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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 3

3.1

This paper describes the first airborne measurements using an Aerodyne Time of Flight Mass Spectrometer during a major international experiment around Mexico City. The paper provides a detailed analysis of the aerosol composition and its variation across the region and links this to different sources. This is a thorough and interesting discussion and one that certainly should be published in ACP.

We thank reviewer 3 for the overall positive evaluation, and thorough comments and

suggestions for improvement of this paper.

3.2

However, the paper does not really offer much insight into the role that dynamics plays in creating the chemical gradients observed. The reader gets no sense of how, for example, the synoptic meteorology mixes pollution emitted from the urban area around the Mexico City basin, aloft and outward into the wider area. Is there significant recirculation and lofting caused by katabatic flows in the basin for example? Is there recirculation or the presence of residual layers? Is it these processes that cause the relatively small geographical distribution of the ammonium nitrate or is it that there are sufficiently large sulfate sources that the ammonium is partitioned very efficiently once it is away from the source region? What is the height of the surface mixed layer and is there any evidence for exchange between this layer and the air above? Though a detailed, quantitative answer to some of these questions may well be beyond the scope of this work, a qualitative description of the main meteorological phenomenon is necessary. I assume that in a campaign as large as this, the meteorological situation is described in detail in other papers, a brief discussion and summary of this should be included to provide the reader with sufficient information to interpret the physical and chemical variability of the aerosol in a dynamical context.

These questions while interesting, are beyond the scope of this paper, and have been and are being addressed by other participants in MILAGRO and previous campaigns who are experts on such questions. For a full analysis of the questions presented here, one would need a detailed meteorological and chemical modeling study. We have added the following text to the paper, in addition to the discussion regarding the Fast et al. paper already in the manuscript, to direct the reader to previous and ongoing modeling studies which have examined some of these aspects, and which describe what we feel are the most relevant meteorological characteristics of the basin, in terms of their influence in the data presented in our paper.

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"The meteorology of the Mexico City basin has been characterized in earlier field campaigns. The meteorology of the basin is very complex in response to synoptic, land/sea, and orographic forcings (de Foy et al., 2006; Fast and Zhong, 1998). These field campaigns examined venting timescales of the basin and concluded that typically the basin vents on timescales less than one day (de Foy et al., 2006; Fast and Zhong, 1998). Mixing heights during the MCMA-2003 campaign were typically around 3000 m with vigorous vertical mixing, implying that pollutants are well mixed in the mixing layer during the day (de Foy et al., 2006). A recently published study examines the basin scale wind transport during the MILAGRO campaign, identifying six episode types and compares the meteorological conditions in March 2006 with previous 10 years (de Foy et al., 2008)."

3.4

I could not find any mention of the altitude of the straight and level runs during the flights. What was the altitude above the ground and was this within or above the boundary layer?

The flight altitude above ground was less than 2 km for the city box. See response to comment 2.4 from Reviewer 2 for more detail.

3.5

I am a little surprised that the NR composition is not related to the black carbon at all when black carbon was measured on the aircraft both by absorption and single particle soot photometry.

This is incorrect, we did relate the NR and black carbon concentrations on P18283 L15-20 as "Based on preliminary data, black carbon makes up 1-3 percent of the submicron mass during MIRAGE (R. Subramanian, DMT, personal communication), and would make up slightly less of the submicron volume due to the higher density values for black carbon (Park et al., 2004) in relation to the dominant organic constituents, consequently the AMS calculated volume is not expected to be significantly impacted by the exclusion

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of black carbon."

Due to the preliminary nature of the data and ongoing work by other groups to reconcile the SP2 measurements and the absorption measurements, we did not feel that including them beyond that statement was prudent. The black carbon content of the aerosol for this campaign and platform will be detailed in subsequent publications by the groups that acquired the data.

3.6

I am also surprised that as a PILS instrument was run on the same inlet as the AMS the data are not compared. The HR-ToF-AMS was being run for the first time in this experiment, if the data is available this should certainly be included in this paper for comparison.

The data from the PILS is available for only 3 flights during the campaign. One flight clearly indicates a strong altitude dependence for the PILS data with Sulfate only measured below approximately 3,500 meters, and during that flight the AMS sulfate follows rapid variations of gas-phase SO2 much better than the PILS. The other 2 flights had levels of PILS Sulfate that were approximately twice the concentration of the AMS sulfate. If the AMS measurements were a factor of 2 too low then the slope of the regression of AMS calculated volume vs SMPS volume (Figs. 2a and 2c) would be approximately 2 rather than the measured value of 1, and similarly the calculated light scattering would be twice the measured scattering (Fig. 2d). In addition the mass scattering efficiency (slope of Nephelometer submicron scattering vs AMS mass) would be a factor of 2 lower at 1.9 m^2/g which is unrealistically low compared to literature values and the value of 3.6 m^2/g from Shinozuka et al. cited in the manuscript (P 18282, L24-25). Lastly the OA/CO ratio measured on our aircraft for aged air was nearly identical to the OA/CO ratio as measured by a different AMS on the G-1 aircraft during the MILAGRO campaign. A factor of 2 change in the AMS concentration would, again, not yield reasonable numbers. For these reasons we believe the AMS concentrations to be more accurate than those from the PILS during MILAGRO, and did not include the

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PILS data, as we did not desire to speculate on why the PILS was measuring a factor of 2 higher than the AMS.

3.7
Pg 18270 Line 6: 12 s averaged data

Changed to “12 second” data

3.8
Pg 18270 Line 12-14: Surely the key point here is that despite Mexico City, NE US and northern Italy being influenced by very different emissions, the OA:CO is remarkably similar in all three. You may then speculate on the reasons why but I am unsure you necessarily have the information to have anything informative to say on these points.

It is indeed surprising that the ratios are similar given the different sources, but the specific comparison is made between the NE United States and Mexico City. Both regions have substantial influence from anthropogenic pollution, but differ in the relative biogenic / biomass burning influences. We feel that this is a relevant observation and that pointing that out this difference is important.

3.9
Pg 18273 Line 23: and elsewhere: plane should be aircraft

“plane” has been replaced with “aircraft” throughout the paper

3.10
Pg 18275: The PILS is mentioned here simply to say that the AMS sampled from the same inlet as it. However, nothing is said about it in the paper. This is intriguing surely for the first reported deployment of an HR-TOF-AMS on an aircraft a comparison with a PILS would be very useful. Why is this not done, it should be.

See response to comment 3.6 above.

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3.11
Pg 18275 footnote Aaerodyne

This typographical error will be fixed in publication.

3.12
Pg 18276 what is the passing efficiency of the inlet system and associated pipework?

We have added the following text to address this point:

"The transmission of particle sizes into the AMS was determined by the AMS inlet (critical orifices and aerodynamic lens) as the losses in the plane inlet and tubing were small for the AMS size range (Dunlea et al., 2008)."

3.13
Pg 18277 line 8: SP2. This acronym is not described and the instrument is not used.

The acronym is now defined. The data from this instrument was indeed briefly mentioned on P18283 L15-20. For additional detail see the response to comment 3.5 above.

3.14
Pg 18280 line 1 Why couldn't the PILS be used to define the CE?

The CE was defined according the empirical correction determined from multiple previous AMS other studies (e.g. Takegawa et al., 2005; Quinn et al., 2006; Canagaratna et al., 2007 and references therein, all cited in the text already), and then checked with comparison to other aerosol measurements (Figure 2a-d). These intercomparisons confirm that the AMS CE varied in the manner determined in previous studies.

PILS data was not available for the majority of the flights. See also the response to comment 3.6 above. To define the CE based on the PILS we would have to be confident

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in the loadings as measured by the PILS, while we think that in this campaign the AMS reported more accurate concentrations.

3.15
Pg 18282 line 4: do you mean averaged or interpolated?

We changed the text to “converted” since in some cases the data were averaged (when the time intervals were different), and some cases the data were interpolated when the sampling intervals were the same.

3.16
Pg 18282 line 9: a 5 time grid, I assume minutes is what is meant?

Yes, this has been corrected.

3.17
Pg 18282 line 12: “native”, original would be better

We prefer to use the word “native” and do not think this will be confusing to the reader.

3.18
Pg 18282 line 23: “equivalent the Mass .. ” insert “to”

“to” has been added.

3.19
Pg 18283-18284: Possible evaporation effects are cited as a possible cause of the reduction in SMPS volume compared to the AMS. However, nephelometers may also suffer similar effects. The correlation shown does not display this, would the authors like to comment on the semi-volatile evaporation in the nephelometer?

The residence time in the Nephelometer is shorter than the residence time in an SMPS system which would lead to reduced evaporation. Additionally (as already described in the text) the SMPS was actively heated to reduce the humidity of the system while the

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nephelometer was not, so the volatile losses in the nephelometer would likely be less than the SMPS. All instruments have potential evaporative losses from ram heating and residence time in the inlet system. This was already described, along with the potential impact on each AMS species (based on thermal denuder measurements) on P18276 L1-6 of the ACPD paper.

3.20

Pg 18284 line 23: There is not only an increased ratio of sulfate to the expense of nitrate but the sulfate concentration away from the city is similar to that close to the city. This is the main evidence for a regional source of sulfate and should be pointed out.

The following text has been added to address this comment:

"...sulfate was more of a regional component to the aerosol with similar concentrations both in the MCMA basin and in the regional airmass,..."

3.21

Pg 18285 line 15: fires should be singular

Corrected.

3.22

Pg 18285 lines 17-22: Are there temperature gradients that might also cause such an NH4NO3 gradient? Is the reason for the low NH3 and HNO3 simply because of distance away from a source region diluting the gas phase of these species, or it also because the acidic sulfate aerosol offers an enhanced sink for ammonia, depleting the availability of the cation?

The following text has been added to address both of these points:

"..., or the loss of NH4+ to sulfuric acid or ammonium bisulfate. Regional temperature gradients do not appear to play a role, as the average temperature measured on the C-130 is approximately 5 degrees C higher above the city than the regional air, which

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would favor evaporation in the city and condensation away from the city."

3.23

Pg 18286 line 5-8: It isn't obvious to me why one needs to look for additional source unless you can budget the flux of organic precursor you do not know if you need an extra source. It may be that oxidant is limiting and not precursor and that is why similar behaviour is observed for example. I believe that the important point is that the OA/CO ratio between New England, Po Valley and Mexico City are all so similar despite having very different precursor pools to develop from.

We are in agreement about the importance of similar asymptotic values for all of these regions. However the larger BB and lower biogenic influence for this study compared to New England is clear in the data from multiple groups. Since both of these sources are expected to be important contributors to regional OA, we feel that this text is justified.

3.24

Pg 18286 line 15: Are the data presented here quantitatively consistent or only qualitatively consistent with those of Morino et al? By how much is the mass of nitrate enhanced aloft? It appears to be the case from your profiles in figure 6 but is this consistent? This behaviour has also been seen over the Po Valley.

We inserted "qualitatively" to clarify this point in the text. A quantitative analysis of the nitrate vertical profiles (such as in Morino et al.) is beyond the scope of this paper.

3.25

Pg 18287 lines 7-9: Whilst the lack of SOA in the acidic sulfate plumes is, consistent with a lack of acid-catalysed SOA formation, you really would need to show that the sources of SOA precursor are still present and it is the process of acid catalysis that does not occur to determine whether or not the process occurs. Another explanation is that the emission of organic compounds is low from the volcanic sources of sulfate, then whilst the aerosol might favor acid catalysis,

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there is no available organic material to drive the process.

This is a valid alternative explanation, and the text has been modified to discuss both possible explanations:

"No enhancement of organics is found in the acidic sulfate layers, consistent with other recent field studies that find no evidence for significant acid-catalyzed SOA formation in the atmosphere (Peltier et al., 2007b; Zhang et al., 2007b), although this may also be due to lack of gas-phase SOA precursors in these layers."

3.26

Pg 18287 first paragraph: There appears to be some evidence of a loss of organic particles in the sub 100 nm size region between the near field city (area I) and the downwind (area III) in the second profile. Is this significant?

The size distributions are noisy and we do not feel the difference mentioned is significant. We are not clear if the reviewer is misunderstanding the locations of the spirals, as they were 112 and 95 km away from Mexico City (see the locations in the new Figure SI-1 in the supplementary information section).

3.27

Pg 18287: Can you discrimate the power plant and volcanic sources of sulfate from other markers? It would be useful to do so and hence get an idea of the relative source strengths and influences of man made and natural sulphur sources in the region.

This has not been attempted in this study and is beyond the scope of this paper. This type of analysis may also be difficult due to the timescale of sulfate formation being similar to airmass mixing and advection time scales in this region. Other studies have looked at the apportionment of the sulfate in the Mexico City region in more detail (e.g. the Raga et al. 1999 paper referenced earlier, and de Foy et al. 2007 ACP 7, 781-801, 2007).

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3.28

Pg 18288 line 9: I assume that the OM:OC is calculated from the HR-ToF-AMS, where is the method description, for the non specialist.

The heading of the section and the first line have been edited to include “OM/OC ratios”, and the reader is directed to the Aiken et al. 2007 and 2008 references

3.29

Pg 18288 lines 9-10: Another possible explanation from what is presented is primary organic material mixing with a residual layer containing oxygenated aerosol from the previous day giving an external population of aerosol but an average O/C ratio of the ensemble.

Figure 8 combines results from five flights, and thus the influence of any one meteorological pattern appears unlikely. In addition the residence time of pollution in the Mexico City basin is typically less than one day with little recirculation (Fast and Zhong, 2008; de Foy et al., 2006).

Also, if a layer contained highly oxidized OA from the previous day, the OA from the previous day had to become oxidized somehow. Rapid SOA formation has been seen in several studies of Mexico City (e.g. Volkamer et al, 2006, 2007 and Kleinman et al., 2008, already cited in the text) is capable of producing rapid increases in O/C.

In addition, the size distributions do not suggest external mixtures of fresh and aged pollution.

3.30

Pg 18288 lines 22-23: How close to the BB source were the measurements made? There are strong indications from BB field studies that O/C ratios are far larger than this (based on a high m/z 44 fraction). I think you need to stress the age of the BB plume and the type of BB that is being burnt here if possible to qualify your statement. It doesn’t hold for very aged plumes I suspect.

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We mention on line 17, that the criteria for these plumes is HCN concentrations greater than 1000 ppt, indicative of fresh BB plumes. We are in agreement that further aging of this plume would result in higher m/z 44 fraction as has been seen in a previous study after aging of several days.

3.31

Pg 18289 line 18-20: The main thing that heterogeneous reaction cannot explain is the high OM/CO ratio compared to source ratios. This is not discussed. The ratio discussion given is consistent with this finding and it is important it is made but both arguments need to included I feel.

Text has been added to more explicitly state that heterogenous reactions cannot explain the large increase in SOA mass.

3.32

Pg 18289 line 22: In contrast formation should read In contrast SOA formation

This has been corrected.

3.33

Pg 18289 line 26-27: An argument is made that there is a net loss of carbon. Why is this evaporation (physical process only) or reaction and re partitioning of products (a chemical effect)?

This is an empirical observation based on our data. We do not have enough information to differentiate between the processes suggested by the reviewer. We have added some text to further discuss this observation, see response to point 2.22 of reviewer 2.

3.34

Pg 18290 last line-Pg18291: A statement is made that the first part of the example flight was used to investigate the ageing of air from the previous day. Why make this statement without discussing the data? Either you have a really good example of ageing in which case it should be discussed or don't mention it here.

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Perhaps the reviewer missed the discussion of this on page 18291 lines 10-23. This portion of the flight (previous day's outflow) was then compared to the other parts of the flight in the text that follows.

3.35
Pg 18292 line 29: this is for relatively fresh biomass burning and should be commented on to that effect.

Text has been added to indicate that these are relatively fresh plumes.

3.36
Figures Some of the figures are rather small and whilst containing impressive detail are difficult to read at times.

This is a limitation imposed by the ACPD format which prints all figures in a half-page irrespective of size, and will be addressed when figures can become larger in the ACP published version.

3.37
Figure 2 caption: "data is averaged" is it averaged or interpolated, both the neph and AMS have the same time resolution.

"Averaged" has been changed to "interpolated"

3.38
Figure 3: grey background on bottom RHS panel

This is there to help differentiate the T0 ground based data from the aircraft data, and has been clarified in the figure caption.

3.39
Figure 4: The boxes identifying the urban area are very difficult to read. The boxes are unlabelled, however, it appear that the sulfate panel and associated labelled sources are in panel a and not in panel b as stated in the caption.

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The error in panel identification has been corrected. The figures will be larger and easier to read in the ACP version.

3.40
Figure 6: It might be worth stating the ground altitude in this figure.

The following text has been added to the caption:

"For both profiles the lowest point corresponds to an altitude approximately 300 m above the ground."

3.41
Figure 9 caption: "ratio of ranging between" alter phrase

This has been corrected.

3.42
Figure 11: This figure is extremely busy and tricky to read. The description of panel e in the caption is worded clumsily.

We agree the figure is busy, but this is due to the limitations of ACPD which publish figures on half pages. For publication in ACP, we expect the figure will be a full page and more easily viewable.

The wording in the caption has been clarified, and in particular part (e) has been re-worded to say:

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

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