

## ***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 #1 for his/her review of the manuscript and useful comments, many of which we have adopted and which helped us improve the manuscript.

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.

*R1.0. This article provides an evaluation of existing SOA modeling approaches for formation of SOA in Mexico City. The modeling approach is based on AMS measurements. All the individual SOA modules used have been previously published, and the*

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*structure of the model is the volatility basis set approach. Thus, the word “new” in the title needs to be removed and the title should be “Evaluation of secondary organic aerosol models for a case study in Mexico City”.*

We apologize for the confusion caused by our title. We have changed the title to “Evaluation of recently-proposed secondary organic aerosol models for a case study in Mexico City” which better conveys what we were trying to convey with the word “new” in the title.

We note that the structure of our model is not only the volatility basis set (VBS) approach, but that we combine a VBS-based model with two-product models for “traditional” SOA precursors such as aromatics, and also with a model of glyoxal uptake into the aerosol water phase. All the models are combined in a VBS-like display in Figure 8 for illustration purposes, but they are each computed within their original framework.

*Specific Comments:*

*R1.1. Division between HOA and OOA. HOA is used as a surrogate for POA, and OOA is used as a surrogate for SOA. The authors use the measured HOA for an estimate of the POA concentration in the model. It is unclear whether NT-SOA (the SOA formed from the oxidation of gases traditionally associated with POA, i.e. low volatility organic carbon) is more consistent with HOA or OOA.*

*Modeled NT-SOA (at least the early generations) may be more similar to HOA than OOA, and thus a strict comparison of SOA (which includes NT-SOA) to OOA may not be warranted. Conceptually, NT-SOA starts out very similar to HOA, as there is only a small reduction in volatility and small addition of mass to represent oxidation. As time progresses, and further generations of NT-SOA form, the NT-SOA probably resembles OOA more and more.*

*Certain model characteristics of NT-SOA indicate it may be more like HOA than OOA:*

*- The NT-SOA volatility from the kinetic calculation (Figure 10b) indicates that NT-SOA*

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*resembles HOA more than OOA as it tends to be more volatile.*

*- The O/C ratio of NT-SOA (about 0.1) is closer to the O/C of HOA ( 0.05) than OOA ( 0.4).*

*- According to Figure 7, the presence of NT-SOA leads to an over-prediction of OOA in the early morning (6:00 to 9:00 am) before OOA rises.*

*Are the above similarities to HOA just a result of the model framework or should NT-SOA actually be more like HOA or OOA?*

We thank the referee for bringing up this point, and we agree that in principle it is a plausible hypothesis that the chemical structure of freshly formed NT-SOA could resemble HOA more than OOA. However, chamber experiments starting from diesel and wood burning emissions have shown that the AMS spectrum of the SOA formed from these emissions resembles OOA (in particular the subtype of OOA known as OOA-2) very quickly (Sage et al., 2008; Grieshop et al., 2009b). This surprising observation is being investigated in detail in the laboratory starting from IVOC precursors (Presto et al., 2009).

Fresher SOA will indeed be less oxygenated than more aged SOA. The separation of fresher and more aged SOA from AMS spectra is a topic that we and others have explored in detail recently (Zhang et al., 2007, Lanz et al., 2007; Nemitz et al., 2008; Ulbrich et al., 2009). It is for this reason that we updated the CPCA results used by Volkamer et al. (2006) to new results using PMF, as already presented in the ACPD manuscript. Both set of results are compared in Fig. SI-1 in the Supp. Info. of the ACPD paper, which shows that OOA-2 (the less oxidized component) rises faster in the morning than OOA-1 (the more aged an oxidized component). Indeed taking into account the less-oxidized OOA more directly results in a small reduction in the HOA and an increase in the total OOA with respect to the results used in Volkamer et al. (2006).

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A final piece of evidence is the good correlation between the time series of HOA and other primary tracers shown in Fig. 1 of the ACPD paper. If the HOA determined with PMF had a major contribution from less-oxidized SOA, it should show an increase above the relative levels of the other primary tracers in the afternoon, but it does not within the variability of the measurements. Thus, we conclude that HOA and total OOA are indeed best interpreted as surrogates for total POA and total SOA respectively. We have added the following text to page 4422, line 7, to clarify this point: **“Figure SI-1 also shows that OOA-2 (the less oxidized component) rises faster in the morning than OOA-1 (the more aged and oxidized component). In principle, fresher SOA should be less oxygenated than more aged SOA, and thus the chemical structure of freshly formed SOA could resemble HOA more than OOA. However, chamber experiments starting from diesel and wood burning emissions have shown that the AMS spectrum of the SOA formed from these emissions resembles OOA (in particular the subtype of OOA known as OOA-2) very quickly (Sage et al., 2008; Grieshop et al., 2009b). This surprising observation is being investigated in detail in the laboratory starting from IVOC precursors (Presto et al., 2009). Finally, and as shown in Figure 1, there is a good correlation between the time series of HOA and other primary tracers. If the HOA determined with PMF had a major contribution from less-oxidized OOA, it should show an increase above the relative levels of the other primary tracers in the afternoon, but it does not within the variability of the measurements. Thus, we conclude that HOA and total OOA are indeed best interpreted as surrogates for total POA and total SOA respectively.”**

*R1.2. Box model method. Equation 11 may under-predict the amount of VOC oxidized if the oxidation reaction depletes the VOC in the atmosphere unless emissions (solving equation 4 with the emission and loss terms) are taken into account. Are any emission estimates for VOC precursors (for example, benzene) used?*

This appears to be a confusion on the part of the reviewer. We used the MEASURED VOC precursors and OH at each step in time, and we DO NOT attempt to calculate

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the VOC concentrations from emissions, dispersion, and removal as e.g. a regional 3D model would do.

*R1.3. Page 4426. This section describes mixing of air from aloft with a background concentration of 1.4 ug/m<sup>3</sup>, which implies there should be a term in equations 4 and 5 to represent this addition of mass to the box. The mixing of air aloft was implemented by addition of a constant 1.4 ug/m<sup>3</sup> background instead of a flux term through the top of the box. Clarify this approach in this section.*

The computations were done correctly, but we agree with the referee that equations (4) and (5) need to have an additional term to account for this effect. We have added the term VMin to these equations, which we define as the input of background SOA from vertical mixing with the air aloft. We also changed the sentence on page 4426, lines 7-8 to read: “As described below, a background of 1.4  $\mu\text{g m}^{-3}$  OA above the PBL is used in our model as an upper limit for this effect.” to: **“As described below, the air mixed in from aloft and diluting the species in the box-model is assumed to have a constant background SOA of 1.4  $\mu\text{g m}^{-3}$  as an upper limit for this effect.”**

*R1.4. Page 4429. Eqn. (9), the authors introduce product VOC (PVOC) and COx terms in the mass balance equation in the updated traditional model (UT-SOA). Later, the authors show that the PVOC is the major SVOC in the UT-SOA and is likely the potential source of additional organic mass. On page 4439, line 1, “Figure 5c shows that UT-PVOC comprise by far the largest fraction of the mass arising from the reaction of these VOC precursors.”. The value of  $\alpha_O$  of the model species in UT-SOA is not given in the paper. How was the value of  $\alpha_O$  determined for the model species?*

The reviewer is mistaken in both of these points. According to the traditional models that we are using in the paper (Koo et al., 2003; Ng et al., 2007) pVOC are not SVOC (i.e. semivolatile species which can partition to the particle phase) but rather highly volatile VOC species that are not considered to partition to the particle phase at all. They are traditionally ignored completely in SOA modeling, but we decided to account

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for them directly in order to show that they do contain a very large amount of organic mass which could potentially form additional SOA upon further reactions, even if this is not the case within the timescale and conditions of chamber experiments.

The choice of  $\alpha_O$  parameter was described on page 4429, lines 15-18 of ACPD manuscript.

*R1.5. Page 4434, line 6-8. Awkward sentence, rewrite. “The OH reactivity is under predicted from that calculated from all measured species... “ should be something like “The OH reactivity based on all measured species under predicts the observed OH reactivity.. “*

We have changed the sentence as suggested by the referee, and the sentence on page 4434, lines 15-18 now reads: **“The OH reactivity calculated from all measured species underpredicts the directly-measured OH reactivity, with the gap between calculated and observed reactivity being the largest during the morning rush hour.”**

*R1.6. Page 4438, line 26. “The measured OOA is several times larger than total SVOC (SOA+gas SVOC) mass in this model, indicating that even if all UT-SVOC mass would partition to particle phase and form SOA, the UT-SOA would still be too small to explain measured SOA by a factor of 3.1.” From Table SI-1, for the one-product precursors, the  $c^*(300K)$  of the model species are low (around  $1-5 \mu g m^{-3}$ ). Also, the mass yields of the model species are small. It is not surprising that there is only a small portion of the model species in the gas phase (i.e., UT-SVOCg is small). Why are the volatilities of the model species so low?*

We have not estimated those volatilities ourselves, but just adopted the reaction yields and partitioning coefficients for UT-SOA species from the work of Koo et al. (2003) and Ng et al. (2007). These parameters are determined by fitting yield curves of SOA mass formed vs. mass of precursor reacted, as first proposed by Odum et al. (1996). The volatilities of the UT-SOA model species have been corrected for temperature effects

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using a lumped enthalpy of vaporization of  $36 \text{ kJ mol}^{-1}$ , as described in the ACPD manuscript. We refer the referee to the Odum et al. (1996), Koo et al. (2003), and Ng et al. (2007) papers for a more detailed discussion.

*R1.7. Page 4442, line 4. The authors point out that about 20% of the total organic species present in Mexico City's atmosphere are accounted for in any of the models considered in this paper on page 4439, line 23. Since a relatively small portion of organic species is being accounted for in the models, how can the total model still predict the SOA mass loading in the case study?*

The majority of OC in total observed organic carbon (TOOC) is arising from highly volatile species such as butane, propane and acetone (Heald et al., 2008), which do not produce SOA according to our current understanding. We wanted to point out this larger total pool of organic species since in reality some of them may produce SOA with a small yield, much like we did not know until recently that species such as benzene, isoprene, and acetylene do produce SOA. Since 80% of the TOOC is not accounted for in our SOA models and/or the pVOC from UT model may form some SOA, there could be an overestimation of total SOA in our model, which would indicate that either the UT or NT models are overestimating the SOA produced by their respective precursors. We were careful to point out in the paper that the relatively good agreement obtained in the total SOA mass does not necessarily arise for the right reasons, and we felt strongly that we should call attention of other researchers to the larger pools of organic species in pVOC and TOOC.

*R1.8. Page 4446, line 21-24. Awkward sentence, rewrite. "the evaporation is closer to the actual residence time" should be something like "the evaporation is closer to the evaporation in the actual residence time".*

We have changed the sentence as suggested by the referee, and the sentence on page 4446, lines 21-24 now reads: **"For very short  $t_{res} = 3 \text{ s}$  there is a significant reduction of the fraction of SOA evaporated, while for the longer  $t_{res} = 22 \text{ s}$  the**

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evaporation is closer to the evaporation in the actual residence time, since both models are already close to equilibrium in either case.“

*R1.9. Page 4447, 4.5.2 O/C ratio section, it is not clear how the authors calculate the model SOA O/C ratio. The O/C ratios of the model species in UT-SOA model and of the volatility bins in the particle and gas phases in different oxidation generations in the NT-SOA model are not given in the paper. How were the O/C ratios of model species and volatility bins determined? What is the sensitivity of the model SOA O/C ratios to the assigned O/C ratios of model species and volatility bins?*

The reviewer perhaps missed these details in the manuscript. We estimated the O/C for UT-SOA as 0.37 based on chamber experiments with aromatic precursors (Aiken et al., 2008), and as stated on page 4447, lines 20-22 of the manuscript. We estimate the O/C ratio of G-SOA as 1, as stated from page 4447, line 22 to page 4448, line 5 of the manuscript. The O/C ratio for NT-SOA is calculated from addition of oxygen that results in a mass increase of 7.5% for each oxidation generation, and as stated on page 4448, lines 6-8 of the manuscript. The O/C ratio of BG-SOA is estimated to be 0.41, the average observed O/C between midnight and 7 am. We did not include the explanation of background SOA O/C ratio in the manuscript, and thus have added the following text on page 4448, line 5: **“We estimate the O/C ratio of BG-SOA to be the average observed O/C between midnight and 7 am of 0.41.”**

We did perform a sensitivity simulation to a recently proposed alternative of the NT-SOA model (Grieshop et al., 2009a) as discussed in section 5.2 of the manuscript, for which the O/C is shown in figure SI-24 in the ACPD manuscript and indeed the change in O/C is very significant. With the information above about the values used for O/C for each model it is possible for readers to infer the qualitative sensitivities of the model O/C to the chosen parameters. Since the paper is already very long and already includes multiple sensitivity studies, we prefer not to add another one to explore further sensitivities to the additional O/C parameters.

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We agree with the referee that it is interesting to report the O/C ratio in every volatility bin of model OA. We calculated the O/C ratios of NT-SOA in every volatility bin at four different times during our case study, as shown in new Figure SI-16. We also added the following text on page 4448, line 11, after “from the measurements.“: **“The evolution of NT-SOA O/C ratio in different volatility bins at four times during the case study is shown in Figure SI-16. The increase of NT-SOA O/C ratio in the afternoon is mainly due to the species with  $c^*$  between 1 - 100  $\mu\text{g m}^{-3}$ , as those species have gone through several generations of oxidation by 2 pm.“**

*R1.10. Page 4448, line 11. “Finally, the average model SOA O/C ratio is 0.3, which is 0.1 below the observations, indicating that this combination of models produces SOA which is somewhat less oxygenated than the OOA measured O/C ratio, but within the uncertainty of the model and measurements.“ What are the uncertainties of the O/C ratios measurements using the AMS and model SOA O/C ratios?*

We estimate the uncertainty of measured OOA O/C ratio to be about +/- 30%, based on the results of Aiken et al. (2007, 2008). The uncertainty of the model results is hard to estimate but it is likely at least as large. We have added error bars to OOA O/C ratio in Figures 11 and SI-24 and added the following text to the revised paper on page 4447, line 19: **“Based on the results of Aiken et al. (2007, 2008), the uncertainty of measured OOA O/C ratio is estimated to be +/- 30%. The uncertainty of the model SOA O/C ratio is difficult to estimate but it is likely at least as large as for the measured OOA.“**

*R1.11. Page 4449, line 27 to page 4450 line 1: Authors assert correlation with primary anthropogenic pollutants implies hydrocarbons are of anthropogenic origin. One doesn't necessarily imply the other. There could be an urban enhancement effect that allows biogenic precursors to form SOA more efficiently in anthropogenic environments. The model could be missing this anthropogenic enhancement. The key factor is that the UT-SOA precursors that formed SOA were of anthropogenic origin and the origin of the POA is somewhat unknown but likely anthropogenic.*

*The 14C section could be shortened as there no direct 14C measurements for the day modeled and the model doesn't predict 14C.*

During our case study, biogenic precursors were measured but are not present in significant amounts, as described in detail in Section SI-2 of Supplementary Information and also by Volkamer et al. (2006). Thus, a possible effect of more efficient formation of SOA from biogenic precursors in urban environment is not relevant to our study.

In response to the comments of all three referees on Section 4.5.3 on modern carbon we have removed this section. We have kept a shorter discussion on the contribution of biogenic SOA to UT-model at the end of page 4438. The new text reads: **“The UT-SOA fraction arising from the oxidation of nominally biogenic VOC (isoprene and terpenes) during our case study is 2% of the total UT-SOA. We also note that a recent modeling study concludes that the isoprene observed in Mexico City is most likely of anthropogenic origin (Hodzic et al., 2009). Wildfires and agricultural fires were very low in the period around April 9, 2003 and would be unlikely to reach our site in the morning due to low wind speeds (see Section SI-2). Based these arguments, the low levels of BB tracers described in Supp. Info Section 2, and the absence of a BB factor when running PMF for this period alone (PMF can generally retrieve factors from AMS datasets whose average mass fraction is above 5%; Ulbrich et al., 2009), we estimate that BBOA from non-urban burning contributed less than 5% to OA during our case study. However, some of the measured hydrocarbons could be from urban sources such as food cooking and trash burning, and thus some of the UT-SOA may be derived from modern sources. Similarly if some of the HOA arises from modern sources, some of the S/IVOC should contribute modern carbon to the NT-SOA. Finally, for similar reasons some of the glyoxal may arise from modern sources of anthropogenic VOC. Overall the sum of these sources may contribute significantly to the modern carbon (14C). Unfortunately no 14C aerosol measurements are available for our case study. Questions on modern carbon have already been highlighted as a**

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**key focus of future research (Hallquist et al., 2009; de Gouw and Jimenez, 2009), and an attempt should be made to perform 14C measurements with as high time resolution as possible and at the same location as the highly time-resolved VOC, oxidant, and aerosol measurements in order to reduce ambiguities in the interpretation of the 14C data.“**

*R1.12. Page 4453, line 6. “The total model SOA O/C ratio after 3-days of aging is 0.34. OOA O/C ratios observed for aircraft measurements during MILAGRO- 2006 range from 0.64 for OOA-2 to 1.02 for OOA-1 (Aiken et al., 2008; DeCarlo et al., 2008) indicating that aged OOA has much higher oxygen content than our model SOA.“ Do the authors have any explanation for this? What is the range of the O/C ratios of the model species in the UT-SOA model and the volatility bins in the NT-SOA model before and after aging?*

This finding indicates that current SOA models do not lead to a gain of organic oxygen as quickly as it is observed in the ambient atmosphere. We already stated this in the ACPD paper at this point, and resolving this discrepancy is the focus of ongoing studies by other groups such as Presto et al. (2009).

As stated in response to comment R1.9, we assume a constant O/C ratio of 0.37 for UT-SOA based on results from chamber experiments (Aiken et al., 2008). A detailed analysis of the evolution of model O/C with aging will be presented in a forthcoming publication. Note that the NT-SOA precursors (primary SVOC and IVOC) are assumed to not contain oxygen.

*R1.13. Table 1: make T1-SOA, T2-SOA, etc as rows to be more consistent with Figure 4.*

We thank the referee for this suggestion and have exchanged columns for rows in Table 1 in the final version of the manuscript.

*R1.14. Figure 5: Pie chart too small.*

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We have increased the size of the pie-chart in the final version of the manuscript.

*R1.15. Supp. Info lines 222-224 missing.*

We thank the referee for catching this omission of text. The complete figure caption of Figure SI-5 reads: **“Figure SI-5: Parameters related to the calculation of the low- and high-NO<sub>x</sub> branching ratio for the UT model. Panel (a): measured NO concentration. Panel (b): measured HO<sub>2</sub> concentration. Panel (c): estimated RO<sub>2</sub> concentration as  $RO_2 = 0.85 * HO_2$  (Volkamer et al., 2007b; Sheehy et al., 2008). Panel (d): fraction of RO<sub>2</sub> reactivity through each of the three possible channels.”**

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