

Interactive comment on “Global mechanistic model of SOA formation: effects of different chemical mechanisms” by G. Lin et al.

Anonymous Referee #2

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This paper is interesting in that it makes use of a chemistry-based scheme to explore the possible importance of different pathways to SOA. It is very useful that the community explores different approaches, and such chemical mechanisms do offer new insights compared to those arising from the popular VBS approach. Many of the results are indeed interesting, and useful to the community, but I am less sure that the results are convincing. This isn't helped by the fact that the text is often confusing and makes statements that aren't backed up by results presented in this paper.

Firstly, I think that what the authors present is an interesting sensitivity study. They claim though (most prominently in the abstract, line 18) that their model "realistically" predicts the organic carbon mass observed in the Northern hemisphere. A quick look at the Figures would give a rather different impression. (Even if the scatter plots were

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perfect I would assume this was largely fortuitous or tuned, as I still doubt that today's knowledge would allow any group to "realistically" simulate OC!). The paper then has a tendency to interpret any problems in terms of just two or three specific processes, for which actually little or no evidence is presented (again, see abstract for the example of having too high update rates of two compounds).

Further, the model comparison with observations is limited in some important ways, and I think more should be done here (see below).

As a final general comment, the paper needs a thorough read through by the authors, to make sure that every sentence makes sense in itself, and to likely readers. All statements should be either supported by the material presented, from other literature, or omitted. I give examples below.

Specific Comments (major)

* Firstly, I thank the authors for their response to my query on the terminology concerning non-evaporative other SOA (ne_oSOA). As this term did seem to cover both real ne_oSOA (the oligomers) and "traditional" SOA (let's call it sv_SOA for semi-vol) which is in dynamic equilibrium, an interesting follow-up question is then why the real ne_oSOA and the sv_oSOA are not documented separately? This would be consistent with the other species treated here e.g. from glyoxal, and would allow the reader to see the importance of the oligomerization assumptions.

* On a similar issue, how do the oligomer products fit into the results shown in Table S1?

* Page 26359. The issue of vapor pressure is critical to SOA schemes (shown in several papers), but there is hardly any mention of its importance here. How sensitive are your estimates to this parameter?

* It would have been useful to show or discuss what happens if you assume 0.5 or 2 day lifetimes for oligomer formation.

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* This chemical mechanism makes specific predictions of which pathways contribute to SOA formation in the atmosphere, e.g. (p. 26368) that 66% of the production rate is from methylglyoxal and epoxide. What is the observational evidence that these specific products account for such a large fraction of ambient OC?

Other Comments

* Page 26349, 1st paragraph. It might be good to mention already here the IVOC and OPOA concepts briefly (Robinson et al, 2007). The simple distinction between POA and SOA is fading rather quickly these days.

* Page 26349, line 24. The Simpson et al study seemed to do quite well for Nordic sites, so I didn't interpret that as a general failure to model SOA? Actually, that study demonstrated how the SOA results were very sensitive to vapor pressure assumptions.

* Page 26350, The Slowik paper year is wrong

* Page 26350, line 27. The text states that the problem "requires" a rigorous and thorough gas-phase chemical mechanism. Donahue has argued in several papers (e.g. Donahue et al 2009) that the complexity of SOA requires the opposite - an approach where we know that we cannot know the individual species and reactions. A short discussion or rephrasing might be appropriate here

* Page 26351, 1st line. What does "As a consequence" mean here? The previous sentence mentioned that isoprene was 1/3 of VOC emissions, nothing to directly support the consequence stated here.

* Page 26351, line 3, "some measured data". Actually, there is a wealth of data on this now, not just some.

* Page 26352, line 9 grammar: better "has been" than "was also".

* Page 26353, line 4 grammar: what do you mean, "we also"? ("we" might do?)

* Page 26354 - explain where the short names used here (e.g. ACO₂) are explained

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* Page 26356. It was confusing to read the sentence starting "Therefore ", when the previous sentence seems to have nothing to do with the text following "Therefore". Please re-phrase.

* Page 26358. The formatting of the list at the end needs to be improved

* Page 26358, line 17. Add "and properties" to distribution. Many things can go wrong even if the products were captured perfectly, and we seem to be very far from that stage at the present time.

* Page 26365, line 13 - reference for terpene emissions?

* Page 26366, lines 5-7 - formatting of rate coefficients mangled.

* Page 26369 - it is important that the vapor pressure be sub-cooled if necessary.

* Page 26366 - how was the dry deposition of semivolatiles treated? Bessagnet et al. (2010) showed it to be quite important, as also noted by Hallquist et al., 2009.

* Page 26367, paragraph starting on line 18 - this paragraph started a distracting discussion in the section entitled results. Move later in the text.

* Page 26369. I found the chemistry description here confusing, partly as the authors do not distinguish between RO₂ in general, and the specific RO₂ compounds that form their products. I suggest a more explicit approach using more numbered equations, and greater clarity.

* Page 26369, what does "may" originate ... "potentially" mean. A little over kill on the qualifiers I think!

* Page 26370 suffers similar problems. The last 2 sentences say that the only pathway to form epoxides is through the RO₂ + HO₂ reaction (R3), but RO₂ includes CH₃O₂ as well as any more complex radicals.

* Page 26373. As this model has explicit chemistry, I was confused to read that it only

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predicts OM. Don't you have the full chemical formula of each product, and hence both OC and OM?

* Page 26374. You say the larger particles are not captured very well by the model. Do you have any large particles at all?

* Page 26374, line 13 ... since isoprene emissions are low I would have thought it just as relevant that POA sources are high (e.g. biomass burning). (The Simpson et al. CARBOSOL paper mentioned there used levoglucosan to demonstrate that accounting for wood-burning very well "fixed" the wintertime OC concentrations.)

* Page 26374. Many Szidat papers have shown similar results, e.g. Szidat et al., 2007

* Page 26374. I wonder why the one Gilardoni paper was used for this comparison. The site involved is rather subject to local emissions within the Po Valley, and GEOS-CHEM cannot resolve such areas I think. The CARBOSOL sites would have provided a more regional data set for comparison to GEO-CHEM. In addition, the referees had some concerns about the summertime results of the Gilardoni et al. paper that I do not think were adequately addressed. Relying on only one such study in one location is rather dangerous though.

* Page 26375. On a similar theme, why compare with urban sites from Zhang et al. 2007? GEOS-CHEM isn't designed for that, and these sites just confuse the results. I think this should be removed.

* Page 26376, line 15. Clarify where this 10% came from? Do you have observed POA?

* Page 26376-26377, general. I am not convinced that comparing a model with 4x5 degrees resolution with local isoprene data can provide much information on the reasons for over or underestimation of SOA. This paragraph is attempting too much detail. Some of the speculation could be moved to the discussion section, some could be omitted. * Page 26378, line 9. Looking at Fig. 7a I don't see support for the statement

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that the results "compare favorably with the INTEX-B results". The most interesting part of the figure is that the observations cover a very wide range, and GEOS-CHEM fits within that, closer to INTEX-B at high altitude.

* In general, why do all simulations give the same results for Fig. 7a? They are hardly distinguishable here. Over North America (Fig 7b) there are modest differences at least.

* Page 26378, same paragraph. I don't think 3 significant figures are needed when comparing OC data.

* Page 26378. It would be good with a summary of the model performance for SO4. One cannot draw many conclusions about SOA predictions without knowing how well a model performs for the easier compounds.

* Page 26380, line 22. I didn't see much evidence that you underpredict POA in winter. I agree it is likely, but not shown.

* Page 26380, line 28. Did the model "significantly overestimate OM". The model has coarse resolution, and the data are sparse.

* Page 26380, last line. I disagree.

Figures:

Fig. 1 has no units on y-axis

Add year of modeled and observed data to all plots

Tables:

S1 - is this the global total? Which temperature is K valid for? Format numbers using decimals where possible: it is hard to spot the large contributors when all are in scientific notation.

S3, S4: number reactions please.

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Add year of modeled and observed data to all plots

Extra Refs:

Bessagnet, B.; Seigneur, C. & Menut, L. Impact of dry deposition of semi-volatile organic compounds on secondary organic aerosols *Atmos. Environ.*, 2010, 44, 1781 - 1787

Szidat, S.; Prévôt, A. S. H.; Sandradewi, J.; Alfarra, M. R.; Synal, H.-A.; Wacker, L. & Baltensperger, U. Dominant impact of residential wood burning on particulate matter in Alpine valleys during winter *Geophys. Res. Lett.*, 2007, 34, L05820

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 26347, 2011.

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