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Interactive comment on “Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass Spectrometry – Part II: overview of the results at the CENICA supersite and comparison to previous studies” *by* D. Salcedo et al.

D. Salcedo et al.

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FINAL RESPONSE

In a previous comment published in the interactive discussion of this manuscript, we explained the major changes to the manuscript, which are:

1. The manuscript was expanded into a more comprehensive paper. It now includes the comparison between AMS+BC+soil and PM2.5 (previously in part I of the

manuscript) which justifies the speciation of PM2.5 that we present (section 3.1). In addition to the description of concentrations and size distributions of the aerosol in Mexico City, we included a more detailed analysis of the particle size distributions (section 3.4), particle ion balance (section 3.5), nitrate and sulfate production (sections 3.6 and 3.7), and chloride plumes (section 3.8). In the revision process, we have included seven new figures (figures 10, 11, 12, 13, 14, 15, and 16) and one new table (table 3); we also moved here three figures previously in part I (figures 2, 3, and 4); and we modified five of the previous figures (1, 4, 7, 8, and 17). 2. We moved 4 figures to a supplementary figures section (figures S1 and S2 were previously in part I of the manuscript). 3. The list of authors has been changed. 4. The title was changed to: " Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass Spectrometry: results from the CENICA Supersite". 5. We removed the previous section 2.1 "Brief review of previous Mexico City PM studies" because the focus of the paper has changed and comparison with previous studies is not a main objective anymore.

In this final response we answer specific comments of each one of the referees. Sections and figures in this response refer to the numbering in the revised manuscript, unless otherwise noted.

Response to referee # 2.

One of the general concerns of this referee was that the manuscript failed to reference some previous reports of high time and size resolved measurements in Mexico City. We had omitted some references due to the fact that some of them present measurements outside Mexico City and others present results on CCN or PM10 which could not be directly compared with our measurements. In the revised manuscript, we have removed the previous section "2.1. Brief review of previous Mexico City PM studies"; however, at the beginning of section 3.9, we reference previous particle studies in Mexico City. In there, we have included the references that referee #2 was probably referring to.

Specific Comments:

1) Why was the Cenica site chosen? Does it represent a geographically important site in MCMA? Has this site ever been used previously? The majority of measurements that have been published were made in areas specifically selected because they represented different types of local sources of emissions, e.g. CCA and Merced. How can comparisons be made between measurements at the Cenica site and those at Merced or CCA unless you can argue that the sources of emissions are similar?

The CENICA site represents an urban area where the main local sources of pollutants are traffic and some small industries, which makes it a suitable site to study fresh traffic related emissions, along with regionally processed pollutants. In addition a large fraction of the particle material in Mexico City during MCMA-2003 was formed by gas-to-particle conversion, which makes differences in the detailed effect of the local primary particle sources less important. In the previous manuscript, the intention of comparing data from CENICA with data from CCA and Merced was to show the variability of the particles in Mexico City at different times and locations. In the new manuscript, given the change in focus, we now only compare data from CENICA with data at Cerro de la Estrella (a site which within 2.5 km from CENICA) and UAM-I (next to the CENICA supersite) (section 3.9 and figure 17).

2) What is the point of presenting average masses over entire periods when you are using an instrument with the response time and resolution of the AMS?

In the previous manuscript, we mostly presented average mass concentrations because it was an overview paper. In the revised manuscript we take advantage of the high resolution data to discuss sources and compositions of short-lived plumes (sections 3.4 and 3.8 and figures 9, 15, and 16). On the other hand, we average data when appropriate in order to investigate processes occurring daily or on large time scales, such as secondary nitrate and sulfate production (sections 3.6 and 3.7 and figures 12, 13, and 14). One advantage of the highly time-resolved data obtained with the

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AMS is that various conditional averages (diurnal cycles, daily averages, etc.) can be performed when appropriate.

3) What is the advantage of the AMS over other techniques? What information is being obtained that is not possible with other techniques? Why are the pros and cons of the AMS not discussed in this article? What is the objective of this paper?

The main advantage of the AMS is the ability to measure size distribution and composition of particles with high time resolution. The main disadvantage of the AMS is that is can only measure non-refractory material on PM1. This disadvantage was overcome in this study using other measurements of the refractory material in the atmospheric aerosol (BC and soil) (section 3.1). The objective of the revised manuscript is to present an overview of the mass concentrations and trends of the composition and size distribution in the aerosol in Mexico City (sections 3.1 to 3.4). In addition, the manuscript now presents a discussion on the trends, size distributions, and chemistry of the inorganic component of the aerosol (sections 3.4 to 3.8). There is an extensive literature (more than 70 papers, see http://cires.colorado.edu/jimenez/ams.html#Papers-AMS) on the AMS where the various pros and cons of the instrument have already been discussed. We did not think that it was appropriate to repeat that information in this manuscript.

4) Can the AMS differentiate externally mixed from internally mixed particles? If so, what are the implications and if not how important is it that we can't know how the mass is chemically distributed?

The Q-AMS we used for this study cannot directly differentiate externally mixed from internally mixed particles. However, the mixing state of the aerosol can be partially inferred from the comparison of time trends and size distributions of the aerosol components (section 3.4), as well as from beam width profiles for the different species presented in the companion paper (see Salcedo et al. Atmos. Chem. Phys. Discuss., 5, 4143-4182, 2005).

5) What happens to volatile material on particles, such as water or semi-volatile organ-

ics when they are introduced into the high vacuum of the AMS?

Water is partially evaporated as the particles enter the vacuum chamber of the AMS; hence we cannot obtain a quantitative mass concentration of water with the AMS. On the other hand, semi-volatile organics can be measured because their vapor pressure is many orders of magnitude lower than that of water (section 3.1)

6) In comparisons with techniques that sort particle size by aerodynamic diameter, how does the vacuum aerodynamic diameter from the AMS compare? Does this explain differences in the size distributions comparing AMS with MOUDI?

A detailed review of the relationship between vacuum aerodynamic diameter and other diameters is presented by DeCarlo et al. (Aerosol Sci. Technol., 38, 1185-1205, 2004), cited in the manuscript. In order to compare particle sizes measured with other instruments such as LASAIR, we did convert aerodynamic diameter (dp) into vacuum aerodynamic diameter (dva) using the estimated density of the particles (section 3.1). In the revised version, we removed the comparison of the AMS with MOUDI. However, in the original version, we did convert da into dva; thus the different diameters measured by the two techniques cannot explain the differences seen.

7) The aethalometer, contrary to what the manufacturer advertises, does not measure BC. The aethalometer is nothing but a measure of light attenuation from which BC is derived using a conversion factor, the specific absorption coefficient, that is highly variable depending on the type of BC being measured. This has been already evaluated for Mexico City in one of the papers that the authors chose not to review.

What referee#2 is saying is explained in the experimental part of the manuscript. Section 2.2 of the revised manuscript starts "The black carbon content of fine aerosols was estimated from the aerosol light absorption using a seven-channel aethalometer". We have changed sentences such as "BC measured with an aethalometer" to into "BC estimated with an aethalometer" in the rest of the manuscript. The paper that referee#2 seems to refer to is referenced in the revised manuscript. In the original version, it was referenced in part I of the manuscript:

Baumgardner, D., Raga, G. B., Peralta, O., Rosas, I., Castro, T., Kuhlbusch, T., John, A., and Petzold, A.: Diagnosing black carbon trends in large urban areas using carbon monoxide measurements, J. Geophys. Res., 107, 8342, 2002. doi:10.1029/2001JD000626

8) If you are going to compare with results from other cities, then you have to convert the measurements to sea level equivalents.

We did in the revised version.

9) Why are the data not analyzed with respect to the local meteorology? Previous papers, for example, have shown that the relative fractions of sulfate and organics are highly sensitive to the relative humidity. Was there no weather station at this “supersite”? The Cenica site is located in an area where the measurements are likely to be very sensitive to wind direction. The “highly time and size resolved” measurements are averaged into intervals where any useful information on smaller scale variations is lost. This is an opportunity to look at how size distributions of the chemical constituents change with temperature, RH, wind direction, wind speed and radiation at small time scales. Surely a research site that was as highly instrumented as the one for this experiment had a complete set of meteorological measurements, including radiation and rain rate. How can you discuss secondary organic aerosol production with no associated correlations with the UV radiation?

The AMS dataset from this study is enormous, with species concentrations, size distributions, beam width profiles, and mass spectra for over 10,000 4-min averages. As this is the first publication on this dataset we have focused on the major patterns observed, which requires some averaging. With the new focus of the revised manuscript, we have added joint analyses of particle measurements with RH and gas phase concentrations in order to discuss the inorganic aerosol processes (sections 3.6 and 3.7, and figures 12, 13, and 14). An analysis of the highly time-resolved variability of chloride has been

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presented, as this species showed some very rapid variations. The variability was slower for other species and most of the relevant features are captured by the hourly averages presented here. As it has been mentioned, the organic processes are going to be discussed in detail in a future publication.

10) The period of April-May, 2003 was unusually disturbed, weather-wise, with an abnormally high number of cloudy and rainy days. How did this affect the results? When comparing the results from 2003 with other years, were these cloudy and rainy days excluded? If not, how can you interpret any differences that are found in the comparisons? It seems that only measurements of Chow et al and Moya et al were used in the comparisons and these not only were from different areas of the city but under very different meteorological conditions. What useful information can one glean from comparisons under such disparate conditions?

With the new focus of the paper, we removed comparisons with Moya et al. and only left the comparison with the IMADA-AVER and PM2.5 RAMA measurements at UAM-I (section 3.9). The measurements of IMADA-AVER and MCMA-2003 are remarkably consistent (Figure 17). The differences found between the soil mass concentrations during MCMA-2003 and IMADA-AVER may indeed be due to differences in precipitation patterns, as explained in the revised manuscript.

11) Why are the gas measurements not used in this study? The RAMA station at CES, while not co-located, would offer valuable insight into the variations in the particle distributions. Other published studies, for example, have shown that the amount of sulfate in particles is inversely correlated with the SO2 and directly correlated with the RH. It is very strange that the authors are unaware of these previous studies and don't take advantage of the RAMA measurements of SO2, CO, NOx and O3 since these are gases are precursors or surrogates of precursors for particle production and growth. For example, the CO has been shown in previous studies as a very good tracer of the boundary layer growth, as well as the intensity of primary emissions.

We were fully aware of these measurements and intended to carry out such analyses, but as explained above we had originally chosen to leave them for a later manuscript. We added an analysis to the paper regarding the production of sulfate and nitrate using measurements of SO2, NO2, and OH (sections 3.6 and 3.7, and figures 12, 13, and 14). CO is used to determine dilution effects due to boundary layer depth changes during the day (section 3.6).

12) Figure 4 is incomprehensible. The legends are unreadable and the symbols and lines are blurs.

We increased the size and resolution of the figure in the revised version (now figure 7).

13) Figure 6c. The fraction of organics in this figure is meaningless. All it does is fill the remainder of the graph to get 100%.

It is not clear to us what the referee means here. The sum of the percentages of all components in the particles must indeed be 100%.

14) Figure 6 b. What do the different shapes mean? How does this relate to the processes that produced these curves? What is the point of displaying these normalized curves?

A more detailed analysis of the size distributions is included in the revised version (section 3.4). As the text explains, the normalized curves are shown in order to compare their relative shapes.

15) The size distributions in this study are only being compared with those from cascade impactors whose 50% size cuts are broad and extend down to only 0.18 um. If the authors look at the references in the Mexico City review paper that they only briefly mention, they will find that particle size distributions (PSD) have been made with high resolution by a number of other investigators. At least one of these studies was a detailed analysis of the concentration of particles in different size ranges as a function of relative humidity and time of day. That same study also has size distributions of sulfate

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with the MOUDI. Perhaps a comparison with the measurements in that study would be more relevant than those that are currently provided.

Given the changes to the manuscript and the new focus on comparing only to sites very close to CENICA, this comment is not relevant anymore because the measurements that the referee is probably referring to were carried out at a site far away from CENICA. However, at the beginning of section 3.9, we reference the relevant papers.

Response to specific comments of Referee # 3

1) Throughout the manuscript, the authors make several references to nitrate existing in the form of ammonium nitrate. Because there is evidence that soil/crustal material resides in fine material in Mexico City, is it not also possible that the nitrate exists in the fine mode due to uptake on soil? There have been numerous literature manuscripts describing the possibility of this process. The authors state on page 4192 that times when not enough ammonium was present to neutralize nitrate and sulfate could indicate organic nitrates. Are these the times in Figure 3 where it appears that nitrate is not well correlated with sulfate and/or ammonium? Could this data also indicate soil uptake, rather than organic nitrate? Seeing plots of ammonium versus nitrate + 2*sulfate (in equivalents) could help clarify when either organic nitrates or soil nitrates were relevant.

In the revised manuscript, we included a section that discusses the ion balance in the aerosol (section 3.5 and figure11). This section contains an analysis equivalent to the one suggested by the referee and addresses the possibility of nitrate uptake on soil during the periods with apparent deficit of ammonium in the particles.

2) On page 4193, the authors speculate that uniform ozone in the eastern part of the valley is indicative of intense photochemistry despite cloudiness. The authors should actually specify what the mixing ratios were and make a comparison to the mixing ratios representative of Mexico City under different scenarios in order to strengthen their argument.

This is not our speculation. It is a conclusion of de Foy et al. (2005), who discuss in detail the meteorological conditions during MCMA-2003.

3) On page 4193, is the increase in aerosol fraction during the second half of the campaign really clear? There are spikes in the first half of the campaign that are just as high.

What is peculiar about the last days in the campaign is that the concentration of organics is higher than the average concentrations during the rest of the campaign, while the concentration of the inorganic compounds remains at the same level. During the spikes at the beginning of the campaign, high concentrations of all the NR-PM1 components were observed. Also during the first part of the study, the organic aerosol generated during the day decreased to a lower concentration at night. During the latter part of the study, the organic aerosol appeared to accumulate with time (see figure 6).

4) The authors do not discuss Figure 5 in any detail at all.

We now discuss some details of this figure (figure 9 in the revised manuscript; see section 3.4).

5) On page 4195, the authors should define what a ‘good fit’ means. Did they basically perform a multi-parameter minimization technique? Clearly, a lot of previous work shows the appearance of multi-modal behavior for organics. In this case, is this more or less pronounced than in other locations?

We use a built-in fitting procedure which minimized the value of Chi-square. We tried fitting mono-, bi- and tri- modal functions to the size distributions and chose the smallest number of modes which captured the main features of each size distribution In the revised version of the manuscript we extended the discussion of the multimodal behavior of organics. For this, in figure 8, we included size distributions of m/z 44 and 57 (which are markers for oxygenated and hydrocarbon-like organics, respectively). A more detailed discussion of the organics size distributions will be presented in a future publication.

6) A good example of material that could very well be included in this paper is at the top of page 4196. If this is an overview of aerosol results during MCMA and organics make such a big contribution to PM in Mexico City, wouldn't it be relevant to discuss SOA at this point (rather than in a paper in preparation by Dzepina)? Also, the authors (at least some of them) have developed a technique to look at oxygenated versus hydrocarbon-like organic aerosol, which have been argued to be proxies for SOA and POA, respectively. Why not include that analysis here? On page 4196, line 16, do the growth periods in sulfate observed by the authors in Figure 5 coincide with the measurements of Dunn et al.? The authors state that the relative roles of traffic and nucleation in the ultrafine particle population will be explored in a future publication. Why not here?

The analysis of the organic aerosol component will be described in a separate publication submitted by a different (first) author. The main reason is that the techniques for the analysis of organic aerosol data from the AMS are evolving rapidly, and as a consequence the relevant analysis for MCMA-2003 may not be completed for at least six months to a year longer. An analysis of m/z 44 and m/z 57 (surrogates for OOA and HOA) has been included (sections 3.3 and 3.4, and figures 7 and 8. We have also connected the sulfate measurements to SO2 concentrations and nucleation events observed and reported in Dunn et al (section 3.4 and figure 10).

7) In some places, section 3.4 is somewhat redundant with earlier discussions of field campaigns in Mexico City. It would be possible to eliminate some material in the introduction since it is contained in section 3.4.

We did eliminate some of the material in the revised version of the manuscript.

8) On page 4198, the authors state that nitrate was higher in MCMA-2003, but on page 4199, the authors state that it is very similar compared to the other campaign. Which is it? Why would ammonium essentially be the same between the campaigns but a

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switch occur between nitrate and sulfate? Over the course of the 6 years, did ammonia emissions change drastically? If not, then a similar meteorological profile would be expected. Does this then mean that the emissions of SO2 and NOx are vastly different? Since the comparison between the two campaigns is, at best, qualitative, the authors should make more of an effort to compare meteorology and emissions scenarios to explain the differences.

The concentration of nitrate is higher during the MCMA-2003, but the relative diurnal profiles are similar. Differences seen are probably due to the lower concentration of sulfate, which was lower during MCMA-2003. This is now explained in the revised version of the manuscript (section 3.9).

9) On page 4201, lines 10-13 in the conclusion. The authors state about the aerosol species: ‘have diurnal cycles that can be qualitatively interpreted as the interplay of (some or all of) direct emissions, photochemical production, etc., etc.’ This statement really can’t be any more general. All atmospheric species are influenced by all of these processes. How much each of these processes matter is the more interesting part, and the authors should at least attempt to estimate the role that each plays.

In the revised version of the paper, processes that might explain the observed diurnal cycles of the inorganic component are discussed in detail (sections 3.4, 3.6, 3.7, and 3.8).

10) Below is a list of editorial suggestions: Page 4186, Line 20, capitalize c in City Page 4188, Line 19, no semicolon needed Page 4200, line 9, should specially be especially? This is also a bit of a run-on sentence. In Table 1, are organic compounds represented as metric tons of C? Figure 4h is rather difficult to read It is probably possible to combine Figures 6-8.

In table 1, organic compounds are given as actual mass emitted. We added a sentence to the table caption stating this. We increased the size and resolution of previous figure 4 in the revised version (now figure 7). We have moved previous figure 8 to the supplementary material (now figure S4)

Response to referee #3 of manuscript part I

The comments of this referee were posted at the interactive discussion of part I of this manuscript; hence, the general response to his/her comments will be posted there. However, because this referee also commented on manuscript part II, we answer his/her specific comments regarding this manuscript here:

1) Paragraph 2 of section 1.2 should include additional detail of the methods used to characterize aerosol composition during previous field studies in Mexico City. Without this detail it is difficult for the reader to understand the difference between previous missions and this one.

Previous section 1.2 (Brief review of previous Mexico City PM studies) was removed from the manuscript because the focus of the paper was changed, and comparison with previous studies is not longer one of the main objectives.

2) One would assume there was fairly extensive intrusion of biomass burning aerosol during this field mission. This is touched upon in the paragraph between pages 4193 and 4194 by referencing an intrusion of biomass plumes from satellite data. This section should be expanded. How are biomass aerosols determined using the AMS and/or black carbon or soot measurements? Are there clear correlations? Is it possible to tell from the aerosol loading how much of the aerosol mass on these days is from biomass aerosol? What is the size distribution?

These topics are currently under investigation. This discussion will be expanded in the in-preparation paper on the organic aerosol in Mexico City.

3) Another section of interest is described in only another single paragraph (line 15 on page 4192): What is the relation of aerosol to traffic patterns? Is it possible to offer a more comprehensive correlation of this effect? The authors appear to have at least a rough understanding of auto emissions. Can this be correlated in the aerosol signal

beyond the phrases ‘more noticeable.’ And ‘a considerable reduction was observed’?

The objective of having the survey analysis that we presented was to give a sense of the traffic patterns in Mexico City for those readers who do not live there. The phrases that the referee mentions are quantified in the manuscript ("more noticeable (˜25%)" and "a considerable reduction was observed (˜30%)"). However, the available traffic data was obtained in one street of a very large city, which is not near the monitoring site, and for which the traffic volume was likely saturated for a significant fraction of the time. The data is not suitable to attempt a comprehensive analysis of traffic patterns vs. particle levels. We have added this explanation to the revised manuscript.

4) The next paragraph is used to relate meteorology, specifically a ‘cold surge’, to aerosol properties. A reference is made to a paper by Foy et al. [which is not in the reference list ??]. Are AMS data presented in this paper? If not is there an attempt to perform a meteorology correlation in one of the ‘in preparation’ papers? This would seem to be a central topic of this field mission.

The paper is in the reference list and can be accessed through the ACP web page:

de Foy, B., Caetano, E., Magaña, V., Zitácuaro, A., Cárdenas, B., Retama, A., Ramos, R., Molina, L. T., and Molina, M. J.: Mexico City basin wind circulation during the MCMA-2003 field campaign, Atmos. Chem. Phys., 5, 2267-2288, 2005.

The paper does not present AMS data.

Further joint analysis of the AMS and meteorology data (e.g. using back-trajectories) has been carried out by a different author, and might be presented in a future publication.

5) A single paragraph is used to describe an observation of what is assumed to be ammonium chloride (last paragraph of page 4197). What is the formation mechanism of these particles? Although it is a semi-volatile species what does it condense on? How was it produced? Is there lab data to support this finding? It appears the identification

of ammonium chloride is dependant on a correlation by AMS size. Were single particle instruments present? Do they support this assertion?

We assume that chloride exists as an ammonium salt in Mexico City because the observed plumes of chloride are always accompanied by a plume in ammonium and because the AMS is not sensitive to other inorganic chlorides such as NaCl, due to their refractory nature. As it is explained in the text of the original manuscript the ammonium chloride might be condensing on preexisting particles in the morning when the temperature is low and RH high. The revised manuscript includes a section on chloride (section 3.8), where this is explained in more detail.

6) The conclusion are a single paragraph in length. Is there a reason some of these important findings are not reiterated?

We expanded the conclusions in the revised version of the manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 4183, 2005.

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