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Atmospheric
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Discussions

Interactive comment on "Development of a secondary organic aerosol formation mechanism: comparison with smog chamber experiments and atmospheric measurements" *by* L. E. Olcese et al.

Anonymous Referee #2

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General comments This paper is relevant to ACP and presents a new model for secondary organic aerosol formation. It is fairly well written and appropriately titled; its abstract is adequate. However, the lack of detail in certain areas and several errors make it impossible to recommend this paper for publication. A long list of specific comments supports this recommendation.

Specific comments Page 8363, line 6. POA is typically not used to describe primary carbonaceous aerosol that includes organic and black/elemental carbon. Rather, POA should be used to describe only the organic part.

Page 8363, line 20. Generally, the modeling methods described do not use a sticking

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coefficient for semi-volatile organic species. Rather, the chamber parameters used are overall equilibrium descriptors and implicitly include this parameter.

Page 8363, line 22. Catalysis by what?

Page 8363, line 23. References are needed at the end of the sentence describing uncertainties in SOA models.

Page 8363, line 28. The Griffin 2002 approach is not one that uses alpha and K derived from chambers.

Page 8364, line 8. This is not true. Reaction rate coefficients are not derived from chamber experiments. Rather overall average partitioning coefficients of the products are derived. Generally, the reaction rate coefficients of the primary hydrocarbons are known from separate experiments.

Page 8364, line 14. The statement regarding particle-phase reactions not being included is not exactly true. In reality, because the parameters derived from chamber experiments tend to be from the end of the experiments, the effect of any particle-phase reactions are implicitly included in the partitioning coefficients.

Page 8364, line 21. The authors claim to calculate partitioning coefficients differently than other methods. How? Other models are also based on the theory of Pankow. Also, how are hydrophobic versus hydrophilic aerosols treated in the model of the authors? What inorganic aerosol model is used? Is one?

Page 8364, line 28. The authors state that other calculations have been unsatisfactory. How? Why?

Page 8365, line 10. Generally, black carbon is not thought to be an absorptive medium for SOA. Is this included in their calculations for K? If so, what properties are used?

Page 8365, line 15. It should only be the organic compounds that contribute to the average molecular weight for the partitioning coefficient calculation presented here.

This should be specified.

Page 8367, line 3. The authors say that Kroll specifies only small yields but that the Henze paper shows significant SOA globally from isoprene. However, the Henze model is based on the laboratory results of Kroll. This seems to be contradictory.

Page 8367, line 15. The authors cite the Iinuma paper that shows a 40% effect of acidity. The model presented in this paper is closer to observations without including this effect. How is this possible? Does this not imply that the authors model overestimates SOA from the mechanisms presented here? It is known that aerosols tend to be acidic in at least one of the regions discussed (New England).

Page 8368. For this discussion, it must be specified that the partitioning theory presented is only looking at partitioning between gas and a condensed organic phase, not total aerosol.

Page 8369, line 3. Other authors have used the Myrdal and Yalkowsky approach and yet still see underpredicted SOA values. What is the big difference then between this work and that presented previously? Is it all due to differences in the gas-phase mechanism? This needs to be explored in much greater depth as this appears to be the significant improvement of this model over others of the same type (MADRID, MCM, etc.).

Page 8369, line 10. The Pankow and Kamens paper state that activity coefficients of unity are appropriate for chamber experiments. Is this really true in the ambient atmosphere, particularly in urban areas with POA that is vastly different than SOA or in areas with high aerosol LWC? This assumption needs to be better justified. If the method of Bowman and Karamalegos is implemented, how different are the results?

Page 8369, line 28. Why only selected species? Should it not be all?

Page 8371, line 3. The isoprene comparisons should be more quantitative. The experiments of Kroll et al. used ammonium sulfate, which is not acidic. Also, these are

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definitely not the only isoprene experiments described in the literature.

Page 8371, line 20. I would not call a 20K difference small. It implies that there could be issues with the authors' calculations of vapor pressures. In addition, it is very easy for the authors to blame the experimental results. Is there some other temperature-driven process going on then? In addition, the differences in parameters cited should be quantified.

Figure 1 should show the ratio of observed to simulated versus observed, rather than just simulated versus observed. In addition, in the results shown in Figure 1, how does the SOA behave as a function of time? Is it appropriate compared to chamber results? Instead of just showing final results, it is important to determine how the SOA model behaves over the entire course of a set of experiments since the final results are not always what are appropriate for the ambient atmosphere.

Page 8374, line 4. Why no POA emissions?

Page 8374, line 5. 5000m seems high for average mixing height, especially since they are considering one that is constant. This is half the troposphere!

Page 8374, line 8. If the evaporating model is more realistic (at least based on the theory upon which their model is established), it is the one that should be used. The non-evaporating model is essentially a vapor pressure correction (albeit smaller than that needed by other authors). It should not be used simply because it gives better results.

Page 8374, line 17. Five species contribute all of the SOA mass. Does this not seem unrealistically simple compared to the complexity of the real atmosphere, especially since the authors are using a first principles approach. Does this mean that the lumping in the gas-phase mechanism is inappropriate?

Page 8374, line 29. These results are in contrast to those from chamber experiments (Song, Presto) that show decreases in SOA with higher NOx. As a result, the authors

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need to do zero-dimensional runs and compare to these experimental results to ensure that their model behaves appropriately with changes in NOx before applying to three dimensions and making these claims.

Page 8375, line 27. The authors should also consider the results from a Tsigaridis 2007 paper that states higher SOA from biogenic precursors results from increased O3 and OH near urban areas.

Page 8376. It would also be appropriate to compare to the results of Chen et al. (2006) who performed three dimensional SOA calculations in the eastern United States and found dominance of terpenes in SOA formation.

Page 8377, line 4. The authors claim that their model is advantageous because it does not rely on smog chamber parameters. They are not the first to take this approach (MCM, MADRID, among others) and this should be cited.

Page 8377, line 15. The authors say that some anthropogenic pathways may be missing from their model by discussing the modeling of Heald et al. and Volkamer et al. I suggest the authors also do some simulations (similar to what was done for comparison to deGouw) of these scenarios. These results would certainly help strengthen their arguments.

Page 8377, line 25 (and following). Again, the recent results of Tsigaridis need to be discussed here.

Page 8378. The extrapolation to global values is completely inappropriate. If the authors want to estimate global SOA from certain compounds, then the SOA model should be implemented into the GCM that has been used by co-author Penner numerous times over the past years. If this is not done, the global portion of this paper needs to be removed.

Page 8393. Include observations on Figure 4.

Technical corrections Abstract - Should not use ‘0’ but rather ‘zero’-dimensional. Also in the abstract, x should be in subscripts. These should be applied throughout the document. GCM need not be defined in the abstract since it is not used again until the main body of the paper.

Page 8363, line 8. The paragraph contains only one sentence, which is inappropriate grammatically.

Page 8364, line 27 (and throughout). De Gouw should be de Gouw.

Page 8376, line 4. Need a space between influenced and conditions.

Page 8376, line 25. Should be of not os.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 8361, 2007.