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

Anonymous Referee #2

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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.

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.

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 centred 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?

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

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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.

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).

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 oxidise 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?

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.

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?

SOA comprises a distribution of particles of a wide range of sizes in vapours 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 centres. Replication of SOA in

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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.

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).

p32419, line 12, I presume terpenes refers to monoterpenes

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

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 32413, 2015.

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