

***Interactive comment on* “Evaluation of the volatility basis-set approach for the simulation of organic aerosol formation in the Mexico City metropolitan area” by A. P. Tsimpidi et al.**

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In their paper, Tsimpidi et al. present a new approach to modeling organic aerosol dynamics using 3-D atmospheric chemical transport models. As an application scenario, the authors have selected a single episode for Mexico City urban area. The paper is, in general, well written, and contains relevant scientific information that will add to the current level of understanding of organic aerosol dynamics in the atmosphere. I recommend the paper for final publication, after some issues are addressed.

General (major) comments:

- 1. An important part of the study resides in the assumptions made to construct the*

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emissions inventory used in the modeling experiments. Additional details should be provided; at some points the description in Section 2.2 tends to be hard to follow. It would help if the authors provide a summary table indicating total domain-wide mass emissions, and the corresponding contributions from particular sources, as well as how these partition. Were all PM size bins treated equally? One would expect that the composition of ultrafine aerosols be different from coarser aerosols. Comment on the expected uncertainties from only using diesel exhaust and wood smoke data to partition the OA emissions. Are OA boundary conditions also partitioned? It is not clear.

We have modified Section 2.2 in the revised paper providing more details about the construction of the emission inventory. The amount of the total OM emissions and their spatial and volatility distribution are shown in Figures 1 and 2. A table with the total organic mass emissions and their size distribution has been also added to the revised manuscript. The chemical speciation of the emissions was made based on field measurements. Mobile sources are the most significant contributors to primary fine particle mass in MCMA with biomass combustion also being an important contributor during periods. Therefore, the use of the diesel exhaust and wood smoke data to partition the OA emissions is a reasonable approximation for the current application in MCMA. Finally, as far as the OA boundary conditions are concerned, they are treated as non-volatile and non-reactive as they are assumed to be highly aged. These points are discussed in more detail in the revised paper.

2. *Section 4 should be revised since it falls short on the expected level of analysis of the results from the modeling experiments; clarifications also need to be made. When discussing averages (e.g., page 13708, line 2, as well as figures), are these episode averages? 24-hour averages? If these are episode averages, comment on the logic of using this averaging scheme. Long-period averages can be misleading. Explain why only PM₁ data is shown in the Figures and not more conventional PM_{2.5}, or both. It would actually be convenient to show both to get a better understanding of fine PM*

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behavior.

Section 4 provides an overview of the model predictions for OA for the episode under investigation. All the averages discussed in this section are episode averages. Our goal here is to summarize the spatial patterns of OA, the predicted contributions of the different sources to OA, etc. For these objectives, the episode averages are quite appropriate given that this is a short episode and there are not large day-to-day differences of OA characteristics. This is now clarified in the text. We have selected to focus our discussion on PM1 and not PM2.5 because the AMS measures the PM1 composition. The differences between PM1 and PM2.5 OA are minor so our discussion does apply to PM2.5 too. This is now explained in the paper.

3. *No domain-wide information is provided on diurnal/nocturnal dynamics; only time series plots at a single site is provided. Even though only one site is available for comparison, it would be of interest to look at domain-wide variations. Comment on the limitations on just having one station against which comparisons could be made.*

We agree with the reviewer that the availability of continuous PM composition measurements in only one site is quite limiting for any modeling study. We have looked at the diurnal patterns in other locations in increasing distance from the center of the city. As one would expect, the diurnal pattern, which in Genica is mostly due to fresh traffic emissions in the morning, gets progressively weaker with distance from the sources. Unfortunately, there is no data available, other than Genica, to evaluate the performance of the model spatially for this episode. Nevertheless, based on the promising results of the model application during the MCMA-2003 period, we have applied our model during the MILAGRO campaign period where there is sufficient data (in urban, suburban, and rural areas) in order to evaluate the predicted geographic variability of organic mass. The results of this application will be presented in a future study.

4. *Section 5. Be more quantitative in the conclusions derived from the time series:*

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“reasonable agreement” is too vague. Estimate percent bias, percent error or other statistical measures.

The discussion in Section 5 has been rewritten and is now based on the statistical measures suggested by the reviewer.

5. *Please comment on the numerical and computational burden that results from a more detailed representation of organic aerosol dynamics.*

The additional computational cost is mainly related to the addition of simulated species in a CTM. The volatility basis set allows the user-selected lumping of these species (in theory all OA species can be simulated with just 4 surrogate species covering the volatility range) so the computational cost does depend on the desired chemical resolution. In this application, because our objective was to simulate individual OA components (e.g., POA, OPOA, different types of SOA, etc.) we used a lot more species than what is required to simulate just the total OA concentration. The result was an increase in CPU time of PMCAMx of approximately 10 percent. This can be reduced significantly and the CTM can be actually accelerated by a few percent if one uses the simplest representation of the volatility basis set (lumping all OA components into 4 surrogate species).

Specific comments:

6. *Page 13695, line 15 “The model predictions. . .” Awkward sentence construction.*

This sentence has been rephrased.

7. *Page 13701, line 3: Any reason why no specific VOC species were treated individually against just using lumped species?*

The use of lumped species is computationally efficient since the simulated species are

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reduced significantly and the resulted SOA concentration remains almost unchanged. For this application there was no reason to follow specific VOC species.

8. *Page 13704, line 8: How relevant is the fact that glyoxal chemistry was not treated explicitly?*

Glyoxal chemistry is simulated by the SAPRC-99 mechanism, but SOA formation is not. As glyoxal may be important in Mexico City, the model may be lacking SOA formation from this precursor. The magnitude of this problem during the simulated period is uncertain and should be explored in future work.

9. *Page 13703, line 12: Is this PM, PM10? How were PM emissions segregated in the different mass bins? (See first major comment)*

In the revised paper we now explain that the PM emissions are distributed in sections with size varying from 40 nm to 10 μm . A figure with the size distribution of the total organic mass emissions (which are distributed in sections with size up to 2.5 μm) has been also added to the revised manuscript (new Figure 4).

10. *Page 13704, line 22: Lei et al. (2007) – missing reference.*

The reference has been added to the manuscript.

11. *Page 13707, line 12: “OPOA is predicted to be the dominant OA component. . .” This can be misleading. From a relative stand-point the argument is correct. However it would be more convenient to indicate the absolute mass contribution to get an idea of the real importance of each component to the total mass produced. This same comment applies when discussing other relative contributions.*

The absolute mass contributions of the different OA components are now discussed in Section 4.

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12. *Figures 9 and 10. Are the authors showing episode averages hour-by-hour or is this a particular day? If the first is true, please clarify and comment on the reasons to do this.*

These figures show diurnal averages for the whole episode. Such a comparison gives us the opportunity to evaluate the diurnal behavior of the different OA components without the random errors in emissions or meteorology dominating the picture. This is now clarified in the revised text.

13. *Page 13709, line 19: Should read “and”.*

This has been corrected.

14. *Figure 1. “significant fraction”, be more quantitative.*

We have rephrased the figure caption.

15. *Figure 3. Provide coordinates along the map boundaries.*

We have added the coordinates.

16. *Figure 5 and 6. Use the same scale to show contributions.*

The same scale is used in the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 13693, 2009.

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