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

**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.