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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.

**X. Querol et al.**

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Reply to Comments from reviewer #3

We thank a lot all constructive comments on our manuscript ACPD 7, S3637-S3639, 2007 made by reviewer #3. We are revising the original paper and we corrected errors highlighted, included all clarifications requested, as well as new short discussion to support interpretations are being added in the new version. Below is attached the list of changes that are being addressed and also some replies to questions made.

General Comments by referee #3: The authors have sampled atmospheric aerosol and determined its major and minor elemental composition at urban, suburban and rural sites in and around Mexico City. They interpret the results in terms of a small number of sources which are identified from their elemental signature, including the use of

Principal Component Analysis, and provide some quantitative estimates of individual source contributions to PM2.5 and PM10. The methods used are very routine and it may be argued that the results of this paper contribute little which is new to the literature. The results will be of local value within Mexico, but unless their contribution to the overall results of the MILAGRO-2006 campaign is especially important, it is difficult to see a justification for publication. This kind of information is widely available from many sites around the world.

Reply from authors: We agree that we are not proposing new methodologies. We were involved in the part of the MILAGRO campaign aiming with investigations on the export of pollutants from the megacity. We applied conventional methods to: a) Measure PM10, PM2.5 and PM1 levels in the city and also in rural and suburban sites around the city to investigate: a.1.) The variability of PM levels at two urban sites during the campaign. a.2.) Where, how and when the pollution plumes influenced the levels of PM at rural and suburban sites around city. b) Chemically characterise PM10 and PM2.5 in the city and at surrounding sub-urban, rural and industrially influenced sites, with the aim of identifying major components, variability along the campaign and tracers of the emission plume.

The aim was not in any case a detailed source apportionment analysis since we did not apply any quantitative approach, such as PMF or CMB.

Thus, the idea was not developing new tools, but applying conventional measurements to try to supply information on the above topics and to provide speciation information to the other teams of the field campaign. Other papers on MILAGRO 2006 campaign have been presented to characterize scenarios. Examples: the meteorological scenarios along the campaign or the evaluation of the variability of carbonaceous aerosols. Based on this we think that our work may be of interest for the campaign since we provide measurements and interpretations of real time levels of coarse and fine aerosols, a detailed chemical characterisation, an evaluation of dominant sources (not all sources) of aerosol, and an identification of some tracers of pollution, among other outputs.

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Outputs may help to interpret other results obtained during this campaign by means of other methods and teams. Another important feature of the work is that it evaluates not only the pollution within the megacity but in the surrounding areas. Thus, the polluted air masses from this urban climate that are transported elsewhere have a ‘chemical signature’, discussed in this article.

Specific Comments from referee #3: The work is conceptually sound but the following points need to be addressed if the paper is to be finally accepted for publication.

(a) Two different types of quartz microfibre filter were used. It is not explained why different types of filter were used for different samplers. Was any intercomparison made in terms of the collected mass of specific species?

Reply: Two different types of quartz filters were used because this paper summarizes the results obtained by three different research groups. Each of the groups checked the quality of the filters in their respective laboratory for the specific instrument, elements or compounds each team is using or analysing. We will add this clarification in the revised version since we agree it is needed.

(b) The environmental conditions under which filter weightings were conducted are not specified, and need to be. How was the optical particle counter “calibrated” against the gravimetric measurements?

Reply: b.1.In the article, it is stated that ‘Samples were conditioned after sampling (50ś4% humidity and 22ś3 oC during 48 h) prior to gravimetric determination of the PM mass.’ For a better understanding we will substitute this by: ‘Samples were conditioned after sampling (50ś4% humidity and 22ś3 oC during 48 h) prior to gravimetric determination of the PM mass (carried out in the same controlled chamber where filters were stabilized’.

b.2. In the text of the article it is written that ‘Real time measurements of PM obtained with the laser spectrometer (GRIMM) were compared and corrected versus gravimetric measurements obtained with the high volume samplers'. Calibration of the instrument is carried out by the technical assistance once a year. In addition, a comparison of the PM2.5 and PM10 levels (12 h) measured by the instrument with the levels determined by the standard method (gravimetrically, EN-1234-1). With the regression equations (in all cases R2>0.8) obtained between both measurement types and grain sizes, the levels of the optical counter were corrected. This correction was applied to PM10 and PM2.5. PM1 data was corrected with the PM2.5 factor. For a better understanding we will include this late text in the new revised version.

(c) What is the justification for calculating the carbonate concentration from that of calcium? Later in the paper the presence of gypsum is reported and therefore it is very clear that not all of the calcium was present as calcium carbonate. This might therefore be an over-estimate.

Reply: Carbonate concentration is mainly estimated to reach a better mass closure and help us to calculate the mineral fraction based on the frequent identification of calcite by SEM-EDS in the MILAGRO samples (many with a high proportion of mineral matter). In spite that calcite is being identified in many samples, it is true that not all the Ca is present as calcium carbonate (as you mentioned Ca sulphate is also present) and that we may overestimate the mineral load. We are including in the new revised version a comparison of the calculation of mineral matter by deducing the carbonate content together with the other mineral components (see below in question 'f'), an additional calculation of the mineral load by the algorithm used by Chow et al. (2002) (1.89ŒAl + 2.14ŒSi + 1.4ŒCa + 1.43ŒFe). We have effectuated the correlation between the mineral matter content calculated by the two methodologies. We have obtained a very good correlation coefficient (R2=0.99) and our methods overestimate the mineral matter content only a mean of 18% with respect to Chow's methodology. We will add the discussion in the new revised version because we agree that this will improve the discussion.

(d) Why was the electron microscopy carried out with an environmental scanning electron microscope (ESEM)? This is a specialised instrument allowing measurements to be made at significant water vapour pressures. The conditions of operation need to be better defined.

Reply: The text of the articles says that ‘Selected samples were also studied under an environmental Scanning Electron Microscope (SEM, FEI QUANTA 200), with chemical analyses of individual particles being performed manually on uncoated samples using an energy dispersive X-ray microanalysis system (EDX). Microscope conditions were working distance of 10 mm, accelerating voltage of 20 kV, a beam spot size of 2$\mu$m with a beam current of approximately 1.00 $\mu$A, and a spectrum acquisition time of 30 s live time, with particles being analyzed in its centre’. We used this instrument to avoid coating and also because is the one we have rapid access.

(e) Substantial concentrations of PM2.5 (as well as PM10) are attributed to local soil resuspension. This seems quite unlikely. What is the supporting evidence?

Reply: High concentrations of PM2.5 and PM10 are attributed to local soil resuspension at T1, not at the rest of the sites. There are some reasons that led us to the conclusion that local soil resuspension influences highly the levels of PM: - The very high levels of crustal matter in all the fractions (using both of the above algorithms). - The specific characteristics of the sampling site (T1 was a suburban site, surrounded by a wide area not paved, with low vegetal coverage) a lot of resuspenison was induced during measurements. - The extremely dry conditions of the weather in the first part of the campaign (no rain during the first part, and some days of rain in the second half of the campaign). The levels of crustal matter decreased during the second part of the campaign, which is attributed to a lower soil resuspension, reflected on the lower crustal levels. - High wind speed during many measuring days.

It is widely accepted that soil dust also influences PM2.5. In a very lower proportion than in PM10 but if the dust load in PM10 is very high, then PM2.5 is also proportionally influenced.

(f) Some justification of the algorithm used to calculate concentrations of crustal material is needed. This looks very incomplete.

Reply: As previously stated this section will be modified by including two types of algortithms. As indicated in the text of the article in the beginning of point 4.2 PM composition (As shown in Table 4, TSP, PM10 and PM2.5 levels in Mexico City are highly influenced by crustal material (SiO2+CO32-+Al2O3+Ca+Fe+Mg+K), the crustal concentration was calculated by the addition of all the crustal elements in ambient air. The other one that we are now considering for comparison and discussion is the algorithm from Chow et al. (2002) in the revised paper.

(g) What factor was used to convert the OC concentration into organic matter? This can have a significant impact on mass closure.

Reply: Organic matter was calculated as 1.4*OC. It will be added to revised version, in the description of the methodology as follows: ‘Indirect determinations from analytical data were obtained for:ĚĚĚ.c) organic matter, determined as 1.4*OC, based on Eatough et al., 1996; Putaud et al., 2000; Turpin et al., 2000)’.

(h) Masses of secondary inorganic aerosols are reported but the species considered in these masses are not defined. Presumably it was just sulphate, nitrate and ammonium. If so, this needs to be stated.

Reply: Yes, we will introduce an statement: SIA= SO42-+NO3-+NH4+

(i) At a number of points the authors appear to be under the misapprehension that Mexico City is in Asia. They refer to results from “other large Asian cities”. This needs to be corrected.

Reply: Grammar error!!. It will be corrected.

(j) The attribution of the mercury to a point source (an incinerator) seems unlikely given that concentrations of mercury were correlated with sulphate. Sulphate is likely to have a regional origin arising from a large number of point sources of sulphur dioxide which would give a very different directional signature to that of a point source such as an incinerator. Consequently, the results do not appear to support the incinerator being the predominant source of mercury and this needs to be considered.

Reply: Yes we agree. May be we were not very clear in writing this.

The texts says that: ‘Particulate Hg is not higher at the urban sites than at the suburban site T1, consequently, as previously reported, it has an external (regional) origin to the city. A possible source for Hg in the area is a city waste incineration power plant as deduced by a previous study of back-trajectories for days with Hg data available (Gonzalez et al., 2007)’. It was not very clear and we will modify text to clarify the interpretation of the results as follows: ‘Particulate Hg is not higher at the urban sites than at the suburban site T1, consequently, as previously reported, it has an external (regional) origin to the city. However, local sources, such as an hazardous waste incinerator and a petrochemical plant may also contribute to increase Hg in a much minor proportion (Gonzalez et al., 2007)’.

(k) Mean wind directions are reported in Figure 4. How were these estimated? Averaging northerly winds of 360o and 0o gives a value of 180o but this does not imply a southerly wind. Was this pitfall avoided?

Reply: Mean wind directions were calculated properly, i.e. vectorial means were calculated, not arithmetic means.

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