

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.

Anonymous Referee #2

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General comments

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 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

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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.

Specific comments

1. *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.

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 $V\text{-SOA} > S\text{-SOA} \gg I\text{-SOA}$ would be useful.

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.

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.

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.

2. 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.

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

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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 non-volatile ($c^* = 0$) bin.

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.

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.

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

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.

Sixth, the authors state that V-SOA yields in PMCAMx-2008 “are based on the NO_x-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 NO_x-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.

Seventh, the authors state that Henry's Law constants and molecular weights are taken

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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.

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 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).

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**

- 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?

3. *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 “consistently accounted for 50% of OC in the urban area and 32% 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).

4. *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 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?

5. *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.

Specific comments

- The Abstract is very clearly written, informative, and makes unambiguous use of the

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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 Fig. 1 caption indicates that the map represents the modeling domain, but the map is rectangular and the domain is a square.
- 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.
- 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)?
- 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.
- 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.
- *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.

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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).

- *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 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.

- *Figure 2.* At the T2 site, Fig. 2 indicates an OPM concentration of $\simeq 7 \mu\text{g m}^{-3}$ 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.

- 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).

- *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).

- *Figure 10.* In the text describing the sensitivity to the aging rate constant, the authors state that a rate constant of 10×10^{-11} was applied to all SOA types. Comparing this rate to the text in Section 2, one concludes that the aging rate for anthropogenic

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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.

- Aging of V-SOA. The second paragraph of Section 6 indicates that V-SOA increases by only 10% 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)?
- 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.

Minor typographical errors

- 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”

- P27941.17 “low volatility emissions case” would make more sense here
- P27941.20 “changes on the”
- P27941.21 “the partition of the emissions”
- P27942.19 “this sensitivity analyses”
- P27942.19 “inclusion of HONO to”
- P27943.22 “volatility partitioning and aging” this terminology is new and ambiguous; please reword
- P27943.23 “in the”
- P27944.10 “in the Mexico City Center”
- P27944.14 “northeast part of”
- P27944.27 “independed”
- P27944.28 “errors on”
- P27945.21 change “appear” to “appears”
- *References.* The authors have made inconsistent use of lower case and capitalization in the titles of cited papers.
- P27946.25 change “Associates” to “Associated”
- P27948.18 change “Hemmann” to “Herrmann”
- P27948.30 change “Geoph.” to “Geophys.”
- P27949.16 “MILAGO”
- P27949.18 change “A. C.” to “A. G.”
- P27951.15 “atmosbere”

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 27925, 2010.

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