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Discussions

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

X. Querol et al.

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We thank a lot the detailed comments of referee 2 that improved quite much the content of the paper. We applied all changes suggested in the new version. Below you will find the changes addressed and some replies requested.

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 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. We agree with the reviewer’s comments. Real time optical measurements were corrected with reference gravimetric data (with aerodynamic size cut), consequently real time corrected measurements may be considered valid. To clarify this point and the others mentioned by the reviewer, this paragraph will be added to the text:

Real time measurements of PM were obtained with two models of laser spectrometers, GRIMM 1107 and 1108. These instruments perform particulate size measurements by 90-degree laser light scattering. Sampling air (1.2 l/minute) passes through a flat laser beam produced by an ultra low maintenance laser diode. A 15-channel (0.3-25 μm) pulse height analyzer for size classification detects the scattering signals. These counts from each precisely sized pulse channel are converted to mass using a density equation included in the instrument software. In addition, real time measurements obtained by the optical counter were corrected with the regression equations (in all cases R2$>$0.8) obtained between the comparison of gravimetric PM levels (aerodynamic diameter) determined by the standard high volume gravimetric method, and real time (optical counts) measurements, independently for PM10 and PM2.5 fractions. PM1 data was corrected according to the PM2.5.

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

These details will be added to the text 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?

The vacuum time and pressure conditions before the analysis will be added to the text. The vacuum time during the analysis depends on each sample. Regarding the evaporation of certain species, our main interest was mineral matter and metals, which are not affected by this process. The lower limit of the size range of particles that can be analysed depends on the specific vacuum conditions (high or low pressure). Given that our main interest of using this technique was the morphology and the size of particles, low vacuum conditions were applied. Our experience in studying this type of samples allowed us to interpret the obtained results, in some cases combined with single particle chemical analyses.

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.

It is answered 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 levels found in our study are in general higher than those reported by Johnson et al., 2006, and it will be stated in the text as follows:

- Levels in PM10 of As (5-7 ng/m3), Zn (100-500 ng/m3), Cd (1-3 ng/m3) and V (20-50 ng/m3) were relatively high when compared with most urban sites from the US and Europe, or with values reported from Mexico city during 1996-1998 (Mugica et al.,

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2002) or during MCMA-2003 campaign (Johnson et al., 2006). However...

- 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 inter-study comparison.

Diurnal variation of PM levels coincides with that from Salcedo et al., 2006, and this comment will be included in the final version of the paper.

Regarding chemical composition, levels of nitrate, sulfate and ammonium recorded in our study are similar to those reported by Salcedo et al. (2006), which was already stated in the text (P10603/L9-12):

These results coincide with those obtained for PM2.5 at the CENICA site during the MCMA-2003 Campaign, when similar levels of sulfate (3.1 μg/m3), nitrate (3.7 μg/m3) and ammonium (2.2 μg/m3) were registered (Salcedo et al., 2006)

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

We state that levels are relatively homogeneous within MCMA, and that coincides with findings from Molina et al. (2007) and it will be added to the text.

- 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.

The results from this paper quantify PM10-PM2.5 nitrate as 61% of the total nitrate at T1 (not at T0, where this percentage is only 21%). The apparent difference with data from Fountoukis (30% of nitrate in larger particles) is not real, as sampling period is not the same. If we took from our data only those that coincide with the sampling period of Fountoukis (21-30March), the percentage of nitrate in the coarse fraction is 39%, which is closer to the 30% estimated by Fountoukis. This variation in the size distribution of nitrate during the campaign (coarse in the first part and finer in the second part) can be explained by the meteorological conditions. In the beginning of the campaign, weather was mostly dry, so the resuspension was high and therefore ambient crustal matter was high; this crustal material could react with the ambient HNO3 and NOx to form Ca(NO3)2, which has a coarse grain size. To the contrary, in the second part of the campaign, rainfall rate was higher and therefore soil resuspension was lower, with the result that ambient mineral matter was lower and HNO3 and NOx didn’t form Ca(NO3)2 but other compounds such as NH4NO3 with a lower grain size. These similarities will be explained in the text.

- 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 Moffet 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.

Data from our study show that PM1-PM2.5 fraction account for 18-21% of total PM2.5 in the MCMA (T0 and CENICA). This has been added to the text

- 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. It will be included in the text as follows:

- Levels of ammonium (1.1-1.5 μg/m3 in PM10) and sulfate (4-5 μg/m3 in PM10) were homogenous at the different urban, suburban and rural sites, and relatively higher at the industrial sites (2.0-2.5 μgNH4+/m3 and 6.5 μgSO42-/m3 in PM10); this low spatial variability agrees with Salcedo et al. (2006), who concluded that sulfate in MCMA has mostly a regional character. Nitrate levels were relatively low, but….

3) Contribution of biomass burning to PM levels during MILAGRO

- 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. 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).

It is a well-known difficulty that receptor models based on factor analysis present limitations regarding the clear differentiation of sources when source profiles and/or source contributions correlate (Henry, 1987). In the present study, biomass burning (BB) was not detected as an independent source and K mostly correlated with the mineral factor (factor loadings = 0.71 and 0.93 at CENICA-TO and T1, respectively), and only less significantly with the regional+fuel-oil combustion factor (factor loading = 0.36) at CENICA-T0. It is thus clear that BB emissions are mixed within these two factors, even though the current analysis does not allow us to provide a more specific estimate of the contribution from the BB source. However, we believe that in this specific case this limitation is linked more to the limited number of samples available (25-38 samples/site) and the fact that OC levels were not available for all samples (therefore preventing us from introducing OC in the factor analysis), than to correlating source profiles. A larger number of cases and the inclusion of a specific tracer of BB (OC) would most certainly increase the potential of the model to detect and resolve the contribution from BB.

In order to solve this issue, measurements are currently ongoing in Mexico City which will be pooled with the MILAGRO data and previous sampling campaigns, with the aim to focus on this specific source.

- If the authors can rule out a significant contribution from BB based on their data, this should also be stated.

With the current data we cannot rule out the contribution from BB. This contribution is clearly detected by means of the K-OC+EC correlation, and it is therefore a significant source of PM. However, it cannot yet be quantified (with our data).

- Or alternatively, can a time series of the chemical form of K associated with BB (as mentioned in P10602/) be produced?

As stated above, this cannott be done with the current data.

- 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 (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?

A maximum hourly contribution of 19 μgBB/m3 to PM2.5 at T0 (Moffet et al., 2007) would be higher than the results suggested by our data. Taking into account that BB particles are mostly made up of OC, and considering that an average ratio of OC/PM2.5 = 0.31 was obtained during this study for T0, this would mean that for a PM2.5 hourly mean of 53 μg/m3 the estimated hourly concentration of OC would be 16 μg/m3. This OC concentration would be the sum of contributions from all combustion sources (traffic + BB + domestic emissions + others), and if we look at the factor analysis we observe that carbon levels correlate significantly with at least 2 emission sources. Therefore the estimated OC hourly concentration must be split into at least 2 sources (although most probably more). As a result, the OCBB contribution to PM2.5 should be much lower than 16 μg/m3, at most less than 50% of that value (8 μg/m3).

It could be argued that the OC/PM2.5 ratio is not constant throughout the day: even if we assumed a much higher ratio (e.g., OC/PM2.5 = 0.60), then OC levels at 11 am in T0 would be 32 μg/m3, meaning that OCBB $<$ 16 μg/m3.

- 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.

Assuming that OCBB = 16%OC at T0 and OCBB = 32%OC at T1 (Stone et al., 2007) would imply that OCBB = 2 μg/m3 at T0 and 1.2 μg/m3 at T1, with our data. Comparing these OCBB levels to mean PM2.5 concentrations, this would result in mean BB contributions of at least 5% of the PM2.5 mass at T0 and 4% of PM2.5 at T1. These should be considered minimum values, given that BB emissions are mainly but not only made up of OC.

As a result, applying the results published by Stone et al. (2007) to our data would provide much lower BB contributions to PM2.5 (OCBB=4-5%) than if the results from Moffet et al. (2007) are considered (19 μgBB/m3/53 μgPM2.5/m3 = 36%). Even if total OC levels from the present study were boldly taken to represent BB emissions (clear overestimation, given that this would neglect highly contributing sources such as traffic), the BB contribution to PM2.5 at T0 would be 31%. Consequently, our results suggest that BB contributions to PM2.5 at T0 must be much lower than 30%, at most 10-15% when other combustion sources are considered. Conversely, a stronger agreement is found between our results and those from Stone et al. (2007), resulting in an estimated BB contribution to PM2.5 of 5-15%.

- 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.

Our results using current data do not suggest that wildfires are a dominant source, because if that were the case then the chances of detecting them as a separate source using factor analysis would be much higher. In that case, the source profiles of BB and other OC sources (e.g., traffic) would be correlated, but not their source contributions (time series) due to the different geographical locations of the sources (within Mexico City vs. in the outlying sites). The difficulty to detect BB within the city is that the source profile variability is minimal (different sources share similar tracers) and also the source contribution variability is low (e.g. PM levels and composition are mostly determined by meteorological factors, therefore contributions from all sources increase and decrease at the same time). However, if the geographical location of the sources were clearly different, the variability within source contributions would increase and consequently the model's ability to resolve sources would be enhanced.

- 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%.

As described above, our results suggest that BB contributions to fine particles (PM2.5) should be 5-15%, and therefore lower than the estimate provided by Yokelson et al. (2007) for PM1. Furthermore, the duration of our sampling campaign was one month and, to our knowledge, no large wildfires occurred during that period, and therefore it is not possible to evaluate the contribution from peak BB episodes with our data. Finally, the OC gradient observed from the urban site T0 (12 μgOC/m3) to the suburban T1 (4 μgOC/m3) confirms the importance of urban emissions on OC levels.

In order to clarify the contribution of BB during MILAGRO, the following paragraphs have been added to the text

- on P10602, Line25:

Biomass burning episodes and their important influence on PM levels and composition in Mexico were previously reported by Salcedo et al. (2006), Yokelson et al. (2007), Moffet et al. (2007), Molina et al. (2007) and Stone et al. (2007). These studies provided quantitative estimations of the contribution from biomass burning to PM levels, which vary widely according to the different authors. As described above, the influence of biomass burning on PM composition was detected in the present study, even though the current data does not enable us to provide an accurate estimation of the magnitude of this source contribution. By applying the factors relating biomass burning carbon with total OC by Stone et al. (2007) to the data from the present study, our results suggest that biomass burning contributions to PM2.5 at T0 should range between 5-15%.

- on P10608, Line25:

It is interesting to note that biomass burning emissions were not identified as a single source in any of the factor analyses performed. Instead, tracers of these emissions (K) were correlated with the mineral and regional-fuel oil combustion sources. The non identification of this source may be related to its probably low contribution compared to other sources during the study period. Also the limited number of samples available (25-38 samples/site), the short duration of the campaign, and the fact that specific tracers (OC) were not available for all samples may account for the non identification of this source. However, the correlation between OC+EC and K levels described above (section 4.2) evidences the influence of this source on PM levels and composition.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 10589, 2007.