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Atmospheric Chemistry and Physics Discussions

Interactive comment on "PM speciation and sources in Mexico during the MILAGRO-2006 Campaign" *by* X. Querol et al.

Anonymous Referee #2

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Referee Report on Manuscript by Querol and coworkers

This paper reports the results of PM measurements carried out in and around Mexico City as part of the MILAGRO campaign during March-April 2006. Measurements were carried out with several types of off-line samplers (filters and microscopy substrates) and also with optical particle counters. This study reports data on 9 sites, including the main ground sites for MILAGRO (T0, T1, and T2), as well as the CENICA site that was the Supersite during MCMA-2003 campaign, and the UNAM site where several previous studies have also been carried out.

This paper is clearly appropriate for ACP and for the MILAGRO special issue. Its spatial and chemical coverage and the ability to link and compare with other measurements

(during and before MILAGRO) is a significant strength of this study. The reporting of PM1, PM2.5, PM10, and of all chemical components is also very useful and it complements and serves as context for other studies that tend to focus on narrower size ranges or chemical fractions. Finally the detailed elemental analysis is extremely informative and complements a variety of other aerosol measurements during MILAGRO. I strongly recommend this paper for publication in ACP after the issues listed below have been addressed.

Comment on Review from Referee 3

I also read the review from Referee 3, and I was simply astonished by the general comments made in this review about these measurements being "very routine" and "widely available." I have participated in 20 field campaigns around the world where routine and advanced particle measurements have been carried out, and this paper has one the widest elemental composition and number of sites that I recall for any previous campaign. This is an extremely rich dataset, which is very complementary to other datasets collected during MILAGRO, and that clearly deserves publication in my opinion. If anything, I believe that the authors could extract even more information from their data than they present by doing further analyses and comparing in more detail with other studies, as I will describe in more detail in my review.

Main Issues

1) Technical description of measurements

It would be useful to readers if the techniques used in this paper were described in more detail. Specifically:

- A slightly more detailed description of the laser spectrometers (GRIMM 1107 and 1108) would be desirable on P10593. What are the size ranges, flow rates, and size resolution (channels / decade) of these instruments? How are PM1 etc. calculated from the OPC size distributions? Typically those size cuts are defined vs. aerodynamic

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diameter [see e.g. DeCarlo et al., 2004] and not optical diameter. Has particle density (which can be estimated from the composition) been taken into account here? Also the size cuts are typically gradual, so that some particles below 1 um are removed by the size cut, while some particles above 1 um are included in PM1 measurements. See e.g. the figure in page 2 of http://www.urgcorp.com/cyclones/pdf/2000-30EHB.pdf.

- Also additional information on the instruments, manufacturers/models, and detection limits would be useful in section 2.2.

- P10596/L10-16: Evaporation of some species (ammonium nitrate, organic species) under vacuum is a known problem with microscopy techniques. The time under vacuum before and during analysis should be specified to provide a comparison point with other studies in which this has been characterized. Also, what is the lower limit of the size range of particles that can be analyzed with this instrument?

2) Comparison with other studies

While this paper briefly cites some previous studies in the Mexico City area, the paper body is very focused on reporting the results of this particular study and does not make a serious effort of connecting with previous studies in the area. This has already been pointed out in an interactive comment by J. Miranda. Some additional comparisons of interest include:

- The relative impact of biomass burning, as discussed in more detail below.

- The results from Johnson et al. (2006), who reports results from elemental analyses during MCMA-2003, with different techniques but qualitatively similar information as in this study. It should be cited and discussed in the revised paper.

- The diurnal variation and fractional composition of PM2.5 at the CENICA site, where two previous studies have been carried out during the same season. See Fig. 16A and 16G of Salcedo et al., 2006. Perhaps these figures could be reproduced here with the data from this study added to them, which would serve as a useful inter-temporal and

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inter-study comparison.

- P10599/L27: the observation of a relatively broad-scale spatial variation of PM is consistent with results from Molina et al. (2007, Fig. 7).

- Fountoukis et al. (2007) interpret the scatter between inorganic thermodynamic model predictions and PM2.5 measurements to 30% of the nitrate being present in larger particles (which was not measured in that study. The results from this paper (Table 4) quantify PM10-PM2.5 nitrate as 61% of the total nitrate at T0. The qualitative agreement but qualitative discrepancy should be pointed out and briefly discussed.

- Regarding the fraction of the particle mass between PM1 and PM2.5, results from Salcedo et al. (2006) (Fig 3 in that paper) suggest that this fraction is small (5-10%), while results from Moffett et al. (2007) (Fig. 3 as well) suggest that this fraction is much larger, near 50%. The results of this paper appear to be more in line with the first study, but I suggest that the authors comment on what their data suggest in this debate.

- P10603/L1-4: the finding that sulfate is relatively homogeneous in space is consistent with the conclusion from Salcedo et al. (2006) that the sulfate in the MCMA has mostly a regional character, based on the low variability in the temporal profiles of this species.

3) Contribution of biomass burning to PM levels during MILAGRO

As the authors may be aware, there is a vigorous ongoing debate among MILAGRO researchers about the impact of biomass burning (BB) to particle concentrations in Mexico City and in the outflow from the city, e.g. at the MILAGRO meeting and in the interactive discussion of some papers. Two ACPD papers (Yokelson et al., Moffet et al.) suggest that BB is a dominant source of fine PM in/around Mexico City during MILAGRO, while one ACPD paper (Stone et al.) and several not yet published results support an important but lower contribution. I am not aware of any reports that do not include BB as a significant PM source during MILAGRO. This paper with its spatial, chemical, and size coverage should be able to contribute significantly to this debate.

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This point needs to be addressed in detail in the revised version.

Currently the paper only mentions BB as a source in P10602/L20-27, indicating that BB is a significant source due to the fact that K is correlated with EC+OC (but K is also more highly correlated with soil tracers). The interpretation of the factor analysis results section 4.3 does not identify BB as a major source, but associates K with soil factor 1 (at CENICA, T0, and T1) which has a "clearly mineral origin." The authors should directly address the potential impact (or lack thereof) of BB on these data. Factor analysis methods have limitations and cannot always separate sources if the chemical profiles and/or time series or several sources are highly correlated. A mixed factor representing several sources could also be assigned to one of them (e.g. due to more distinct tracers). Also the contribution of BB was likely pretty variable during MILAGRO due to the variable meteorology (as summarized in this paper, also by Stone et al. (2007) and Fast et al. (2007)). Since many measurements (here and in other studies) did not operate for the whole MILAGRO campaign, that may explain some of the apparent discrepancies. The authors should directly address the question of whether BB could be lurking behind some of the sources in the factor analysis (presumably with high OC and K). If yes, the BB contribution should be quantified or at least bounds placed on its contribution at different sites and times. If the authors can rule out a significant contribution from BB based on their data, this should also be stated. Or alternatively, can a time series of the chemical form of K associated with BB (as mentioned in P10602/) be produced?

Some highlights of the ongoing debate about BB impact during MILAGRO are:

- Moffet et al. (2007) report a very large fractional contribution of BB to PM2.5 concentrations at T0, with a maximum in the afternoon reaching 19 ug/m3 at 11 am (Fig 7 in that paper). Jimenez and DeCarlo (2007) suggest a number of reasons why the impact of BB may be overestimated in that study and summarize evidence from other researchers that points towards an important but lower BB contribution. A BB contribution of of 19 ug/m3 would represent 40% of the average PM2.5 reported in this

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(Querol et al.) paper at 11 am. Is such a high BB impact consistent or inconsistent with the T0 measurements reported here? Could such a large contribution, if real, be missed by the source apportionment technique used here?

- Stone et al. (2007) reports average contributions of BB to PM2.5 OC of 16% at T0 and 32% at T1 (average of data in Table 2 of that paper). Since BB particles are dominated by OC, this implies that the fractional contribution of BB to PM2.5 would be about 2/3 of those percentages.

- Yokelson et al. (2007) estimate that wildfires in the hills and mountains surrounding the city may contribute up to 78% of the PM1 in the outflow. DeCarlo and Jimenez (2007) suggest that if the omission of SOA in that study is corrected, the contribution of fires to PM1 in the outflow should be in the range 22-37%. BB is mainly a source of fine PM. Geometrical arguments would suggest that if wildfires surrounding Mexico City were an overwhelmingly dominant source as suggested by Yokelson et al, the fine PM concentrations in the outlying sites should be only slightly lower than those in the core of the city. However the PM1 concentrations at those sites are about half than at the urban sites, which to me highlights the importance of the urban sources, and suggest that the contribution of BB may have been overestimated by Yokelson et al. Also BB PM is dominated by OC, which also decreases significantly between the urban and outlying sites, reinforcing the same conclusion. The times of sampling at some sites in this study were very limited, which could introduce some uncertainty given the variability in the fires. The consistency or inconsistency of the data presented here with the Yokelson et al. study should be explicitly discussed.

Minor Issues

- A minor but important point is to specify the volume convention used for the concentrations reported here (e.g. ng/m3). E.g. Salcedo et al. (2006) report concentrations per unit volume of air at local T and P in Mexico City. Other authors report concentrations per unit volume of air at 298 K and 1 atm, while yet others use 273 K and 1 atm.

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Especially the difference in pressure can result in significant differences in the numbers, so this should be clarified early in the paper. This should be taken into account when concentrations from this study are compared to those from other studies in the literature.

- P10590/L9: Mexico City is in North America, not South America. I suggest replacing "South American" with "Latin American."

- P10601/L21: 7 am seems early for the "rapid growth" of the mixing layer. References for this in Mexico City?

- P10602/L12-14: sentence starting with "In PM2.5..." is ambiguous, not clear which % refers to what, suggest rephrasing.

- Fig 11: this graph has 2 vertical scales, but it is not clear which traces are on which scale.

Typos etc.

- P10614, last line in Table 1: "closet o" should be "close to"

- The word "Mexico" has an accent sometimes and not others (e.g. P10594/L8 and L17).

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Interactive Comment