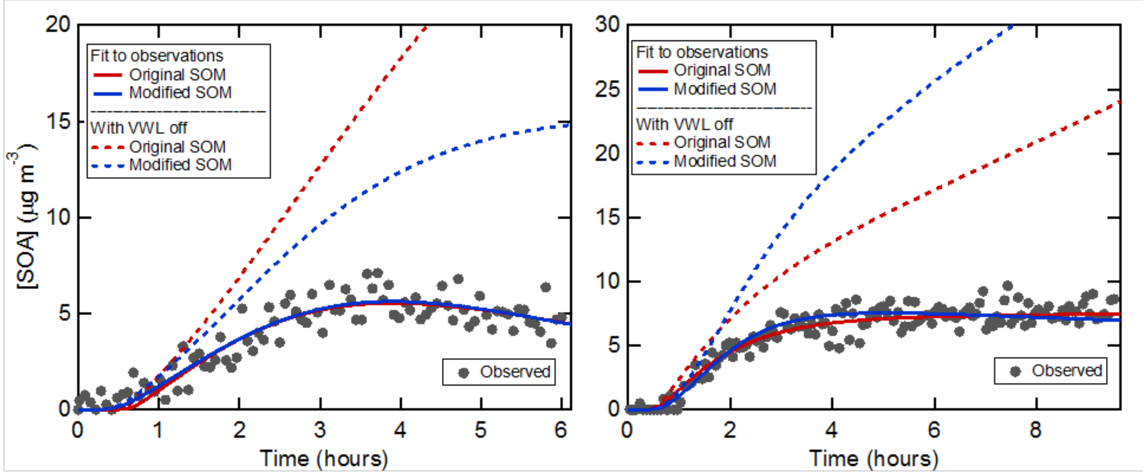

Figure S1. *Observations of SOA formation (gray points) and the resulting SOM fits to the observations (solid lines) for the original SOM (red) and the modified SOM (blue), and where the fits were performed under the assumption that $k_{wall} = 1 \times 10^{-4}\ s^{-1}$. SOM simulation results based on these fits are also shown for the same reaction conditions (i.e. initial VOC concentration, OH concentration), but where k_{wall} is now set to zero (dashed lines) to illustrate the influence that vapor wall losses had on the model fits. Observations and results are shown for low NO_x (left panel) and high NO_x (right panel) conditions, with more experimental details available in Zhang et al. [2014] and Chhabra et al. [2011].*

Additional simulations were run (similar to those in the main text for other species) to determine the long-time VBS product yields that describe the SOA formation from isoprene oxidation. Specifically, simulations were run for 36 h where [isoprene] = 1 ppt, [seed] = 10 $\mu g\ m^{-3}$, [OH] = 2×10^{6} molecule^{-1} cm^{-3}, and where the seed is assumed to be absorbing and instantaneous equilibrium partitioning was assumed. At the end of these 36 h, the SOM products in both the gas and particle phases were binned according to saturation concentration (in $\mu g\ m^{-3}$) into logarithmically spaced bins ranging from log C^{*} of -2 to 3. All species with log $C^{*} < -2$ were grouped into the log C^{*} = -2 bin. The product mass yields for products in each bin were calculated by dividing the total mass concentration of all species in that bin by the amount of reacted isoprene. The SOA mass yield (calculated as new SOA formed divided by isoprene reacted) differed substantially between the simulations using the original and alternate formulations. For both low- and high-NO_x the SOA mass yield was much larger for the original formulation. For the low-NO_x case, this is primarily due to the difference in the predicted yield of species that fall into the log C^{*} = 1 bin. For the high-NO_x case the difference was primarily due to the larger yield of species in both the log C^{*} = 0 and 1 bins. This result indicates that structural assumptions regarding the SOM model can have a large impact on the simulated VBS mass yields and total SOA yield predicted by SOM.

Table S1. The derived SOM parameters for isoprene under low-NO_x and high-NO_x conditions derived from the original SOM formulation and for the alternate case in which some of the products are assumed to be more reactive towards OH radicals. The SOM fits used here were derived assuming that vapor wall losses influenced the observations, with $k_{wall} = 1 \times 10^{-4}\ s^{-1}$.

SOM Parameter[a]	Low-NO_x		High-NO_x	
	Original	Alternate	Original	Alternate
m_{frag}	0.01	0.01	0.322	0.502
DLVP	2.23	2.25	2.23	1.92
P1	0.0003	0.789	0.679	0.994
P2	0.146	8E-05	0.321	4E-05
P3	0.826	0.183	0.0005	0.006
P4	0.028	0.028	0.0002	0.0002

See Cappa and Wilson [2012] for detailed descriptions of these parameters. In brief, m_{frag} characterizes the fragmentation probability with $P_{frag} = (O:C)^{mfrag}$, ΔLVP characterizes the decrease in volatility per oxygen atom added and P1-P4 indicate the probability of functionalization leading to addition of 1-4 oxygen atoms.

Table S2. Derived VBS mass yields for isoprene under low-NO_x and high-NO_x conditions derived from the original SOM formulation and for the alternate case in which some of the products are assumed to be more reactive towards OH radicals. The SOM fits used here were derived assuming that vapor wall losses influenced the observations, with $k_{wall} = 1 \times 10^{-4}\ s^{-1}$.

	Low-NO_x		High-NO_x	
log C^*	Original	Alternate	Original	Alternate
-2	0.011	0.012	0.013	0.001
-1	0.014	0.013	0.008	0.000
0	0.042	0.001	0.079	0.027
1	0.333	0.100	0.083	0.021
2	0.216	0.078	0.059	0.044
3	0.348	0.097	0.178	0.185
SOA yield with 10 μg m^{-3} seed	**0.252**	**0.083**	**0.141**	**0.042**

Table S3. *Derived VBS mass yields for isoprene under low-NO_x and high-NO_x conditions derived from the original SOM formulation and for the alternate case in which some of the products are assumed to be more reactive towards OH radicals. The SOM fits used here were derived assuming that vapor wall losses did not influence the observations, with $k_{wall} = 0\ s^{-1}$.*

	Low-NO_x		High-NO_x	
log C^*	Original	Alternate	Original	Alternate
-2	0.002	0.002	0.000	0.000
-1	0.001	0.027	0.000	0.002
0	0.044	0.000	0.008	0.000
1	0.010	0.019	0.007	0.021
2	0.000	0.023	0.025	0.026
3	0.054	0.003	0.018	0.007
SOA yield with 10 mg m^{-3} seed	**0.049**	**0.041**	**0.013**	**0.015**

RI.7b) P32421, L9. Related to this, SOM was run assuming 10 ug/m^3 OA background, which suggests that the yield curves are more suitable for polluted environments rather than free tropospheric. How does this affect the results of this paper?

Response RI.7b) The reviewer raises an important question regarding how the initial model parameterization influences the results here. We address this in two ways: (i) by modifying the text associated with the SOM+VBS model parameterization to make clearer exactly how this was done and (ii) through the following discussion. Although decreasing the amount of seed does have some influence, the influence is smaller than the reviewer might think for the following reason. We determined the VBS yields used here based on the end-of-run distribution of mass from the SOM. This is somewhat different than fitting a "yield curve" to determine VBS parameters. This may not have been clear in the original manuscript, and thus the text around P32419, L5 has been updated. By using these "end-of-run" results, the derived distributions become less sensitive to the seed concentration. The seed concentration does have a relatively large influence on the distribution between the gas and particle phases, but not on the overall amount of material produced. Thus, although there are some differences in the distributions derived using a seed of 10 vs. 1 μg/m^3, the differences are relatively minor. Changing the seed concentration appears to mainly shift material around between the lowest volatility bins while keeping the total amount of material summed across the lowest volatility bins approximately constant.

This is now explained in the manuscript in section 2.2:

Specifically, synthetic SOA yield curves (i.e. the amount of SOA formed versus the amount of VOC reacted) were generated using the Statistical Oxidation Model (SOM) [Cappa and Wilson, 2012] based on previously-derived fits to chamber data. The SOM accounts for the influence of multi-generational chemistry, including both functionalization and fragmentation. The SOM parameterizations are unique to precursor species and NOx conditions. The SOM parameters are determined by fitting laboratory chamber data, specifically the time-evolution of the SOA formed during oxidation of a given VOC. All experiments considered were performed in the Caltech chambers and results from the fits are summarized in Zhang et al. [2014]. The SOM framework can account for the influence of losses of semi- and low-volatility vapors to the chamber walls on SOA formation using the Matsunaga and Ziemann [2010] methodology, and as described by Zhang et al. [2014]. The appropriate value to use for the vapor wall-loss rate coefficient (k_{wall}) remains a point of discussion, but can vary between chambers due to differences in chamber size and operation. Here, a value of k_{wall} = 10^{-4} s^{-1} was assumed. This is likely a conservative (i.e. low) estimate as Zhang et al. [2014] derived a slightly larger value (2.5 x 10^{-4} s^{-1}) and Matsunaga and Ziemann [2010] a substantially larger value (~10^{-3} s^{-1}), albeit in the latter case for a different chamber. Here, this conservative estimate is used so as to provide an initial assessment of the influence of vapor wall losses, the effects of which may actually be larger than simulated here if the appropriate k_{wall} is larger than 10^{-4} s^{-1} [Cappa et al., 2016]. For isoprene specifically, which contains two double bonds and can form products that react as fast, if not faster than, isoprene itself, especially under lower NOx conditions [Surratt et al., 2010; St. Clair et al., 2015], an isoprene-specific version of SOM was also used to fit the chamber observations. Parameterizations resulting from both the original and isoprene-specific SOM formulations have been described and compared in the Supplemental Material (Figure S1 and Table S2). The primary results in this work are based on the isoprene-specific formulation.

Results from SOM simulations are used to determine parameters for use in the volatility basis set (VBS) model framework. Specifically, after determining a set of SOM parameters for each precursor with vapor wall losses accounted for, a set of simulations were run for each precursor VOC with: constant [OH] = 2x10^6 molecules cm^{-3}; run time = 36h; absorbing seed concentration = 10 μg m^{-3}; precursor [VOC] = 1 ppt. The SOM product species from these simulations were then binned by their *saturation concentration into logarithmically spaced bins (e.g. logC* ranging from -2 to 3, see Table 1) according to their gas + particle phase concentrations at the end of the simulation, and normalized by the total precursor concentration to determine mass yields as a function of volatility. Thus, the long-time (36 h) VBS mass yields can be calculated as:*

$$a_{VBS,x} = \frac{\sum_{\log C^{*}_{SOM,i} \geq x-0.5}^{\log C^{*}_{SOM,i} < x+0.5} C_{SOM,i}}{\Delta[HC]}$$

where $a_{VBS,x}$ *indicates the mass yield in VBS bin defined as* $\log C^{*}_{VBS} = x$, $C_{SOM,i}$ *is the gas + particle mass concentration of a given SOM species i after 36 h of reaction and* $C^{*}_{SOM,i}$ *is the saturation concentration of that species, and Δ[HC] is the reacted amount of a given parent hydrocarbon. All species with* $\log C^{*}_{SOM,i} < -2.5$ *were added to the* $\log C^{*}_{VBS} = -2$ *bin. This produces a VBS for each compound for use in the global simulations that effectively accounts for the influence of vapor wall losses and, to first order, for the long-time influence of multi-generational chemistry. This new set of parameters used in the VBS_NEW model is summarized in Table 1 for low- and high-*NO_X *SOA production from terpenes, isoprene, sesquiterpenes, benzene, toluene and xylene.*

RI.7c) And further, yield-curves and fits are rather specific to the chamber data being modelled, with the implied restrictions on time-scales. How can a VBS system (which excludes ageing) derived from a SOM run over limited chamber data cope with multi-generational chemical ageing?

Response RI.7c) The reviewer is correct in that the VBS framework is an imperfect way to account for multi-generational chemical ageing, and that the SOM fits may be limited by the chamber data to some extent. Here, it is important to note that the multi-generational ageing is intrinsic to all systems. There is no point at which the effects “turn on”. There is simply an evolution of the concentrations of the different product distributions over time (see e.g. Wilson et al. (2015) for a fuller discussion). The aim here was to use the “long time” yields, derived from SOM, to approximate the effects of ageing within the VBS framework. Here, “long time” is 36 hours of continuous reaction at [OH] = 2 x 10^{-6} molecule cm^{-3}, or effectively 3 days of reaction (assuming 12 hours of sunlight per day, on average). Ultimately, it would be preferable to use a model in which multi-generational ageing (including functionalization and fragmentation) is explicitly included, but at this point in time this is not possible. But we reiterate that by using the actual mass yields determined after running SOM or GECKO for a long time, the influence of multi-generational ageing is, at least to first order, accounted for. We also point the reviewer to our response above regarding the details of the SOM simulations.

RI.7d) I don’t understand why only low-NOx yield curves are used for BSOA, since such compounds may clearly undergo oxidation in urban atmospheres too. (Indeed, this might be one reason for anthropogenic enhancement of BSOA production.) In any case, the cited Jo et al. paper just refers back to Henze et al. 2008 for this assumption, so it is better to cite the original source too.

Response RI.7d) We follow the general treatment of BSOA in previous versions of GEOS-Chem (Jo et al., 2013). This treatment of BSOA in GEOS-Chem is uncoupled from gas-phase biogenic chemistry, and the model does not explicitly keep track of the fraction of peroxy radicals that react with HO_2, other peroxy radicals, and NO. We are therefore unable to estimate the impact of using low-NOx yields for biogenics in some model cells where high-NOx yields might be more appropriate. We note that a previous global model study by Pye et al. (2010, Figure 2b) has found that more than 90% of biogenic hydrocarbons react through the low-NOx pathway, and that the difference on surface SOA concentrations between low-NOx and high-NOx yields is small. We therefore choose to use the low-NOx yield parameters for BSOA production as in previous versions of GEOS-Chem.

We address this comment by adding the following text (in red) to Section 2.2:

"Similar to Jo et al. [2013], we use the low-NOx yield values for biogenic species since most of the biogenic emissions occur over low-NO_X forested regions, and since the coarse model resolution cannot resolve high-NO_X conditions. This is also consistent with the previous global model study by Pye et al. [2010] which reported that more than 90% of biogenic hydrocarbon reactions proceed through the low-NOx pathway. ~~and~~ For anthropogenic species, we perform a linear interpolation between low- and high-NOx yields ~~values for anthropogenic species~~ based on the relative ratio of HO_2 and NO at the location and time of VOC oxidation (Lane et al., 2008)."

Note that we only consider yields of these species at low-NOx conditions since most of the isoprene and terpene emissions around the globe occur in remote or rural forested locations (i.e., under low-NOx conditions), and a global model with coarse horizontal grid spacing (~250 km) can barely resolve urban high-NOx conditions

RI.7e) Finally, I am curious, why didn't the authors just use the SOM model, since it seems to underlie their VBS schemes?

Response RI.7e) Jathar et al. (2015, 2016) have applied the SOM directly within a regional air quality model, but the computational expense currently prohibits incorporation into a global model. Indeed, Jathar et al. (2015) included 324 additional gas-phase species and 2592 additional particle-phase SOM model species into the air quality model for the simulations reported in their paper.

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RI.8) Other points:
RI.8.1) P32416, line 3. Better to say 'assumed small' dry deposition velocities, since most such models also neglect the observations of fast particle deposition to forests (e.g. Pryor et al., 2008, below).

Response RI.8.1) we have updated this sentence and used the term "predicted" instead of assumed, as the deposition velocity for aerosol particles is calculated in 3D models.

RI.8.2) P32416, line 5. It can be noted that Hallquist et al (2009) estimated that vapour-phase deposition of OC was substantially greater than particulate phase (800 TgC/yr vs. 150 TgC/yr, c.f. Fig. 1), so this issue of gaseous deposition has been highlighted previously.

Response RI.8.2) Hallquist et al. [2009] have highlighted the large uncertainties associated with the deposition of gaseous VOCs, and have derived the value of 800 TgC/yr for the deposition of VOCs from the global fluxes of VOCs and OA. It seems however that the proposed value refers not only to condensable organic vapors (that we are interested in) but include all VOCs including the precursor species.

RI.8.3) P32422, L12-13. I was puzzled that Heff values for terpenes were used for terpene products. Why would this be a good assumption for compounds such as pinic acid for example?

Response RI.8.3) We agree with the reviewer, and we are not using the values of monoterpenes, but of their oxidation products. This has been clarified in the manuscript:

"For traditional anthropogenic precursors, we use H^{eff} *typical of oxidation products of n-alkanes while for biogenic precursors we use* H^{eff} *values typical of oxidation products of monoterpenes."*

RI.8.4) Notation issues.
- Eqns. (1,4) and elsewhere uses () to represent concentrations, but the normal practice in chemistry is to use [].

We agree with the reviewer, and we have used "[ ]" in our original manuscript, but those were modified into regular parenthesis "( )" when the paper was put into the acpd format. We will insist on having "[ ]" when the paper will be under proofreading.

- P32427, ugsm-3! The use of 's' for STP and not seconds here is very unconventional, in fact downright misleading, and completely unnecessary! I was actually a little shocked to see experienced scientists redefine such a well-known symbol within an otherwise SI-conforming expression. And why? The abbreviation STP has been used in every text book I have seen since my school days. Should readers expect to check the meaning of "m" also, or "g" to see if these were also redefined somewhere in the text?!

This remark has already been made by Dr. Andreae, and we absolutely agree with the use of SI notations. We have updated the manuscript accordingly and modified "sm^{-3}" to m^{-3}(STP)". We note also that previous studies showing the aircraft comparisons have used the "sm^{-3}" notation: Heald et al., 2011: *Exploring the vertical profile of atmospheric organic aerosol: comparing 17 aircraft field campaigns with a global model. Atmos. Chem. Phys. 11, 12673–12696, 2011*.

RI.8.5) P32425, L5. Explain what loses 10% by mass - presumably that means for one molecule of SOA?

Response RI.8.5) It is 10% of the SOA mass that is being lost. This is now clarified in the manuscript: "*We assume that each oxidant lost from the gas phase reacts with one molecule of OA, and that 10% of the OA mass is lost as a result*".

RI.8.6) 32426 Which sampling times are used for IMPROVE and EMEP, and does this matter for the comments about evaporation of the IMPROVE samples?
Response RI.8.6) The IMPROVE network uses the filter-based samples of PM2.5. Filters are collected for 24h every 3 days, and are collected and shipped without cooling every week. Previous studies (e.g. Kim et al. 2015) found that the IMPROVE OC measurements collected in the summer were biases low (up to ~30%) compared to other OC data. This is now explained in the manuscript:

"During the considered period, the mean OC concentration are 2.5 times larger at the EMEP sites (3.46 µg m-3) than at the IMPROVE sites (1.27 µg m-3), which could be due to a greater proximity of urban and industrial centers. Evaporation of OC from IMPROVE summer samples which are kept in the field for several days and shipped without cooling, could also play a role [Kim et al., 2015]."

RI.8.7) P32433, L27. The recent paper by Denier van der Gon et al. (2015, below) reinforces the lessons about wood-burning from these earlier studies.

Response RI8.7) We have made reference to this recent study.

RI.8.8) P32434. As noted above, I don't think we learn much from comparisons against urban sites, and in order to learn anything at all I would have wanted more information on model performance for other pollutants. For SOA the non-linearity of the equilibrium assumptions also make comparison of large grid-cell data against observations in an urban area very questionable.

Response RI8.8) We have followed reviewer's suggestions, and we have removed the comparisons with urban sites.

RI.8.9) Given the importance of free-tropospheric concentrations, I wonder what the authors used for any "background" aerosol assumptions? (Most VBS or SOA models require some kind of background OA, and this is usually assumed to consist of OA from sources not explicitly modelled, e.g. possible marine or other biogenic sources.)

Response RI8.9) We do not prescribe 'background' OA concentrations. Rather, the model is spun up for a year with all emissions (including POA emissions).

Reviewer #2 (Comments to Author):

RII.0) This is an exceptionally well-motivated paper, given the persistent discrepancies between models and measurements of SOA. There are a large number of uncertainties in our fundamental understanding of SOA and its model representation. That the authors attempt to address a number of these in their rethink is commendable and the paper provides a thought-provoking contribution to the area. However, the paper does appear to be a little arbitrary in its chosen areas of uncertainty. These are limited to "corrections" of the chamber yield frequently used to derive model treatments, condensed phase photolysis, surface reaction with oxidants and wet and dry removal. There are a large number of hot topic uncertainties that are not considered that may have significant impacts on the conclusions. This is not to say that every study must address all unknowns in a highly uncertain area, but that care must be taken to construct questions that can appropriately be addressed by the available tools.

Consider four possible hot topic cases - missing SOA sources, SOA formation from condensed phase reactions ("oligomerisation"), formation of so-called "HOMs" or "ELVOCs" from biogenic (or indeed also from anthropogenic) precursors and condensed phase diffusive limitation to evaporation. If the missing OH-reactivity inferred widely from direct OH lifetime measurements were from a class of compound of high SOA yield not represented by the surrogates in a model, this would have significant impact on the goodness of fit to the measurements. If SOA is formed from condensed phase processes in complex mixed multicomponent particles, it would be fortuitous if these were represented by single precursor chamber experiments - indeed this may be one of many contributors to the non-linearities in mixed source (e.g. biogenic / anthropogenic) environments. If low volatility early-generation product formation is significant, the microphysical evolution of the particles will give a very different geographical distribution of mass loading than the generation of mainly semi-volatile SOA. This will also be the case for the evolution of viscous particles, with changes to the "apparent volatility”.

This raises an important (and almost philosophical) question of whether the adjustment of parameters in a model to draw conclusions about processes not treated in a structurally comprehensive manner is appropriate. The authors may justifiably claim that each of these areas is outside the scope and main aims of the paper. However, each of these could significantly impact on the conclusions and the attribution of the magnitude of any of the individual effects they are studying. At the end of the introduction it is stated that the paper focusses on re-assessing "global SOA distribution, budget and radiative forcing in light of new insights into SOA production and loss processes in the atmosphere derived from recent laboratory measurements and theoretical calculations". It appears that a relatively limited subset of recent new insights have been chosen and this subset should be justified. I guess the range of topics addressed and the interesting possibilities raised by the results are worthy of publication, but at the least the conclusions should be much more strongly caveated in light of the points above and questions below. I have a few specific queries about the chosen approaches.

Response RII.0) We thank the reviewer for recognizing that our manuscript presents a though-provoking contribution to the field of organic aerosols. We agree that our study could only present a subset of known uncertainties in 3D models, and we have followed the reviewer's specific comments listed below to more strongly highlight the areas of uncertainties that have not been addressed by the present study.

RII.1) On line 15 of p32415, the underprediction of SOA is stated as being a consequence of underprediction of yields because of lack of wall-correction. This is one of very many possible reasons and can be argued to be a minor reason when compared with the potential for significant missing sources and the inappropriateness of chamber yield extrapolation to ambient conditions. It is difficult to see how chamber yields can be "corrected" to be applicable across a range of atmospheric conditions beyond those in the chamber. A brief discussion of the robustness of drawing conclusions concerning the production and loss rates of SOA from application of "corrections" to such models should be included.

Response RII.1) We agree with the reviewer that there are number of issues related to the use of chamber-derived yields in 3D models. One of them is the loss of condensable gases on the chamber walls which has been quantified in a number of studies (e.g. Zhang et al., 2014) but that has not been consistently included in 3D models. Therefore one of the goals of our study is to evaluate whether SOA parameterizations that account for this "correction of wall-losses" can be reconciled with ambient measurements of SOA. To address reviewers' concerns, in the introduction we have more clearly stated the limited/specific goal of our study:

"We perform a series of model sensitivity simulations using the GEOS-Chem global model to evaluate the importance of the wall-corrected SOA yields, the additional emissions of semi-volatile and intermediate volatility organic species, as well as the effect of additional removal pathways discussed above on the SOA spatial distribution and budget."

We have also added the following sentences to the conclusion to caveat more strongly the limitations of our study:

"One should keep in mind that the proposed VBS parameterization for the VOCs are derived from empirical fitting of laboratory experiments, which are performed on individual precursors and are highly dependent on experimental conditions. Further work is thus needed to fully understand the limitations associated with the use of the chamber-based SOA yields available for a small subset of surrogate precursors in 3D models to represent complex atmospheric mixtures and ambient conditions."

"We also recognize that our study has accounted for a subset of known SOA formation pathways, leaving out in particular the potentially important aqueous-phase formation of SOA in clouds droplets and wet particles [e.g. Ervens et al., 2011; Knote et al., 2014], or the condensed-phase processes that lead to the formation of low-volatility compounds [e.g. Shiraiwa et al., 2013]."

RII.2) The OVOC wet removal treats the solubility as a function of volatility. The solubility at any given volatility will depend on the polarity of a molecule (and hence O:C ratio). Since a 1-D VBS is used, the distribution of solubility at any volatility must be represented by a single value. These are centered on different values for biogenic and anthropogenic precursors (table 2). Have the authors thought about the impacts of the variability at each volatility, which can range over several orders of magnitude? Would the wet removal rate be skewed by non-linear scavenging rate response to this range in solubility?

Response RII.2) We agree with the reviewer that H^{eff} can vary within the same volatility bin. We have already discussed the sensitivity of the deposition velocities to the choice of H^{eff} in our previous studies [Hodzic et al., 2014, Knote et al., 2015. Hodzic et al. [2014] showed that the variability associated with the bin-averaged H^{eff} typically varies by 1 to 2 orders of magnitude for oxidation products from biogenic and anthropogenic precursors species, and that this uncertainty does not impact the results for $H^{eff}>10^7$ M/atm which is the case for dominant biogenic compounds considered in our study. In the present study, we have also shown that increasing H^{eff} from 10^5 M/atm to larger values predicted from GECKO-A, typically 10^7-10^{11} M/atm for biogenic compounds (dominant fraction in our study) does not strongly impact the predicted SOA concentrations.

This is already explained in the manuscript:

"The comparison between the NY simulation, which uses a constant H^{eff} of 10^5 M atm^{-1} (default value in GEOS-Chem), and the sensitivity NY_D simulation, which uses values determined from the explicit chemical modeling (see Table 2), shows a modest decrease of tropospheric SOA, ranging from of 5 to 10% over water surfaces and from 5 to 20% over continents (Figure 3c,i)."

RII.3) It is stated that "in particular, the updated model predicts larger SOA concentrations in the boundary layer" in section 3.1.2. This raises the perennial problem of boundary layer representation in the model, particularly in assessing the magnitude of removal processes (it is definitely the case that the boundary layer schemes in the WRF-Chem model cause considerable problems with comparison with aircraft measurements). Some discussion of the reasonableness of the BL structure in the model and consequent confidence of the conclusions about removal processes would be welcome.

Response RII.3) The meteorology is taken from the Goddard Earth Observing System - version 5 (GEOS-5). GEOS-5 provides meteorological analysis, which means that the system assimilates available meteorological observations. Jordan et al. [2010] have evaluated the boundary layer height predicted by GEOS-5 against the CALIPSO lidar observations, and have shown that the predicted PBL height is within 25% of the observed values most of the time.

This is now explained in the revised manuscript:

"The comparison of surface concentrations could also suffer from uncertainties in the boundary layer parameterizations, and it should be noted that the GEOS-5 meteorological analysis were found to reproduce reasonably well (within 25%) the boundary layer height as compared to the CALIPSO data [Jordan et al., 2010]."

Jordan, N. S., R. M. Hoff, and J. T. Bacmeister (2010), Validation of Goddard Earth Observing System–version 5 MERRA planetary boundary layer heights using CALIPSO, J. Geophys. Res., 115, D24218, doi:10.1029/2009JD013777. Link.

RII.4) Can the authors state why there was no increase in O:C with oxidation in the base run (p32418) and suggest what the implication might be on the conclusions? A "1.5D" VBS approach, such as that implemented in WRF-Chem might go some way to addressing this at modest expense. It is also stated on 32418 that "biogenic precursors are not artificially aged", implying that the "ad hoc" ageing is somehow artificial. Some justification for the inconsistency should be stated (in the light of the further comment below).

Response RII.4) For the reference simulation (REF) described p32418 we are reproducing the base GEOS-Chem configuration that was used in Jo et al. 2014, and the choices on the ageing of anthropogenic and biogenic oxygenated compounds follow strictly those made in Jo et al., 2014.

RII.5) I'm not sure that there is as much constraint on the oxidation rate of precursors and intermediates as inferred by the approach. The fitted VBS includes "to some extent" (p32419, line 23) the ageing. This is the ageing under the chamber conditions from which the fit is derived (oxidant concentration, illumination, VOC:NOx ratio etc.). It is indeed inconsistent to use an arbitrary additional "ad hoc" ageing rate, but it is a rather substantial assumption that the chamber-derived VBS will meaningfully capture the evolving VBS as the precursors dilute and oxidize and mix across a range of photochemical conditions. It is not completely clear that an "ad hoc", but empirically tuned set of rates is an inferior approach. Indeed, this is very likely no worse than "ad-hoc" particle deposition velocity or solubility, particularly if a bulk representation of aerosol is used. How would the authors suggest that there can be confidence in one approach over another? Can they suggest a means of obtaining a better constrained approach rather than fitting a 6-product yield model that implicitly includes oxidative perturbation of the VBS?

Would a combination of dilution and thermodenuding of instantaneous grab samples from particles throughout a chamber experiment allow time-resolved retrieval of the evolving VBS, and hence VBS and ageing rate independently?

Response RII.5) We agree with the reviewer that the SOA modeling suffers from many uncertainties on both production and removal sides. The use of unconstrained ageing parameters in 3D models is one of many examples. Traditional chamber-derived yields already account for ageing of organic compounds that have occurred during the experiment. The additional ageing is often added to those yields in 3D models but without considering or refitting the experimental data. The used values are not constrained by laboratory data, nor empirically adjusted to any data, but are rather arbitrarily chosen, different values are used in different studies although they all are based on the same laboratory derived yields. The reason why our approach can be considered as an improvement is that it uses the SOM model to extrapolate to longer times and include the ageing parameter into the VBS fit. There are of course limitations with our approach and additional laboratory measurements or explicit modeling results are needed to further constrain VBS fits. From the laboratory experiments, although dilution and thermodenuding can provide information on particle behavior, there have been challenges in relating volatility distributions derived from growth measurements to those from such evaporation measurements (see e.g. Vaden et al., (2011), Cappa and Wilson (2011) or Kolesar et al. (2015)). This is because the evaporation measurements are especially sensitive to the influence of condensed reactions on particle volatility whereas the particle growth and the volatility distribution derived in this manner is much less sensitive to particle-phase reactions (see Cappa and Wilson (2011) or Zaveri et al. (2014)). As such, volatility distributions derived from evaporation experiments do not necessarily provide information on the volatility distribution of the condensing products, which determines whether they end up in the condensed phase in the first place. Thus, we believe that the volatility distributions based on growth experiments can be used to improve the current model parameterizations, but where the influence of multi-generational oxidation is included in the analysis of these experiments and derivation of volatility basis sets is appropriate. We feel that the discussion on experimental constraints is beyond the scope of the present paper.

RII.6) Extending this discussion, given the scale of the uncertainty surrounding the rich diversity of potential SOA precursors (and their diversity in yields) in real source mixtures, is it unlikely that VOC emissions inventories that are not designed to focus on SOA precursors miss a significant proportion of them. Over and above the other limitations of the structural treatments in the host model, the authors should comment on the suitability of an attempt to represent the rich mixture of real VOCs and OVOCs by a very limited number of surrogates (isoprene, monoterpenes, sesquiterpenes, a couple of aromatics and a few n-alkanes) with their own uncertainty in emissions and a limited ability to represent the range of SOA-forming behaviour to answer the questions posed in the paper.

Response RII.6) We agree with the reviewer that emission inventories are highly uncertain, and that the use of a limited number of precursor species adds to the uncertainty.

Those points have been acknowledge in the updated manuscript:

"Further work is thus needed to fully understand the limitations associated with the use of the chamber-based SOA yields for a small subset of surrogate precursors in 3D models to represent complex atmospheric mixtures and ambient conditions. Although we have considerably improved the emissions for the purpose of this study by adding S/IVOC emissions, we note that large uncertainties remain in emission inventories of biogenic and anthropogenic precursors [Goldstein and Galbally, 2007]."

Goldstein, A. H. and Galbally, I. E.: Known and unexplored organic constituents in the earth's atmosphere, Environ. Sci. Technol., 41, 1514–1521, 2007.

RII.7) It is interesting that photolysis leads to a loss of one carbon atom per molecule. Can the authors justify cleavage at the end of each molecule?

The 10% mass loss from each SOA molecule for each oxidant accommodated in the heterogeneous oxidation is stated as leading to an upper limit at the stated uptake coefficients for the various oxidants. Given the huge complexity of the inorganic / organic matrix across a wide population of sizes, the surface reactivity differences across this population and the volatility change of the products in the mixture in each particle, I am amazed that the authors consider that there is enough constraint to say whether it is an upper or lower limit. Can they justify further this statement?

Response RII.7) Photolysis can cause cleavage at the end of a molecule e.g. photolysis of carbonyl compounds (formed under low-NOx) that leads to the breakage of the alpha-carbon bond on either side of the C=O group. We refer the reviewer to Hodzic et al. [2015] Table S1, which shows the typical products of various gas-phase photolysis reactions. Given the limited data on the condensed-phase photolysis, we have chosen the loss of 1 carbon atom as a conservative lower loss due to this process. This is now mentioned in the manuscript:

"*We assume that absorption of each photon by an SOA molecule leads to the irreversible loss of one carbon atom (as the lowest possible limit) from the molecule with a quantum yield of QY.*"

We agree with the reviewer's comment related to the uncertainties on the heterogeneous uptake and have removed all qualitative judgment in the manuscript:

~~*"Our calculations of the heterogeneous loss should thus be viewed as an upper limit."*~~
"We note that the additional effect of heterogeneous loss of SOA in our simulations is small ~~although we have considered used an upper limit estimate for the uptake coefficient.~~"

RII.8) SOA comprises a distribution of particles of a wide range of sizes in vapors of wide ranging volatility. The mixing and dilution of pollution will give rise to highly non-linear partitioning (and consequent deviation from equilibrium) that will determine PM mass on a range of temporal and spatial scales that will confound comparison of even very detailed high resolution models with explicit microphysics with point measurements. I agree with their removal, as they have done for the aircraft data. The authors should be consistent in their exclusion of polluted conditions in comparisons with measurements and in predictions of urban pollution for the purposes of exposure. I understand that the population-weighted SOA enhancement factor is only stated as relative to the base run, however I share the concerns of the other reviewer in the comparison of GEOS-Chem for concentrations over the urban population centers. Replication of SOA in urban hotspots / population is an unrealistic challenge for current global models and I struggle with the meaning of calculation of enhancement factors on which to base exposure estimates. I agree with the authors that a "more in-depth study to evaluate the contribution of SOA to PM-related human health effects" is needed, and this should be at higher resolution with more microphysical detail.

Response RII.8) We have removed the comparison with urban measurements, and have more strongly caveated the application to health-studies. See **Response RI.2.**

RII.9) p32419, line 9, it appears that this rate coefficient is inconsistent with the lifetime of a few tens of minutes found by the Ziemann group. If these are correct, what is the effect on the wall-corrected yields and how does this impact on the findings of the current study (presumably increasing the production and loss rates significantly).

Response RII.9) The wall loss rate coefficients that one should use are chamber specific, as they are linked to both molecular diffusion (chamber non-specific) and turbulent diffusion (chamber specific). This is discussed at length in McMurry and Grosjean (1985) and in the supplemental material of Zhang et al. (2014). Put another way, one cannot simply take a value from one chamber and apply it to another. The value used here was determined to be reasonably appropriate for the Caltech chamber based on observations (discussed in Zhang et al., 2014). The use of a larger value for k_{wall} (such as that found by Matsunaga and Ziemann (2010) for their chamber) would lead to a larger apparent influence of vapor wall losses, thereby necessitating greater losses to balance. It is for that reason, that we refer to our use of $k_{wall} = 10^{-4}\ s^{-1}$ as a conservative estimate.

RII.10) p32419, line 12, I presume terpenes refers to monoterpenes

Response RII.10) We have changed “terpenes” to “monoterpenes” throughout the manuscript.

RII.11) p32419, line 13, Why low NOx biogenic yields - in anthropogenically-perturbed cells, surely the higher NOx yields should be used.

Response RII.11) This has been explained above - see Response RI.7d.

Additional references:

Cappa, C. D. and Wilson, K. R.: Evolution of organic aerosol mass spectra upon heating: implications for OA phase and partitioning behavior, Atmos. Chem. Phys., 11, 1895-2011, doi:10.5194/acp-11-1895-2011, 2011.

Kolesar, K. R., Chen, C., Johnson, D., and Cappa, C. D.: The influences of mass loading and rapid dilution of secondary organic aerosol on particle volatility, Atmos. Chem. Phys., 15, 9327-9343, doi:10.5194/acp-15-9327-2015, 2015.

McMurry, P. H. and Grosjean, D.: Gas and aerosol wall losses in Teflon film smog chambers, 19, 1176-1182, doi:10.1021/es00142a006, 1985.

Vaden, T. D., Imre, D., Beránek, J., Shrivastava, M., and Zelenyuk, A.: Evaporation kinetics and phase of laboratory and ambient secondary organic aerosol, Proc. Nat. Acad. Sci., 108, 2190-2195, doi:10.1073/pnas.1013391108, 2011.

Zaveri, R. A., Easter, R. C., Shilling, J. E., and Seinfeld, J. H.: Modeling kinetic partitioning of secondary organic aerosol and size distribution dynamics: representing effects of volatility, phase state, and particle-phase reaction, Atmos. Chem. Phys., 14, 5153-5181, doi:10.5194/acp-14-5153-2014, 2014.

Zhang, X., Cappa, C. D., Jathar, S. H., McVay, R. C., Ensberg, J. J., Kleeman, M. J., and Seinfeld, J. H.: Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, Proc. Nat. Acad. Sci., 111, 5802-5807, doi:10.1073/pnas.1404727111, 2014.