**Atmospheric
Chemistry
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Discussions**

Interactive comment on "Evaluation of new secondary organic aerosol models for a case study in Mexico City" *by* K. Dzepina et al.

K. Dzepina et al.

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We would like to thank Anonymous Referee #3 for his/her review of the manuscript and useful comments, many of which we have adopted and which helped us improve the manuscript. The referee agrees that this is an important paper on implementing recently published SOA mechanisms to SOA models, and that it should be published after taking his/her comments into account.

In this reply all the original comments were copied, and *italicized*. Our reply is given after each comment in non-italic font. All the references cited in both this reply and the manuscript are given with the same format as in the manuscript and are included in the reply.

This is an important paper describing the modeling of secondary organic aerosol (SOA)

formation in Mexico City. The study follows up on the seminal paper by Volkamer (2006), it updates the modeling in that study and adds several additional mechanisms. The paper should be published after taking the following minor comments into account:

R3.1. Page 4423, lines 1-2: This sentence is unnecessarily vague. Which tracers for primary emissions and secondary formation were used and what specifically do the correlation coefficients refer to?

We have replaced the sentence starting on page 4422, lines 27-28 and ending on page 4423, lines 1-2 with the following text: "**To characterize the correlation between AMS HOA and OOA and other tracers, we calculated *r* values between AMS HOA and OOA and primary and secondary tracers, respectively, for April 9, 2003 between 6 am and 6 pm. There is a strong correlation between AMS HOA and CO, black carbon, NO_x, benzene, toluene and AMS PAH, resulting in *r* values of 0.68, 0.75, 0.62, 0.78, 0.66 and 0.76, respectively. AMS OOA is strongly correlated with OH, ozone, glyoxal and AMS nitrate, with *r* values of 0.92, 0.95, 0.94, and 0.99, respectively, which indicates very similar behavior of all secondary species.**"

R3.2. Page 4431, lines 3-4: I am not sure the manuscript returned to explain why this specific choice of model was made.

This was described in item (a) a few lines below, but the fact that this confused the reviewer suggests that this connection was not clear. In the revised paper version we have replaced the sentence on page 4431, lines 3-4 with the following text: "**In this paper, we use the results of MCM_{Heff} model as the formation of SOA from glyoxal appears to be dominated by uptake into the aerosol aqueous phase and enhanced with reactions with water soluble organic species (Volkamer et al., 2009).**" The next paragraph has also been modified accordingly.

R3.3. Page 4433, lines 5-8: Ignoring the fragmentation pathways suggests that the model provides an upper estimate to SOA formation. If the authors agree, it might be good to add a statement to that effect.

The model structure does indeed have a number of uncertainties, and indeed if the gas-phase species in NT model would be fragmenting upon oxidation, the amounts of SOA produced in NT model would be smaller. However another structural uncertainty of the model is the lack of particle-phase accretion reactions (e.g. Barsanti and Pankow, 2005), and if included these would increase the amount of model SOA produced. To clearly stress both possibilities, we have changed the sentence on page 4433, line 8 of ACPD paper and the new text now reads: "**The current formulations of the NT model do not include SVOC fragmentation upon oxidation, which would likely reduce the amount of SOA formed. Another structural uncertainty of the NT model is the lack of particle-phase accretion reactions (e.g. Barsanti and Pankow, 2005), which if included would increase the amount of model SOA produced. According to this mechanism, S/IVOC$_{i,j,p}$ do not react while in the particle-phase (Robinson et al., 2007).**"

R3.4. Page 4436, lines 15-19: I suggest using background OOA instead of background SOA. It is likely that this OOA is indeed SOA, but ultimately the AMS only determines the composition and not the source of the aerosol.

We agree with the reviewer that the AMS determines only the composition of OA. However, the point here is that during our case study there was a small amount of OOA already present BEFORE the onset of photochemistry which was most likely aged SOA, and we include that small amount of OOA in the model as BG-SOA. Thus, we think it is appropriate to call that mass within the model BG-SOA.

R3.5. Page 4440, section 4.2: The G-SOA model does not seem to be new in this manuscript. If that is the case, can the description of the model and the results be shortened by adding the appropriate references?

The referee is right in that the G-SOA results have been adopted from those of Volkamer et al. (2007a). However this is the first time to our knowledge in which the G-SOA model is included on a larger SOA model and tested against field study results. For

this reason many readers may be unfamiliar with this model and a short description is useful. In that context, the description of G-SOA model is quite short, and we do give the appropriate citations for a reader interested in a more detailed discussion of G-SOA. In Section 3.4 which describes G-SOA model, we merely give the main glyoxal parameters, briefly describe the model and justify the choice of glyoxal partitioning to the water phase. Section 4.2 very briefly describes the main results from this model. We believe that these brief sections are very useful within our paper. Thus, we have not shortened the sections on the G-SOA model.

R3.6. Section 4.5.2: As described by the authors, there is a significant difference in the description of the thermal denuder results depending on the assumption of equilibrium or of kinetic limitations to the evaporation. Based on this, are there any recommendations on how to do thermal denuder measurements better?

This is indeed an important issue, as there can be a large difference in species evaporation especially for short residence times. Increasing residence time allows evaporation closer to that under equilibrium, but however it can also exacerbate particle losses in the denuder, especially for the smaller particles that result from evaporation and which have much higher diffusion coefficients than the original particles (Huffman et al., 2008). However there are significant uncertainties in e.g. evaporation coefficients and enthalpies of vaporization which have an important influence in the calculated evaporation, as discussed in the manuscript. Exploring these issues in further detail is beyond the scope of this paper. We tentatively recommend that the thermal denuder measurements use plug flow residence times (PFRTs, Huffman et al., 2008) particle residence time between 10-15 s to allow approaching equilibrium based on the calculations presented here, and have added the new paragraph to the revised manuscript on page 4447, line 6: "**As described above, there is a significant difference in the description of the TD results depending on the assumption of equilibrium or of kinetic limitations to the evaporation. This is an important issue, as there can be a large difference in species evaporation especially for short residence times.**

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Increasing residence time allows evaporation closer to that under equilibrium, but however it can also exacerbate particle losses in the denuder, especially for the smaller particles that result from evaporation and which have much higher diffusion coefficients than the original particles (Huffman et al., 2008). There are also significant uncertainties in e.g. evaporation coefficients and enthalpies of vaporization which have an important influence in the evaporation, as discussed above, and exploring these issues in more detail is beyond the scope of this paper. Based on the calculations presented here, we recommend that the TD measurements use plug flow particle residence time between 10-15 s to avoid the most severe kinetic limitations to evaporation."

R3.7. Section 4.5.3: This section is relatively weak, since there really were no C-14 data for comparison with the model. The authors merely assume that C-14 would have indicated a predominantly modern fraction of carbon like in the MILAGRO study. They may be right about this, and the ensuing discussion is not without merit, but still there does not seem to be enough concrete data to warrant such an extensive discussion.

In response to the comments of all three referees that Section 4.5.3 on modern carbon should be shortened or removed, we have removed the section and kept a much shorter discussion on the contribution of biogenic SOA to UT-model at the end of page 4438, as explained in more details in response R1.11 to Referee #1.

R3.8. Page 4450, line 14: I am not sure that "ambiguity" is the right word here. The interpretation of the C-14 data seems very straightforward.

We disagree with the referee on this point. The detailed interpretation of organic aerosol sources from 14C data is challenging as modern carbon in aerosols can arise from very different sources such as cooking, brake pads, wildfires, the use of bio-fuels, biogenic SOA, primary biological particles, and even hot sources of radicarbon from medical waste incinerators, cement manufacturing etc. However a detailed discussion this point is not needed in the paper since we have removed the 14C section from the

paper.

R3.9. Figure 2: It would good to explain in more detail how the graph was put together using the results of Kleinman (2008) and de Gouw (2009).

This issue has been addressed in response to a similar comment by reviewer 2 (R2.4).

R3.10. Figure 8: This graph confused me. Between 6 am and 2 pm, the composition of the particle phase clearly changes, but the relative contribution seems to be rather constant. I was expecting to see the contribution from particles to increase due to gas-to-particle conversion?

We are not sure what the referee's confusion is. It is clear that by 2 pm the particle-phase species (full bars) amounts grow substantially when compared to the gas-phase species (dashed bars) amounts, and that the relative contributions of the different types of species change substantially. Perhaps the referee is confusing the 12 pm panel with the 6 am one?

R3.11. Figure 9: While looking at this figure, I kept thinking what could be learned about semi-volatiles if an ambient sample were cooled. Perhaps the authors care to speculate about this?

We thank the referee for this interesting point, as we have wondered about and discussed the same topic multiple times. Indeed an experiment in which semivolatiles were captured at several temperatures lower than ambient and then chemically analyzed (or more practically, captured at a very low temperature and desorbed with a slow temperature ramp on the collection surface a la Ziemann, see e.g. Tobias and Ziemann (1999, 2000)) could in principle provide information that would be of great value for constraining SOA models such as those used in this paper. This is quite challenging experimentally but we do know of at least two groups which are pursuing variations of this approach. We have added this suggestion in the paper on page 4445, line 9, after "in Fig. SI-11.": "**Figure 10 also shows that model SOA increases sig-**

nificantly upon cooling, and future research is needed in order to characterize the SOA partitioning at low temperatures. An experiment in which semivolatiles were captured at several temperatures lower than ambient and then chemically analyzed (or more practically, captured at a very low temperature and desorbed with a slow temperature ramp on the collection surface similar to the TDPBMS instrument of Paul Ziemann, see e.g. Tobias and Ziemann, 1999, 2000) could in principle provide information that would be of great value for constraining SOA models such as those used in this paper. "

Please note that Fig. 9 mentioned in Question R3.11 has been changed to Fig. 10.