

## ***Interactive comment on “Sources and production of organic aerosol in Mexico City: insights from the combination of a chemical transport model (PMCAMx-2008) and measurements during MILAGRO” by A. P. Tsimpidi et al.***

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### *General comments*

1. The authors apply the PMCAMx-2008 model to a domain encompassing the Mexico City Metropolitan Area (MCMA) in an effort to explain organic particulate matter (OPM) levels observed at an urban, suburban, rural, and high-elevation site during March 2006. In previous work, these authors (Tsimpidi et al., 2010) established useful terminology for distinguishing the different types of OPM (i.e., V-SOA, S-SOA, I-SOA, fresh

C14859

POA, transported OOA) which they simulated across the MCMA for a 5-day period in April 2003. That study laid the foundation for evaluating numerical model results against the HOA and OOA levels that are often reported in the current literature. Such evaluations are necessary for piecing together the new information arising from Aerodyne aerosol mass spectrometry (AMS) measurements and from volatility-based models of organic aerosol. However, the model evaluation of Tsimpidi et al. (2010) was limited to a 4-day period at a single urban site. In the present study, the authors have expanded their evaluation to 3 sites and a 27-day period during the MILAGRO campaign. Their previous study also concluded that a larger modeling domain is needed to test the hypothesis of large OPM contributions from the surrounding regions, so the modeling area has been doubled in the present study. In addition, the authors have improved the meteorological inputs (now using WRF instead of MM5) and emission inputs for their air quality simulation. In their model, primary organic aerosol (POA) is distributed across a broad volatility range (9 orders of magnitude) and its gas-phase constituents react with OH to form less volatile material that may subsequently partition to the particle phase (I-SOA and S-SOA). In addition, traditional precursors of secondary organic aerosol (SOA), such as monoterpenes and toluene, are oxidized to form material that spans 4 orders of magnitude in volatility. That material can partition to the particle phase as V-SOA and a subset of its gas-phase components may react with OH to form lower-volatility material that will eventually favor the particle phase, thereby augmenting the V-SOA. The model results are evaluated against measurements of total OPM and factor analysis results of Aerodyne AMS measurements (HOA and OOA factors). The authors are commended for continuing to study this important problem, but several shortcomings in their manuscript must be addressed before final publication.

This is an excellent overview of the contents of the manuscript.

### *Specific comments*

C14860

**2. Unexplained sources of organic mass.** *The authors fall short of their stated goal on P27932, “to provide a concrete understanding of the sources of organic mass in Mexico City.” First, they fail to report the modeled contributions of different sources to the total OPM. For example, they report in the abstract that the model predicts  $18 \mu\text{g m}^{-3}$  of OPM at T0 of which 4.4 is fresh POA and 7.5 is OOA (sum of V-SOA, S-SOA, I-SOA, and transported OOA). This leaves  $6.1 \mu\text{g m}^{-3}$  of unaccounted material. Similarly, there are  $4.2 \mu\text{g m}^{-3}$  unaccounted at the T1 site. It seems like the modeled values in Fig. 4 should equal the sum of Fig. 7 and Fig. 8, but they do not.*

The points made by the referee are valid. In this paper we do not attribute the OA to specific source types (e.g., transportation, industry, etc.) so our statement in P27932 may be confusing. We have rephrased this statement and it now reads “to improve our understanding of the formation pathways of organic aerosol in Mexico City”. This is now consistent with our major emphasis on processes and not individual sources.

The average biomass burning source contribution was missing from the list of numbers in the abstract. This is introduced in the model through the boundary conditions as explained in the text. These boundary condition values of the OA concentrations at the boundaries of the domain were chosen based on results of the GISS-II' global CTM for the month of March. The biomass contribution was estimated using the measurements and analysis of Crouse et al. (2009) for the MILAGRO period. We now clearly state the mass concentration from biomass burning ( $6.1 \mu\text{g m}^{-3}$  and  $4.2 \mu\text{g m}^{-3}$  in T0 and T1 sites respectively) in the revised Abstract. We also clarify in the text that this biomass burning contribution is not included in Figures 7 and 8 (to be consistent with the AMS analysis) explaining why the sum of Fig. 7 and 8 does not equal the total concentration.

**3. Second, the authors provide no information about the relative contributions of different OOA types.** *The only information available must be gleaned by inspection of Figs. 8 and 11, but some explanation of why V-SOA > S-SOA > I-SOA would be useful.*

V-SOA is the dominant component of OOA (accounting for approximately 80 percent  
C14861

of the locally produced OOA). I-SOA contributes approximately 5 percent of the OOA with the other 15 percent coming from S-SOA. The V-SOA dominance is mainly due to the high emissions of its precursors compared to the IVOC and SVOC emissions (see Table 1). The relative contribution of the different OOA types together with a brief discussion explanation have been added to the text.

**4. Third, there is virtually no discussion of the actual source contributions (e.g., vehicle exhaust, trash burning, meat cooking, industrial emissions, etc.) to the modeled OPM.** *Without such discussion, the authors are unable to confirm or refute earlier findings (e.g., those listed on P27929 – P27930) nor resolve any controversies surrounding the present understanding of MCMA air quality.*

According to the emission inventory used in this study, 65 percent of the POA is emitted by mobile diesel sources with the rest coming from mobile gasoline (15 percent), area (10 percent), and point (10 percent) sources indicating that the modeled fresh primary organic mass is dominated by mobile sources.

Aromatic VOCs are the major precursors of our V-SOA in our simulations. Transportation contributes 48 percent of the emissions (35 percent gasoline and 13 percent diesel), area sources 40 percent, and point emission sources around 12 percent. While there is some spatial variability to the contributions inside the city, the transportation and area emissions are predicted to be the dominant sources of V-SOA and therefore the locally produced OA. These results are consistent with the findings of Wöhrensimmel et al. (2010) who identified vehicle exhaust as one of the principal emission sources of VOCs, accounting for 32 percent (during the night) to 62 percent (during the evening) of the total measured VOC concentration. A detailed source attribution of the OA is outside the scope of this work. A discussion of the contribution of each type of emission source to total emitted POA and aromatic VOCs has been added to the revised manuscript.

**5.** *Fourth, the authors invoke rather large boundary concentrations to reproduce the observed OPM concentrations at each site. The sources of this long-range transported material are not elucidated by the present study and its concentration is unverified.*

We should first clarify that the boundary conditions used in this study are not invoked in order to reproduce the observed OA concentrations. They are based on results from the GISS-II' global CTM which uses present-day emissions. These results generate a climatological background of aerosols in the area around the PMCAMx-2008 model domain with the aerosol values representing a 5-year average for the month of March. Although this approach of calculating the boundary conditions is not optimal, it does provide a reasonable approximation to the OA in the boundaries. These boundary condition values used in our study are consistent with measurements on the T2 site which is the only available site close to the boundaries of our model domain (north boundary) and is largely affected by the boundary conditions and little by Mexico City. Recognizing the uncertainty introduced by this choice we have devoted a subsection of the paper to the investigation of the sensitivity of our results to this choice. Unfortunately, PMCAMx-2008 cannot provide insights about the source of this material as it is emitted outside of the model domain and it is not included in the emission inventory. According to the global model the major source of these emissions is fires, but also there are significant contributions from biogenic VOCs and anthropogenic sources. This is clearly an important issue that deserves further investigation.

**6.** *Fifth, the authors acknowledge several OPM formation processes that are missing from their model simulation (e.g., SOA from glyoxal, aqueous-phase SOA production, and oligomerization of semi-volatile OPM) which leave the reader wondering if their good agreement with the observations is a fortuitous result of overestimated boundary concentrations coupled with missing sources.*

There are several potential explanations for this result. The first is that these formation pathways were not major OA sources during the study period. The second is that their

C14863

effects are indirectly included in our parameterization of the production of SOA and its subsequent aging. The third one is the one suggested by the reviewer, that other sources are overestimated in the model (especially the boundary conditions).

It is of course difficult to give a definite answer about which of the third explanations is right due to our lack of understanding of these missing processes. There is a good chance that all of them are at least partially true. Cloud processes probably had a small effect on locally produced OA because both of the low cloud cover during the study and the spatial and temporal scales involved in this process for an urban area. Clouds could have been involved of course in the formation of OA transported into the city from outside the modeling domain. The role of glyoxal in OA production in this episode has been recently investigated by Li et al. (2011). They reported a relatively small contribution (10 percent of the SOA inside the city and 4 percent outside) which would not affect our results significantly. We believe that the oligomerization effects are probably indirectly included in our aging mechanism. We have added this discussion to our disclaimer about what is not included in the model.

**7.** *Model description needs improvement. While I appreciate the conciseness of Section 2, I found myself referring to 4 earlier papers by the authors in order to understand the model formulation. In spite of that effort, several aspects of the model formulation are still unclear to me. I suspect that some of my confusion arises from inaccurate statements in Section 2, which should be corrected and/or clarified in the final publication.*

The model details were described extensively in our previous application of PMCAMx in the Mexico City area for MCMA-2003. This is the reason why in this study (which is a continuation of our previous application) we have chosen to just provide a summary of the model techniques. However, as the reviewer has pointed out, we may have overdone it. In the revised manuscript we have enriched Section 2 with all the information needed by the reader to fully understand the organic aerosol module used

C14864

by PMCAMx-2008 and we have also corrected the few typos and that may have some confusion. These are described below.

**8.** *First, the authors state that a volatility distribution is applied to POA emissions such that the material is allocated to 10 volatility bins following the treatment by Tsimpidi et al. (2010). However, both Table 3 and Fig. 3 of the cited paper reveal that the POA emissions are distributed to only 9 bins and none of the material is assigned to a nonvolatile ( $c^* = 0$ ) bin.*

The volatility distribution applied to the emitted POA species consists of 9 volatility bins, ranging from  $10^{-2}$  to  $10^6 \mu\text{g m}^{-3}$  saturation concentrations. The 10th bin (zero volatility) is used only for the boundary conditions.

**9.** *Second, the authors state that IVOC emissions are distributed among the  $c^* = 10^4$ ;  $10^5$ , and  $10^6 \mu\text{g m}^{-3}$  bins but P27933.10 indicates that IVOC includes the  $c^* = 10^3$  bin and Figure 1 of Tsimpidi et al. (2010) also shows 4 bins of IVOC emissions.*

IVOC emissions are distributed among the four bins ranging from  $c^* = 10^3$  to  $10^6 \mu\text{g m}^{-3}$ . The typo has been corrected.

**10.** *Third, the authors state that the emissions of IVOC in the  $c^* = 10^4$  bin equal 0.2 times the original POA emission rate. The corresponding factor in Table 3 of Tsimpidi et al. (2010) is 0.4, but the authors indicate on P27934.3 that the emissions processing is identical. The authors should elaborate on their rationale for reducing those IVOC emissions or clarify the text if no change was made.*

IVOC emissions rates are equal to 0.3, 0.4, 0.5, and 0.8 times the original non-volatile POA emission rate, distributed among the  $10^3$ ,  $10^4$ ,  $10^5$  and  $10^6 \mu\text{g m}^{-3}$  effective saturation concentration bins respectively. The typo has been corrected.

**11.** *Fourth, the authors describe their gas-phase chemical mechanism as having*  
C14865

*77 species and 217 reactions. This contradicts the authors' earlier reports (Lane et al., 2008a; Murphy and Pandis, 2009; and Tsimpidi et al., 2010) which describe the same mechanism as having 74 species and 214 reactions. If any species or reactions were added to SAPRC-99 for the present study, those should be described here.*

The correct number of species is 74 (56 long-lived gas-phase species and 18 free radicals) and 211 reactions. This is the same as in Tsimpidi et al. (2010) and Lane et al. (2008a). Murphy and Pandis (2009) mentioned that they used 217 reactions and 77 (total) species in the gas phase. None of these studies used 214 reactions. The small difference in reactions and species in the Murphy and Pandis paper is due to the way that the number of volatility bins and aging reactions were treated by that model. The correct number of reactions is mentioned in the revised paper and a sentence explaining the difference has been added.

**12.** *Fifth, the authors state that I-SOA and S-SOA are described with 10 volatility bins including one at  $c^* = 0$ . This differs from Fig. 1 of Tsimpidi et al. (2010) but, more importantly, the authors do not explain how S-SOA or I-SOA could enter the non-volatile bin.*

We only use 9 volatility bins (we do not use a volatility bin with  $c^*=0$ ). See also our response to comment 8. This has been corrected in the revised manuscript.

**13.** *Sixth, the authors state that V-SOA yields in PMCAMx-2008 "are based on the NOx-dependent yields of Lane et al. (2008a)." It appears that the authors made several inaccurate references to the two papers by Lane et al. (confusion of 2008a with 2008b) because the 2008a paper does not have any NOx-dependent yields. More importantly, the yields tabulated by Lane et al. (2008b) differ substantially from those in Table 2 by Tsimpidi et al. (2010) for example, compare the yields tabulated for ALK4, ALK5, OLE1, and OLE2 in each paper. If the authors did indeed revert to the earlier yields of Lane et al. (2008b) for the present study, they should elaborate on that decision.*

C14866

The citations to Lane et al. (2008a) and Lane et al. (2008b) have now been corrected. The SOA yields originally used in PMCAMx were the baseline NO<sub>x</sub>-dependent stoichiometric yields of Lane et al. (2008b). However, in the following work (Murphy and Pandis, 2009, Tsimpidi et al., 2010) the anthropogenic yields for the low-NO<sub>x</sub> case correspond to the high-yield case investigated by Lane et al. (2008b). Recent laboratory studies (Ng et al., 2006; Hildebrandt et al., 2009) have indicated that these higher yields are closer to the truth. SOA density of 1.5 g cm<sup>-3</sup> is assumed (Kostenidou et al., 2007) so the yields used in this work have been calculated by multiplying the experimentally determined volume yields by 1.5. This information is now added to section 2 to clarify the source of these yields.

**14.** *Seventh, the authors state that Henry's Law constants and molecular weights are taken from Lane et al. (2008b) but I didn't find those parameters reported in either of the Lane et al. papers. Similarly, I couldn't find a Henry's Law constant for S-SOA or I-SOA in the paper by Shrivastava et al. (2007). Overall, there are enough questions pertaining to the model description that the authors should consider rewriting Section 2.*

The corresponding parameters affecting V-SOA, S-SOA, and I-SOA partitioning and removal processes, including effective Henry's law constants, molecular weights and enthalpies of vaporization, are taken from Tsimpidi et al. (2010). This clarification has been added to the revised manuscript. The same parameters though have been used in Lane et al. (2008b) and Shrivastava et al. (2008) work. We have revised the model description to a large extent following the suggestions of the reviewer.

**15.** *One very puzzling aspect of the model description in this manuscript as well as Tsimpidi et al. (2010) is that neither make reference to the paper by Murphy and Pandis (2009) which, from my read, appears to describe a model formulation that is very similar (if not identical) to that used in the present study. If the model formulation is*

C14867

*identical, the authors could consider replacing the current version of Section 2 with a single sentence citing that paper. But on the discussion page, it may satisfy the curiosity of other readers if the authors were to reveal their rationale for not citing Murphy and Pandis (2009).*

Murphy and Pandis (2009) and Tsimpidi et al. (2010) were in the publication process at the same time and therefore we avoided cross referencing these two studies of our group. In the current study, the reference of Murphy and Pandis (2009) does not add any more information than the Tsimpidi et al. (2010) reference and therefore was omitted. Nevertheless, in the revised version of the manuscript we have added this reference following the recommendation of the reviewer.

**16.** *Apart from clarifying the issues enumerated above, it would be helpful to model users who are less familiar with the VBS if the authors would state the number of species required to track the various organic aerosol constituents in PMCAMx-2008. Such information would be analogous to the statistics commonly reported for gas-phase chemical mechanisms (e.g., number of species and reactions). By my count, the VBS treatment in PMCAMx-2008 requires 425 extra species:*

- *For V-SOA, one needs 8 OPM species per size bin (4 volatility bins for anthropogenic V-SOA and 4 for biogenic) plus the 8 corresponding gas-phase species. n = 88*
- *For S-SOA, one needs 10 OPM species per size bin plus 9 gas-phase species to account for all the semi-volatile bins. n = 109*
- *For I-SOA, the requirement appears the same as S-SOA. n = 109*
- *For fresh POA, one needs 10 PM species per size bin plus 9 gas-phase species to track the fresh emissions that have never reacted with OH. Although Tsimpidi et al. (2010) report that POA is emitted into only 6 size bins, I assume that material can grow into the larger bins via condensation. n = 109*

C14868

- For long-range transported OOA, one PM species per size bin is sufficient.  $n = 10$

*This raises a practical concern. How much computational burden does the VBS treatment add to PMCAMx? Are all 425 species transported and diffused throughout the modeling domain? Have the authors found some time-saving shortcuts that do not impact the PMCAMx model results?*

The number of species required by the VBS theory depends on the desired chemical resolution of the application and the aging scheme used. For example, in our application of the VBS in a Global Chemistry Model (Farina et al., 2010) we used only 12 aerosol and 12 gas-phase species. This can still produce results that are quite close to the full VBS implementation but with less information about the sources and the size distribution of the OA. In this study we have used 296 species which are:

- 88 species for V-SOA (4 volatility bins for anthropogenic + 4 for biogenic by 10 size bins and 8 gas phase species)
- 99 species for fresh POA (9 volatility bins by 10 size bins and 9 gas phase species)
- 99 species for S-SOA and I-SOA (9 volatility bins by 10 size bins and 9 gas phase species)
- 10 aerosol species for long range transport OA (10 size bins)

All of the above species are transported throughout the modeling domain. The result was an increase in CPU time by approximately 10 percent. This can be reduced significantly if someone uses lower number of size and/or volatility bins to describe the OA formation and growth (i.e. Farina et al., 2010; Shrivastava et al., 2010).

**17. Introduction.** *Paragraphs 3 – 6 are poorly focused and ought to be rewritten. Instead of just rehashing one or two conclusions from each of the past studies, the authors should focus on the key findings from those studies that this paper will seek to clarify and/or refute. For example, the authors state on P27929.26 that motor vehicles*

C14869

*“consistently accounted for 50 percent of OC in the urban area and 32 percent on the periphery” in a previous study by Stone et al. (2008). This is rather large compared to the HOA and fresh POA that the authors report in their abstract, but this contrast is never discussed. Also when describing past studies, the authors ought to refrain from using ambiguous terminology (e.g., “primary urban” on P27929.15).*

Following the reviewer’s recommendation, in the revised manuscript, we also compare the key findings of the current study with the results of the studies reported in the introduction section. This will help the reader to better evaluate not only the key findings of this work but also its limitations. In particular, the results of the current study are compared with the findings of: Querol et al. (2008), DeCarlo et al. (2008), Yu et al. (2009), and Kleinman et al. (2008) in the “overview of model predictions” section; Stone et al. (2008) and Wöhrnschimmel et al. (2010) in the “emission inventory” discussion; Yokelson et al. (2007), Crouse et al. (2009), DeCarlo et al. (2010), DeCarlo et al. (2008), and Fast et al. (2009) in the “boundary conditions” discussion; Aiken et al. (2009), Stone et al. (2010), and Hodzic et al. (2009) in the “Model performance evaluation” section; De Gouw et al. (2009) in the “Comparison with PMF analysis” section.

Regarding the Stone et al. (2008) study mentioned by the reviewer the comparison is a little more involved than a comparison with the fresh POA. Stone et al. (2008) used the tracer method for their estimates which neglects evaporation of the POA, oxidation of the resulting vapors and then their recondensation. Therefore a more appropriate comparison would use the sum of the POA coming from transportation, the corresponding oxygenated POA and also a fraction of the long range transport OA coming from transportation outside the modeling domain.

**18. Originality.** *Section 6 is largely duplicative of Section 6 by Tsimpidi et al. (2010). In addition, the Conclusions of this study are very similar to the Conclusions of Tsimpidi et al. (2010). To be suitable for publication in ACP, the authors must make a greater effort*

C14870

*to distinguish the findings of this study from their previous investigation. For example, what unique lessons were learned by evaluating the model against observations at multiple sites and a longer time period? What was gained by using a larger study domain?*

Some similarity of the two sections is unavoidable given the use of the same model in the same Megacity even if the application is for a different time period (spring of 2006 instead of spring of 2003). Given the uncertainty introduced by the boundary conditions and the volatility distribution of the emissions it is important to recheck the robustness of our results. For example, the boundary condition sensitivity is needed to address comment 5 of the referee. Repeating these studies confirms the conclusions of Tsimpidi et al. (2010) for the 2003 MCMA-2003 study using a better dataset (multiple sites inside and outside and simulation period that is four times longer). In addition to these we also quantified the effect of HONO formation aging reaction constant on the results.

The major new insight is the agreement between the model predictions and the observations not only in the center of Mexico City (as in Tsimpidi et al., 2010) but also in the suburbs and far away from the city. The use of a much longer dataset (one month instead of one week) is also a methodological plus. This is now stressed in the conclusions. Additional contributions include the quantification of the role of the Tula emissions in the domain, the role of biogenics and the various other OA formation pathways. These additional contributions are now stressed in the revised manuscript.

**19.** *Editorial quality. While quite good overall, I found an increasing number of grammatical errors in the later sections of the manuscript. In particular, the editorial quality seemed to drop sharply in Sections 6 and 7 so those sections should be edited carefully before the final submission.*

All the manuscript has been edited carefully.

C14871

#### *Specific comments*

**20.** *The Abstract is very clearly written, informative, and makes unambiguous use of the relevant terminology. The second sentence from the end describes the relative contributions of different OPM types, but I found no information supporting that statement in the main body of the manuscript. The last sentence should be clarified so that readers know whether the statement pertains to only the T0 site or to the entire MCMA. In terms of editorial quality, I believe there is some error in the tense used – shifting from present tense at the beginning, to past tense in the middle, and reverting to present tense again at the end. In addition, the authors should consider a better choice of words on line 8: “based on the volatility-basis set.”*

The relative contributions of the different OA components are now also discussed in Section 4 of the revised manuscript. The last statement of the abstract has been rewritten so as to provide the contribution of OA components in total organic mass for both the T0 site and the entire MCMA domain. Errors in the tenses and in the use of words in line 8: “based on the volatility-basis set” have been corrected.

**21.** *The Fig. 1 caption indicates that the map represents the modeling domain, but the map is rectangular and the domain is a square.*

We replaced Figure 1 with a map that defines exactly the modeling domain used in this study. The location of the monitor sites used in this work is also included.

**22.** *A major conclusion of Tsimpidi et al. (2010) was that a larger modeling domain is needed to test the hypothesis of large OPM contributions from the surrounding regions. In this study, the modeled area is doubled yet the concentrations along all 4 boundaries are also increased relative to the study by Tsimpidi et al. (2010). It would seem that the domain expansion did not have its desired effect, yet the authors again conclude (Section 5.2) that a larger modeling domain is needed. The discussion of this topic should be given extra thought in the final publication.*

C14872

The reviewer makes a good point. The boundary conditions can play a crucial role in CTM applications in relatively small domains especially if the boundaries are located in polluted areas. The boundary conditions for this application, as mentioned above, are based on the climatological background of aerosols in the area around the model domain for the month of March. These values happened to be larger than the corresponding results for the month of April (used in Tsimpidi et al., 2010). Moreover, a big limitation of this work is the lack of biomass burning emissions which have a large contribution on the OA in MCMA as discussed in the conclusion section. Therefore, the best option to eliminate this problem is to include these emissions in our emission inventory and at the same time further expand our modeling domain in order to have its boundaries in relatively clean areas (i.e at the Ocean). Unfortunately, there was not sufficient data to do so in the current application and therefore we were forced to implement all this OA exists in the area through the boundary conditions. In order to bind the uncertainty introduced from the boundary conditions we have also tested the sensitivity of the results to changes on their values.

**23.** *Table 1. It seems that the emission rate of SVOC+IVOC in the present study is almost five times as large as in Tsimpidi et al. (2010). Is this entirely attributed to the domain expansion or have some additional sources been added? Also, is it purely coincidental that the SVOC emissions in this study (55 tons per day) equal the SVOC+IVOC emissions reported by Tsimpidi et al. (2010)?*

This increase is attributed to the domain expansion. There is no additional type of source added in the inventory. Nevertheless, due to the expansion, major sources, such as the Tula industrial area, have significantly contributed on the OA emissions. The fact that the SVOC emissions in this study are equal to the SVOC+IVOC emissions reported by Tsimpidi et al. (2010) is indeed purely coincidental. The emission rate of non-volatile OA in the previous study was 22 tons per day and in the current study 110 tons per day (5 times higher). The SVOC emissions are approximately 0.5 times the non volatile emissions and the IVOC emissions are approximately 2 times the non

C14873

volatile emissions. This gives  $22 \times (0.5 + 2) = 55$  tons per day of SVOC+IVOC emissions in the previous study and  $110 \times 0.5 = 55$  tons per day of SVOC emissions in the current study.

**24.** *P27934.6 Why is the definition of SVOC limited to only 3 orders of magnitude in this description? Everywhere else, 5 orders of magnitude are mentioned.*

It is a typo. It has been corrected in the revised manuscript.

**25.** *P27934.9 Insert "which is subsequently oxidized by OH" right after "gas phase material" because some material that is initially emitted in the gas phase could condense to the particle phase before aging and ultimately would be counted as fresh POA.*

This is good suggestion that we have made the corresponding change.

**26.** *Boundary conditions. In this part of Section 3, the authors ought to state that the long-range transported OOA is non-volatile. That fact is not revealed until Section 6. Also, the authors should describe the size distribution of this material. Finally, it would be helpful if the authors introduce a new acronym for the long-range transported OOA so that there is no ambiguity when referring to that OPM component later on (e.g., P27940.7 and in the Fig. 13 legend).*

The non-volatile nature of long-range transported OOA and its size distribution are now explained in Section 3 of the revised manuscript. We have also adopted the reviewer's suggestion to introduce a new acronym for the long-range transported OOA. We now refer to it as LT-OOA.

**27.** *Ground observations. In this part of Section 3, the authors should describe all measurements used to evaluate the model results. From the text in this section, readers should be able to discern why the model results at T2 are not evaluated separately*

C14874



for OOA and HOA, how semi-continuous OPM measurements were obtained at T2 (e.g., were they estimated from a Sunset OC analyzer by assuming an OM/OC ratio?), and why there is no total OPM reported at the PTP site. In addition, much of the first paragraph in Section 7 should be moved here because the site descriptions are not conclusions.

To evaluate the model results for POA and SOA within the city basin we used AMS measurements of submicron aerosols collected at two supersites at the Instituto Mexicano del Petroleo (designed as T0) and Universidad Technologica de Tecamac (T1). Data collected by the Aerodyne Mobile Laboratory located on an elevated site of Pico Tres Padres (PTP, 900m above city ground), a mountain within the Mexico, are also used for comparisons of model predictions against OOA and HOA. PTP is 10 km northeast of "T0" and 19 km southwest of "T1". The AMS at T0 was a high-resolution time-of-flight AMS (DeCarlo et al., 2006) while those at the other two sites were compact time-of-flight versions (Drewnick et al., 2005) which report unit mass resolution data. Detailed analyses and intercomparisons of the AMS data are reported in other publications (Aiken et al., 2010;2009;Herndon et al., 2008;Yu et al., 2009;de Gouw et al., 2009;Wood et al., 2010). The AMS spectra are analyzed with the PMF technique (Paatero and Tapper, 1994) as described by Ulbrich et al. (2009) and Aiken et al. (2009). Moreover the model predictions of total OA were also compared against measurements in the T2 site which is a regional background site located around 90 km to the north of the city of Mexico, in the surroundings of a farm isolated from major urban agglomerations, and around 2 km from the closest road. In this site the measured OC derived from OCEC analyzers which were manufactured by Sunset Laboratory Inc., and are similar to the thermal-optical instrument described in Birch and Cary (1996). Detailed analyses of the measurements and description of the used instruments can be found in Doran et al., (2007). AMS measurements were not collected at this site and therefore the model evaluation was limited to the total OA comparison. This discussion has been now added in Section 3. Furthermore the average OM concentration in PTP is now reported on Section 5 and is compared against the measured average

C14875

total OPM concentration in this site.

**28.** *Figure 2. At the T2 site, Fig. 2 indicates an OPM concentration of  $7 \mu\text{g m}^{-3}$  but Fig.6c suggests that the concentration is about  $10 \mu\text{g m}^{-3}$ . Also, model predictions along the domain boundaries are much smaller than the fixed boundary conditions that were prescribed (e.g., western boundary =  $8 \mu\text{g m}^{-3}$  but those cells are dark blue). These discrepancies should be fixed or explained in the final publication.*

Figure 2 has been redrawn with a more appropriate color scale (it now goes from 0 to  $20 \mu\text{g m}^{-3}$ ). The new scale removes the ambiguities caused by the large area of different shades of blue in the original figure.

**29.** *In some parts of the manuscript (e.g., P27938.10 and Fig. 5 caption), the authors use the term "fresh" to describe material that is emitted inside the domain. Many readers may find this confusing, so the authors ought to consider using a different term (e.g., locally-emitted).*

In the revised manuscript the term "fresh" has been replaced by the term "locally-emitted".

**30.** *Figure 6. The y-axis limits are so broad (0 to  $50 \mu\text{g m}^{-3}$ ) that it is not possible to corroborate any information in Section 5.1 by inspecting this figure. Given that the purpose of this figure is to describe the hourly variation in OPM, the y-axis limits should be narrowed to an extent that the daily amplitude, maxima, and minima are visible (e.g., 10 to  $30 \mu\text{g m}^{-3}$  for T0 and 5 to  $15 \mu\text{g m}^{-3}$  for T1 and T2).*

This figure has been modified following the suggestions of both reviewers.

**31.** *Figure 10. In the text describing the sensitivity to the aging rate constant, the authors state that a rate constant of  $10 \times 10^{-11}$  was applied to all SOA types. Comparing*

C14876

this rate to the text in Section 2, one concludes that the aging rate for anthropogenic V-SOA is being enhanced by a factor of 10 while the S-SOA and I-SOA aging rates are increased by only a factor of 2.5. However, the caption of Fig. 10 suggests otherwise as does the text on P27945.19. This discrepancy should be removed before final publication.

A rate constant of  $10 \times 10^{-11}$  was applied to all SOA types. This discrepancy no longer exists in the revised manuscript.

**32. Aging of V-SOA.** The second paragraph of Section 6 indicates that V-SOA increases by only 10 percent when the V-SOA aging rate is enhanced by a factor of 10. Does this imply that V-SOA is essentially insensitive to the choice of aging rate or is it just that V-SOA in the MCMA region is dominated by biogenic precursors (which are not being aged)?

The 10 percent increase of V-SOA is predicted at the T0 site where the fraction of biogenic to total V-SOA is approximately 20-30 percent. Therefore this small increase is due more to the low sensitivity of V-SOA to the aging rate than to the presence of the biogenic V-SOA. This discussion has been also added to the manuscript.

**33. Conclusions.** The authors incorrectly state that “Most of the organic mass at these sites [T1 and T2] is coming from the urban center...” but in fact the OPM at those sites is dominated by the long range transported OOA.

The purpose of this sentence was to point out that the OA concentration peaks at these sites depend mostly on the meteorological conditions and the OA formed in the center of Mexico City. This sentence has been changed to “Most of the locally produced organic mass at these sites is coming from the urban center...” in order to avoid confusion.

**34. Minor typographical errors**

C14877

- P27928.27 “surroundings”
- P27933.18 “fifteenth”
- P27933.26 “emissions emitted”
- P27933.27 “northeast of the model domain” implies those biogenic emissions came from outside the domain. I assume those emissions were outside the previous domain but are inside the present domain, but the wording should be corrected to reflect this.
- P27934.8 Mismatching tense – “remains” and “did not”
- P27934.17 All 2-author papers should be cited using the names of both authors instead of “et al.” This line should read “Racherla and Adams, 2006” and the authors ought to check their manuscript for other errors of this type.
- P27935.5 “hereinafter”
- P27935.14 “road traffic fresh emissions”
- P27935.17 “an suburban”
- P27938.3 “tent”
- P27940.18 remove the first “respectively”
- P27941.10 change “Wameck” to “Warneck”

All of the above typos have been corrected in the revised manuscript. We would like to thank the referee for the effort in reviewing the paper and providing constructive criticism and useful suggestions.

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C14878

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C14879

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C14880

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C14881

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C14882

C14883