Atmos. Chem. Phys. Discuss., 7, S8505–S8510, 2008
www.atmos-chem-phys-discuss.net/7/S8505/2008/

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.

Anonymous Referee #3

Received and published: 17 January 2008

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.

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 re-

circulation 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.

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?

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.

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 avaiable this should certainly be included in this paper for comparison.

Specific points (some of these are editorial, others scientific) Pg 18270 Line 6: 12 s averaged data

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

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necessarily have the information to have anything informative to say on these points.

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

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.

Pg 18275 footnote Aarodyne

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

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

Pg 18280 line 1 Why couldnt the PILS be used to define the CE?

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

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

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

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

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?

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.

Pg 18285 line 15: fires should be singular

Pg 18285 lines 17-22: Are there temperature gradients that might also cause such

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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?

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.

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.

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, there is no available organic material to drive the process.

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 scond profile. Is this significant?

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.

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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.

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.

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.

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.

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

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)?

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.

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

Figures Some of the figures are rather small and whilst containing impressive detail

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Interactive Comment

are difficult to read at times.

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

Figure 3: grey background on bottom RHS panel

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.

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

Figure 9 caption: “ratio of ranging between…” alter phrase

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

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