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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Fast airborne aerosol size and chemistry measurements with the high resolution aerosol mass spectrometer during the MILAGRO Campaign" *by* P. F. DeCarlo et al.

**P. F. DeCarlo et al.**

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**Responses to Anonymous Referee 2**

**General Comments:**
**2.1**
**This paper presents new and interesting data on aerosol chemistry measured with an aircraft-based High-Resolution ToF-AMS above Mexico City and Central Mexico during the MILAGRO project. The paper is well organized and fits well into the scope of ACP. The overall data quality is good, however, I discovered a few shortcomings, especially with respect to the description of the different**

**measurement systems and data sources, as well as in the discussion and interpretation of the measurements. I recommend publication after the specific comments listed below have been addressed.**

We thank Reviewer 2 for his/her thorough review of our paper and suggestions for improving the manuscript.

**Specific comments:**
**2.2**
**Title: I suggest to change the title into something more science-related, e.g.: "Fast airborne aerosol size and chemistry measurements over Mexico City and Central Mexico during the MILAGRO campaign", because the focus of the paper is on the results and not on the instrument**

We have changed the title as suggested by the reviewer. Originally we wanted to highlight that this was the first aircraft deployment of the HR-ToF-AMS instrument, but we agree that the paper focuses more on the observations than the instrument.

**2.3**
**Methods: I miss a description of the ground sites T0 and T1. What was the instrumentation used there? Are there references on this issue? Was an identical HR-ToF-AMS used at the ground as on the aircraft? The Stone et al. (2007) paper doesn8217;t mention an AMS, and the Aiken et al. (2007a) conference contribution is not available to the reader.**

The following text was added to give a brief description of the ground sites:.

"2.2 Ground Supersites
The ground supersites, named T0, T1, and T2 are described in (Fast et al., 2007). Some additional information on the ground supersites is given in Querol et al.(2007) and Stone et al. (2007). Briefly T0 was inside the city, and T1 and T2 were outside the city to the northeast about 30 and 63 km away from T0 respectively. The names



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were chosen to indicate the relative ages of air for pseudo-lagrangian experiments when city air flowed to the northeast. A more detailed discussion of these sites will be given in the forthcoming MILAGRO overview paper (Molina et al., 2008). Notably at the T0 supersite another HR-ToF-AMS was deployed jointly by the Jimenez group and Aerodyne."

**2.4**

**page 18273, lines 17-29: What were the flight altitudes?**

The following text was added: "Flight altitudes were typically less than 6 km above sea level (ASL) (approximately 96 percent of data), and approximately 97 percent of city data (defined in section 3.2) taken at less than 2 km radar altitude. Vigorous turbulent mixing in the boundary layer with a timescale of about half of an hour implies a well mixed boundary layer over Mexico City during the afternoon. The regional data average altitude is 4.0 km ASL and 3.2 km radar altitude."

**2.5**

**page 18277, lines 18-20: Regarding the HCN measurements: Crounse et al. (2006) focus on H2O2. They do not say much about about HCN, and I couldn8217;t find the detection limit for HCN in that paper.**

The reported sensitivities are based on laboratory calibrations performed by the Caltech group subsequent to the publishing of the Crounse et al. (2006) instrument paper. The placement of the reference to Crounse et al. could be the source of the confusion. We have moved the reference to a more appropriate location in the text.

**2.6**

**page 18277, line 8: The SPS2 is not mentioned elsewhere in the paper. Were the black carbon data mentioned on page 18283 measured with this SP2? If so, please give a short explanation.**

Yes, they were measured with the SP2. The data SP2 at the time of publication were



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still preliminary, see also response to comment 3.5 from reviewer 3.

**2.7**

**page 18280, line 12-13: Was the gas-phase CO2 fraction of m/z 44 found to be dependent on flight altitude?**

We have added the following text to the manuscript to explain this point:

"Variations in the gas-phase CO2 would produce only a very small effect in the aerosol CO2+ ion signal. The typical gas-phase CO2 background of approximately 380 ppm is equivalent to approximately 100 ng $m^{-3}$ of organic-equivalent (org.-eq. (Zhang et al., EST, 2005) aerosol signal at m/z 44. This signal is subtracted from approximately 2600 ng $m^{-3}$ of org.-eq. m/z 44 aerosol signal in the city and approximately 1000 ng $m^{-3}$ in regional air. Variations on the order of 40 ppm for gas-phase CO2 would change its contribution to total m/z 44 by $+/-$ 10 ng $m^{-3}$, which is within the noise of the measurement. Note that this correction can be much more important for studies with low OA concentrations."

**2.8**

**page 18281: Again the T0 Supersite is mentioned, this time also with "W-mode data...". Please give a description of the measurements or a reference for these data.**

See response to item 2.3 above.

**2.9**

**page 18282, line 9: Replace "5 m time grid" by "5 min time grid" to avoid confusion with horizontal flight distance.**

This has been changed as suggested.

**2.10**

**page 18283: The good agreement between AMS and SMPS implies that no mineral dust is found in below 1 $\mu$m. Is this expected for Central Mexico?**



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We discussed the influence of mineral dust on the submicron aerosol on pages 18287 lines 19-24 of the ACPD version:

"A comparison of the supermicron volume (likely dominated by mineral dust) and submicron volume from the Optical Particle Sizer, operated by the University of Hawaii, indicate that with the exception of a few short plumes submicron volume was typically a factor of 2 or more larger than supermicron volume. This suggests that the contribution of mineral cations to the charge balance due to the submicron tail of the dust mode was small"

We have added the following text to further clarify this point:

"Assuming a dust size distribution similar to those from Maring et al. (2003), this implies that only a few percent of the submicron volume would be due to dust, which is consistent with previous observations in Mexico City (Salcedo et al., 2006) and with measurements at T0 during MILAGRO (Aiken et al., 2007a)."

**2.11**

**page 18284, line 12: I would prefer "12:00 - 18:00" instead of "noon-6 PM" (as in the legend of Figure 3)**

This has been changed as suggested

**2.12**

**page 18284: Again the T0 Supersite is mentioned without further information.**

See response to comment 2.3 above

**2.13**

**page 18285, description of Figure 4: Please indicate the flight altitudes. Did the flights take place in the PBL or above? Would it be possible to present the data as averages in "grid boxes", e.g. 0.5 degrees x 0.5 degrees? And leave grid points empty that contain no data? What is the reason for not including NH4 in Figure 4?**



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Regarding the altitude of the flights, please see comment 2.4 above describing the typical altitudes of the flights.

While it is possible to report the data as 0.5 x 0.5 degree boxes, we prefer to show the data as is to preserve day to day variations and differences between time of day for flights which have similar tracks.

The altitudes have been added in response to comment 2.4 above.

As shown by Figure 7. NH4 typically tracks the NO3 and SO4 concentrations, and does not add additional information for this overview. Further the measurement of Ammonium has more noise associated with it, so the patterns on the NH4 map are less clear.

**2.14**
**page 18285, line 24: What is "excess CO" here?**

See answer to comment 1.7 from reviewer 1.

**2.15**
**page 18285, lines 25ff: Be careful: The ratio NO3/CO shows a reduction, while the ratio OA/CO does not. The absolute concentrations of OA decrease (as shown in Figure 4)**

We agree the statement was confusing, and have changed it to specifically say that NO3/CO shows a reduction while OA/CO does not.

**2.16**
**page 18286, line 3: SOA formation? Is there evidence? If CO and OA are just diluted, the ratio will stay constant. How is the time scale for SOA formation of 1 day determined?**

There is overwhelming evidence for the dominance of SOA for the urban pollution aerosol sampled here. See a detailed explanation in response to comment 1.9 from



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reviewer 1.

**2.17**

**page 18286, line 14: "... at altitude as ..." What altitude?**

We have added the following text:

"at radar altitudes less than 2 km"

**2.18**

**page 18286, line 19 ff and Figure 6: It would very valuable to show more vertical profiles, for example one plot with data from all flights, averaged for measurements over Mexico City and off the city.**

We chose not to show averaged vertical profiles as the topography of Central Mexico, and the altitude of Mexico City complicates their interpretation. Mexico City is a large aerosol source at approximately 2240 meters, but there are other sources closer to sea level. The meteorology over and around Mexico City is very complex (Fast and Zhong, 1998; de Foy et al., 2006), and transport away from Mexico city can detach from the ground and stay at a similar altitude, or it can follow the topography and descend towards sea level. These processes blur out information about the vertical structure of the plumes, and neither radar altitude (above ground) or altitude above sea level (ASL) can do justice to these complex transport phenomena. Further the flights directly above Mexico City were all at less than 2 km radar altitude, and typically within the boundary layer so there is limited information on the vertical structure of the atmosphere for the city.

**2.19**

**page 18286, line 20: Is the Popocatepetl always active? Or was it only active during the measurement times? Maybe one sentence on the volcano in the introduction would be helpful.**

We have added the following text on Pg 18285 line 8 (of ACPD version):



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"Emissions of SO2 from Popocateptl were also monitored directly during MILAGRO, when the volcano was a continous source of SO2 and its emissions varied from a minimum of 0.56 Gg/day to a maximum of 5.97 Gg/day (Grutter et al., 2008)."

**2.20**

**page 18287, lines 14 - 29: Please give description or reference for the optical particle instrument.**

The following text was added to the methods section:

"2.1.3 Optical Particle Counter (OPC): An optical particle counter (OPC, a modified LAS-X, Particle Measurement Systems, Boulder, Colorado) measured the dry (RH < 30 percent) aerosol size distribution between 0.1 $\mu$m and about 10 $\mu$m (Clarke, 1991). The He-Ne laser operates at 633 nm detecting light scattered by individual particles over 35 8211; 145 degrees. The particle size was calibrated up to 2 $\mu$m with polystyrene latex spheres whose refractive index is 1.59. For calibrating the coarse mode, glass beads with a refractive index of 1.54 were also used. The data was obtained every 3 seconds, but averaged over 30 seconds to reduce error due to low counting statistics at about 1 $\mu$m or larger."

**2.21**

**page 18288, line 9: flights "through the city": At what altitude? What is the timescale of transport of the emissions to the measurement altitude?**

This has now been clarified in the text as "flights through the mixed layer above city." As described in response to comment 2.4 above, the flight altitudes above the city were less than 2 km above the ground.

**2.22**

**page 18289, lines 22-27: The discussion is not clear: What is the reason for the increasing O/C ratio: Additional aerosol formation by SOA? This would imply that the aerosol mass increases. Then why does the ratio OA/OC remain con-**



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**stant? What is meant by "loss of carbon"? How and why does this occur?**

Appendix 1 has been added to the paper, the calculation has been redone with even more conservative assumptions, and the text has been modified as follows to clarify the discussion for the points alluded to by the reviewer:

"However, heterogeneous oxidation of the emitted primary aerosols cannot explain the large mass of SOA rapidly formed. Also, heterogeneous oxidation proceeds with longer timescales of the order of 1 week or longer (Molina et al., 2004; Murphy et al., 2007; Schauer et al., 1996; Zhang et al., 2005a). An order-of-magnitude calculation (See Appendix 1) comparing the gain of O observed in Figure 8 vs. an upper limit of what could be expected from heterogeneous oxidation from OH shows that heterogeneous oxidation is too slow by a factor of approximately 10-200 to explain the rate of O increase observed here. I.e. only approximately 0.5-10 percent of the increase in O/C can be explained by heterogeneous reactions. This is consistent with the results of the only study of heterogeneous aging on ambient particles to date (George et al., 2008), which observed a gain of O/C (estimated from their results and the correlation of m/z 44/OA and O/C of Aiken et al. (2008)) about 16 times slower than than observed here. As SOA formation has a timescale around 1 day (de Gouw et al., 2005; Peltier et al., 2007a), additional SOA formation (from urban and BB precursors) or additional gas-phase oxidation of semivolatile SOA species are the most likely reasons for the observed increase in O/C."

And

"Downwind of the city basin the increase in the O/C ratio while OA/CO stays approximately constant implies that there is a loss of organic carbon from the OA (e.g. by evaporation upon dilution), since the addition of oxygen to the OA without subsequent loss of organic carbon would increase the OA/CO ratio, but this is not observed. Significant loss of carbon due to heterogeneous reactions is unlikely, given the constraint provided by Murphy et al. (2007). These observed the timescale of this process to



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be of the order of several months for tropospheric accumulation mode particles (dominated by sulfate and organics, very likely OOA) in the lower stratosphere despite high oxidant levels. High rates of carbon loss due to heterogeneous reactions have only been reported in the laboratory for very reduced particle compositions which are not representative of atmospheric OOA (e.g. Molina et al., 2004)."

**2.23**
**page 18291, line 11: what are "day tagged CO emissions"?**

This has been clarified in the caption to the figure 11:

"Part (e) shows the contribution in percent of CO emitted from sources in Mexico City based on the emissions and transport from the MOZART model for the flight day and each of the previous 6 days."

**2.24**
**page 18292, line 18: Is the reference Lee et al., (2008) work that was submitted to the conference that will be held in 2008?**

Yes this is from the submitted conference abstract. This has also been recently observed by our group while sampling aged Asian biomass burning from the NASA DC-8 during the 2008 NASA ARCTAS campaign, and this a short mention of this has been added to the text.

**2.25**
**Figure 2b: All error limits equal 0.01? Please check. Error limits to the slope of a regression in Igor are calculated by: (formula removed, see original comment)**

As described in the figure caption, "Reported errors in slopes in plots b-d are the 1-$\sigma$ estimate for the fitted variables returned from the fitting algorithm."

Also we note that the errors listed were not in fact identical, but were all rounded up from values between 0.005 and 0.009 to 0.01.



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Finally, with this large number of points the distribution is approximately normal, and a reader can easily estimate the 95 percent confidence interval by multiplying the 1-$\sigma$ errors quoted by 1.96.

**2.26**
**Technical corrections:**
**page 18275, line 20: replace second “with” in the sentence by “and”**

This has been changed.

**2.27**
**page 18280, line 22: “...the flight one city...” please check sentence**

text has been corrected

**2.28**
**page 18285, line 17: “...the their...” check sentence.**

Corrected.

**2.29**
**page 18292, line 24: should it read “Fig. 12b and c” ?**

This now correctly reads Figure 12b and c

**2.30**
**Figure 4: only panel (c.) is denoted. The letters (a), (b), (d) are missing Figure 5: (a), (b), (c) are missing in the figures**

This has been corrected.

**2.31**
**Figure 6: denote panels with (a) (upper part) and (b) (lower part)**

Text has been added the figure.

**2.32**



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**Figure 11: The legend is confusing. The graph is very busy. It might help to plot the flight altitude into the first panel, and also include vertical lines into the plot, because the reader has to compare panels d) and a) for time periods I, II, and III.**

As suggested, the figure has been updated with vertical lines to aid the reader in comparing the different sections of the plot. The altitude trace has also been moved to the top panel and the text changed to reflect this.

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Interactive comment on Atmos. Chem. Phys. Discuss., 7, 18269, 2007.