

***Interactive comment on “Mexico City aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0) – Part 1: Fine particle composition and organic source apportionment” by A. C. Aiken et al.***

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We thank Referee #2 for his/her time and support of the paper for publication with minor revisions.

(R2.1) Page 8384 line 21: I think that the discussion about AMS collection efficiency requires some improvements. First, for the ease of the reader, the author should clearly define the meaning of this CE; second, verification of the collection efficiency here

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stated partially relies on the plot in Figure S3. Though discussing in depth all the challenges in instruments inter-comparison (mostly related to different size cuts and to different kinds of measured diameters), the authors should better provide evidence for the 0.5 CE assumption.

Response: This topic has been address in response to comment R1.1 from reviewer #1.

(R2.2) Page 8384 line 9: It had better to specify the averaging time for time series data.

Response: The reviewer missed this detail as in line 3 of the same page we stated "AMS data were saved every 2.5 min."

(R2.3) Page 8394 line 24: The authors make some interesting consideration about night-time OOA and nitrate background levels but they should explain the way the estimate these levels.

Response: We have added the following text to explain this point: "(defined as the average from 8 pm – 4 am)."

(R2.4) Page 8402, section 3.4: I think that the comparison of experimental data with Mexico City emission inventory is a little bit questionable. The authors compare the observed morning peak-hour PM/CO ratio to the same ratio from Mexico City emission inventory in order to draw conclusions about inventory accuracy for PM. This approach is sound but some points need to be better explained. Since emission inventory data are normally referred to the annual basis, while comparing observed and inventory PM/CO ratios the authors should be aware that all the sources considered in the inventory are active during the period of the field campaigns and affect air quality at the T0 supersite, which appears as a representative site for the urban MCMA. Moreover, the considerations are based on data observed on a 20 days period only. Comparison is based on PM<sub>2.5</sub>/CO ratio but it is not clear how PM<sub>2.5</sub> concentration is estimated based on AMS data. For comparison purpose PM<sub>2.5</sub> is related to \_CO (CO concentra-

tion minus regional background): if possible, I suggest to compare also  $\text{PM}_{2.5}/\text{CO}$  ratio to the inventory ratio, with  $\text{PM}_{2.5}$  being observed concentration minus regional background. This latter ratio should better represent the real anthropogenic contribution to  $\text{PM}_{2.5}$  levels. Morning peak hour is typically dominated by traffic as emission source. Though T0 supersite is supposed as representative of urban MCMA, it would be interesting to have some information about the inventory ratio for the traffic source just as verification of this assumption. Finally, it is not surprising that afternoon  $\text{PM}_{2.5}/\text{CO}$  ratio largely exceeds the inventory ratio since PM inventory data normally consider primary PM only. If this is not the case for Mexico City inventory, the authors should state that the inventory ratio considers both primary and secondary emissions. Anyway, the comparison of observed morning and afternoon  $\text{PM}/\text{CO}$  ratios provide an insight in the potential strength of secondary aerosol formation.

Response: We appreciate the referee supporting the use of our data for comparison to MCMA emissions inventories. Several of the issues raised by the reviewer were already discussed in the text:

Response: The issue of the representativeness for the MCMA of the ratios determined in this study was already addressed in P8402 L11-16 with the following text: "Since most of the PM species and components vary slowly in time (Fig. 1), are observed at consistent ratios at different times during the campaign, and show similar fractions and ratios to the data from MCMA-2003 from a different location in the city, we conclude that our observations at T0 are generally representative for Mexico City."

Response: We will add the following text to clarify the importance of the traffic source:

"The 2006 MCMA emissions inventory attributes 62% of the  $\text{PM}_{2.5}$  emissions to motor vehicles and most of the rest to a variety of area and point sources, whose activity is not expected to be strongly dependent on the time of the year."

Response: The species included in our measurement-based approximation of primary  $\text{PM}_{2.5}$  were already described in P8402 L16-19 with the following text: "When HOA,

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LOA, submicron soil, metals, and BC mass concentrations are summed during the morning rush hour period (06:00–08:00 a.m.), which is most strongly influenced by direct emissions, we obtain a  $\text{PM}/\Delta\text{CO}$  ratio of  $11.5 \mu\text{g am}^{-3} \text{ppm}^{-1}$  ( $13 \text{ g/kg}$ )."

Response: We have added the following sentence to clarify that this is a conservative estimate of the inventory underestimation:

"Since several of the species included in this sum are submicron or (such as BC) do not extend to  $2.5 \mu\text{m}$ , the calculated underestimation of the emission inventory is a lower limit, as additional small amounts of those species in the  $\text{PM}_{1}$  to  $\text{PM}_{2.5}$  range would increase the measured-to-inventory ratio."

Response: Our calculation assumes a negligible background for these primary species during the morning rush hour. This is justified since the concentrations of these species in the morning rush hour are very large and are dominated by urban sources.

Response: A separate report of the underestimation of the traffic source in the MCMA inventory has been recently published by Zavala et al. (2009), which we already cited in the manuscript. To clarify this point we will change that text to: "This underestimate is consistent with the results of Zavala et al. (2009) for the mobile source emission inventory."

Response: We agree with the reviewer that it is not surprising that the inventory only includes primary emissions. However, the importance of secondary species is not clear to everyone in the research community, for example Christian et al. (ACPD 2009) estimated the total contribution of Mexico City to regional PM levels as only the primary emissions inventory. Thus, it is important to document in the literature how large secondary formation is relative to primary PM emissions.

Response: In response to the final comment about "the comparison of observed morning and afternoon  $\text{PM}/\text{CO}$  ratios provid[ing] an insight in the potential strength of secondary aerosol formation" we already quantified the ratio of secondary to primary for

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these estimates, and included it in the abstract, as an example ratio for the importance of secondary production within a megacity (lines 20-22 p8379):

"The 2006 Mexico City emissions inventory underestimates the urban primary PM<sub>2.5</sub> emissions by a factor of  $\sim 4$ , and it is  $\sim 16$  times lower than afternoon concentrations when secondary species are included."

Response: To further clarify this point, we had add the following text to the conclusions: "Additional secondary species formation over longer time scales (e.g. Dzepina et al., 2009) will likely increase this ratio."

Minor comments:

(R2.5) Figure S-17. Autocorrelation plot for BBOA factor shows a peak for a lag time of about 8 hours. Though R<sup>2</sup> value is rather low, it would be interesting to have some possible explanation for this behavior.

Response: This is most likely an artifact due to the short duration of the campaign and the even shorter time during which BBOA had very large plumes, so we do not think it has any significance.

(R2.6) Figure S-19. I find this plot very interesting and I suggest its inclusion in the manuscript (Section 3.2.3).

Response: In response to this suggestion we have moved Fig. S-19 to the main text (Figure 11).

References:

K. Dzepina, R.M. Volkamer, S. Madronich, P. Tulet, I.M. Ulbrich, Q. Zhang, C.D. Cappa, P.J. Ziemann, and J.L. Jimenez. Evaluation of New Secondary Organic Aerosol Models for a Case Study in Mexico City. *Atmospheric Chemistry and Physics*, in press, 2009.

Zavala, M., Herndon, S. C., Wood, E. C., Onasch, T. B., Knighton, W. B., Kolb, C. E., and Molina, L. T.: Evaluation of mobile emissions contributions to Mexico City's emis-

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sions inventory using on-road and cross-road emission measurements and ambient data, *Atmos. Chem. Phys. Discuss.*, 9, 6363-6395, 2009.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 9, 8377, 2009.

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