Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Evaluating the impact of new observational constraints on P-S/IVOC emissions, multi-generation oxidation, and chamber wall losses on SOA modeling for Los Angeles, CA" *by* Prettiny K. Ma et al.

Anonymous Referee #1

This paper is interesting in that new constraints on S/IVOC emissions are used together with recent VBS yield suggestions, and the results compared to a wide range of measurements. The measurement data range from near-surface to aircraft data, all evaluated using the concept of photochemical age and with SOA/CO ratios. The use of OFR data is also beneficial I think, in helping to place limits on the SOA formation and ageing-process at long photochemical ages.

Although the paper does present some interesting analysis, I think that there are some significant problems, and I cannot recommend the paper for publication until these are

addressed.

One problem is that there have been so many papers by now in which somebody identifies a problem with model-measurement discrepancies in SOA, and by tweaking the VBS parameters in some way one can get better agreement. This paper falls into that pattern, and although the authors have good reasons for their particular choice of parameter-tweaking the fact remains that there are an infinite number of ways of improving SOA predictions. The authors need to demonstrate some advantage of their schemes over others, and this requires a reliable model study.

1 Why a box-model?

In order to demonstrate that the merits of the tweaks used here are real, I would have wanted to see a thorough demonstration of improved model-observation performance across a range of scales. The box model used here cannot in my opinion provide such a demonstration; this study should have been conducted with a well-evaluated 3-D chemical transport model. In fact, with only four mechanisms being evaluated, and over a short period, I cannot think of any reason not to use a CTM.

Although box models are often useful for examination of, for example detailed chemical processes, or basic principles, they are not well suited to studies where comparison with ambient measurements is in focus. This has been well established for years, and is a major reason why air pollution modelling moved from the earlier EKMA-type moving-box models to 3-D models such as CAMx or CMAQ. The measurements used in this study also range from near-surface data to aircraft, which places additional constraints on the abilities of a box model. Although the authors (and those of the previous Hayes et al 2015 study which preceded this work) have put a lot of effort into the box model setup, I do not believe that any amount of effort can overcome the basic limitations of such models. Box models simply cannot account for the 3-D nature of atmospheric

dispersion, and they cannot be expected to cope with pollutant situations where non-linearity of photochemical/SOA production is expected.

The authors may argue that by scaling with CO that they remove dispersion errors but this is only partly true. This does not account for the fact that SVOC partitioning is dependent on absolute OA concentrations, and so requires simulation of e.g. urban plumes and vertical gradients.

More fundamentally, the assumption in this box-model work is that one can predict Δ VOC concentrations from Δ CO alone. There may be some merit in this for transport-derived VOC (and the VOC profiles shown in Hayes et al 2015 show surprisingly good agreement for such VOC), but such a relationship cannot hold for VOC from solvents and various production processes. Thus, we have sources of VOC and hence SOA which are not constrained. I didn't find a discussion of this in the paper.

These problems are even more difficult to deal with when comparing SOA formation at longer photochemical ages, e.g. 3 days as is done here. I would expect problems with any pollutant when running a box model over such time-scales.

The authors (also in Hayes et al 2015) do not even demonstrate that the model is capable of reproducing pollutants such as CO or NO2 reliably, and without this it is impossible to explain model-measurement discrepancies in SOA in terms of VBS parameters alone.

It was disturbing that the text didn't acknowledge these limitations, but instead all model-measurement discrepancies are assigned to VBS/SOA formation parametrizations.

Given that CTM models have already been set up and used for the CalNex campaign (Baker et al., 2015, Hayes et al., 2015, Woody et al., 2016), I would suggest that the authors re-do their work in collaboration with one of these teams.

2 Experiment design

I found the approach confusing in several respects.

To start with, the paragraph at the end of P9 (start of 2.2.2) is worrying. The initial POA is calculated from Δ POA/Δ CO emissions, which implies that POA is an inert pollutant. At the same time the authors use Robinson's volatility distribution to estimate all emitted P/S/IVOCs. How can this be reconciled?

At the end of 2.2.2 (P10) we read that the important ratios of IVOC or VOC to CO are derived from measurements made between 00:00 and 06:00 local time in Pasadena, 'when the amount of photochemical ageing was very low'. There are several problems here, associated with the reliability of such ratios for daytime modelling, and the assumption that other ageing processes are negligible. My guess would be that CO concentrations have a larger component of long-range transport than IVOC for example, and also that night-time chemistry would be more important than assumed here.

Thirdly, it is usually a good idea to change one aspect at a time of model simulations, in order to investigate the effect of that one change. Here though the authors move from a set of 'Tsimpidi' cases to cases where wall-loss are accounted for. At the same time they switch off the ageing of secondary SVOCs. Thus, one cannot evaluate the importance of the ageing effect alone. This would have been a useful step between the TSI and the various wall-loss cases.

Further, on p8-9, we read that ageing of secondary SVOC from 'VOC' is not included, partly because of poorly-constrained chamber data, but ageing of secondary SVOC from P-IVOCs and P-SVOCs is included for the MA cases. These choices feel rather random, and indeed seem like tweaks to give the model a decent chance of fitting the observations.

Finally, the text on p9,L301-304 anyway seems to confirm that the refit was not able to reproduce the chamber data. Although non-equilibrium reasons are given for this, I am

a little confused about the benefit of a refit that cannot reproduce the data.

3 Yield data?

Can the yields in Table S4 be correct? According to the manuscript (p8,L277-), this Table presents the upper limits of the SOA yields, but the numbers look rather odd compared to Table S1 which is supposed to be the lower limit. For isoprene the total yield is 0.039 in both Tables, and for other compounds the differences are sec are quite small (0.194 vs 0.200 for Ole1, 0.382 vs 0.392 for Ole2, 0.932 vs 0.939 for Aro2, 0.835 vs 0.855 for Terp). The main difference seems to be that Table S4 has mainly 0.0 for the 19 ug/m3 bin. A mistake maybe?

4 3-day simulations?

As noted above, I have grave reservations about the use of a box model for this study, and the extension of the simulations to 3-days in Sect. 3.1. seems hard to defend. The authors suggest that they limited the runs to 3-days to minimize the importance of missing processes such as deposition, but a box model misses all processes of dispersion, transport and even chemistry in the correct photochemical regimes when run over such a long time. I simply do not believe that such long runs with such an artificial setup can be compared with measurements in other than a superficial way.

In any case, many SVOC species will show substantial deposition over 3-days (Karl et al, 2010, Hodzic et al, 2016), as indeed would ozone and various NOy species (e.g. N2O5).

5 Some other questions

p3, L86 and generally. Actually VOCs are the only precursor of SOA (though of course other precursors such as NOx can be involved). VOC is a general term (defined here on L80-81) which includes SVOC and IVOC. If the authors want to use the term VOC for volatile organic compounds which are not S/IVOC then they need to refine and clarify their notation.

p3, L99. I was surprised not to see some more recent references here, since much has been done in the last years. For example, Hodzic et al 2016 seem to cover some of the same themes (wall-loss corrected VBS) as this paper, with an evaluation at global scale. Another relevant work would be that of Dunmore et al 2015 and Ots et al. 2016, where IVOC emissions from diesel were suggested to be a major source of ambient SOA.

p4, L105-107. If discussing VBS as a conceptual model, the 2-D version (Jimenez et al., 2009) deserves a mention. Actually, why was this version not used? Box/Lagrangian models have few restrictions on CPU usage, so would be a natural place to test 2-D VBS schemes.

p4, L118. loses should be losses. (There are other some small typos/English problems throughout, which should be checked.)

p6, L185-189. The text states that the potential source of error from omission if cold-starts does not apply to the total amount of vehicular POA emissions. This may be true if the absolute emission rates are not used, but surely the volatility distribution of cold-start VOC is different to that of warm-running engines?

On the same paragraph though, presumably the Worton et al data could be used to produce a new estimate of total vehicle (S/I)VOC emissions. Why wasn't this done?

p8,L276-279, 281-288. Quantify these time-scales for the reader.

P11, L370 and elsewhere. Define whether mass or volume fractions and stoichiometry are used. This can be an easy error, especially when the cited Donahue paper redefined Raoult's law in terms of mass rather than mole fractions.

P11, L396. 'shorter' ... than what?

P15, L519-523. Too wordy and repetitive.

P15, L531. The work of Dunmore and Ots mentioned above would support this statement.

P15, L543 on. This paragraph is a good example where the authors attribute all problems to SOA mechanisms. It may well be that the box model setup is responsible for the problems.

P17, Sect. 3.2. Given my reservations about the validity of the box-model, and its obvious lack of treatment of VOC degradation with transport time, I wasn't convinced that this section had a good basis. In addition, the manuscript is already quite long, and this section feels like a side-issue.

6 Additional References

Dunmore, RE et al., Diesel-related hydrocarbons can dominate gas phase reactive carbon in megacities, ACP, 2015, 15, 9983-9996

Karl, T et al., Efficient Atmospheric Cleansing of Oxidized Organic Trace Gases by Vegetation, Science, 2010, 330, 816-819

Hodzic, A et al., Rethinking the global secondary organic aerosol (SOA) budget: stronger production, faster removal, shorter lifetime, ACP, 2016, 16, 7917-7941

Ots, R et al., Simulating secondary organic aerosol from missing diesel-related

intermediate-volatility organic compound emissions during the Clean Air for London (ClearfLo) campaign, ACP, 2016, 16, 6453-6473