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Atmospheric
Chemistry
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Discussions

# *Interactive comment on* "Primary and secondary contributions to aerosol light scattering and absorption in Mexico City during the MILAGRO 2006 campaign" *by* G. Paredes-Miranda et al.

**G. Paredes-Miranda et al.**

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**Reply to reviewer comments for ACPD 8, 16951-16979, 2008, Primary and Secondary ...by Paredes-Miranda et. al.**

The authors thank the reviewers for comments that were helpful for us in improving the revised version of the manuscript. Detailed comments from the reviewers, and our replies, are given below.

**1st Referee Comments**

**1. P16956, Section 2.2. Please include estimates of measurement uncertainty for all of the instruments used.** The following was added to the revised version on page

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16956 line 17 after "...as a reciprocal nephelometer (RN) (Rahmah et al. 2006)". "The reciprocal nephelometer measurements of scattering coefficient have a systematic relative uncertainty of 15%, and the photoacoustic absorption coefficient measurements have a 5% relative uncertainty (Lewis et al. 2008) associated with systematic errors noted during repeated calibrations".

The following was added to the revised manuscript on page 16957 line 22, after "...(Aiken et al. 2008)". "The mass concentration measurements obtained with the AMS have an uncertainty of about 20%, mainly due to the uncertainty of particle collection efficiency (Huffman et al. 2005; Salcedo et al. 2006)".

**2. P16957, Line 1- 5. What wavelength dependence for absorption do you apply to convert from 520nm to 532nm? The choice is not critical, just curious as to the number and justifications. In converting the aethalometer mass back to absorption, what is an appropriate uncertainty range? It seems like a rather uncertain transformation process.** The spectral variation over this small range is not worth worrying about since the LEDs in the aethalometer likely have bandwidths of 25 nm. The photoacoustic bandwidth is around 0.1 nm. A model with inverse wavelength dependence was used, commensurate with the bulk of the aethalometer spectral measurements at T0. The athaelometer actually measures absorption and then uses an algorithm to report the mass assuming a specific mass absorption coefficient at the various wavelengths. The same algorithm was reversed to give aerosol absorption.

**3. 16957 Line 10. What collection efficiencies were applied to the AMS data and were they based on determinations from this field campaign?** A collection efficiency of 0.5 was applied to the AMS data, which was based on the observed composition/CE relationships determined in previous campaigns, and verified through intercomparisons with collocated instruments at T0 (Aiken et al. 2008) .This value is also consistent with multiple other AMS experiments in Mexico City (DeCarlo et al. 2008; Herndon et al. 2008; Salcedo et al. 2006).

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**4. Figures 1 and 2. Why not report data at 1 standard wavelength? Conversion to 532nm should be available. I am confused as to what wavelength the aethalometer data are reported. The text says there is a conversion from 520nm to 532nm but the figure has both.** See the answer for comment 2.

**5. Figure 4. Can you put uncertainty bars on the SSA or mention the propagated uncertainty in this value?** Considering the systematic errors for absorption and scattering, the range of absolute error for the SSA as propagated by the extremes of the systematic errors when added and subtracted from absorption and scattering was 0.02 to 0.07, with an average relative error of about 3%. This is discussed further below in item 8.

**6. P16959 Line 14. There are several references to photochemically generated SOA. I believe this mechanism in explaining much of the data and the latter section on fraction of secondary contribution demonstrates this nicely. I would make a reference early on to say that you investigate the contribution of secondary processes. The last paragraph of the introduction may be the best location for this statement.** Add at the end of the introduction, page 16955, line 10: "The diurnal variation of aerosol chemistry and optics is used to estimate the contributions of secondary aerosol formation to particulate mass and light scattering".

**7. Figures 3 and 4. The darker shaded regions for nighttime should have more contrast.** Done

**8. P16959 Line 14. The McComiskey work demonstrates that SSA uncertainty is a large uncertainty in radiative forcing calculations. Can you demonstrate your SSA uncertainty (ideally on the figure and in the text) and comment if your measurements will help in this regard?** The following was added: P 16959 line 9 after ...Fig3 "The SSA absolute uncertainty varies somewhat during the day, but it is typically about 0.03, just as in (McComiskey et al. 2008)".

**9. P16960 Line 3. "our 2006 study" should refer to this manuscript. It sounds like**

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**there is some other body of 2006 work.** The following was used as a replacement for "... our 2006 study..." In the current study...

**10. P16960 Line 10. Uncertainty for the mass scattering efficiency? I think it is necessary to put uncertainties on all derived parameters to get a sense of the measurement uncertainty relative to the absolute change you are reporting (i.e. for SSA and mass scattering efficiency).** Done

**11. Figure 7. The sigma values have a lot of variation and a significant drop at about hour 12 for 2 hours. Is this drop real? Is there a change in meteorology that accounts for a different air mass at that point or are we looking at measurement variability?** The data reported for the variation of the value of sigma are averages of 20 measurements carried out in different days (at the same hour of the day). Considering the uncertainties involved, the significant variation observed in the sigma values cannot be positively charged to a change in meteorology.

**12. P16960 Line 21. An MAC number of 8.8 m2/g was derived from Las Vegas data. Does this represent the data from Mexico City? I assume it indicates some form of processing if an MAC for fresh soot is 7.5 m2/g?** The Las Vegas data represented fresh soot also.

**13. P16961. I like the analysis of the fraction of scattering and mass from secondary processes. However, as the authors point out there is some uncertainty here. I am curious as to just how much there is. When all of the uncertainties are propagated through I feel that this could be rather large. This does not take away from the analysis however it must be presented with necessary uncertainty. I am also not 100% clear on the definitions for this analysis. The background aerosol prior to initiation of photochemical processes will dictate the fractions of primary vs secondary. Do you suspect that the conditions you sampled under are representative of the primary background? You assume that secondary contribution only results from a single photochemical cycle right? There are a number**

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**of variables that will determine your background. Primary emissions vs second-day carry over vs rain out vs differences in boundary layer dynamics.** We do not assume that the background is only determined by primary aerosol. Actually we stress the importance of secondary aerosol carried over from the previous day or which may be part of the regional background advected into the city, and which represents a significant fraction of the measured mass (page 16963, line 4). What we assume is that the abrupt increasing at sunrise from the baseline in the fraction of aerosol scattering and mass is dominated by photochemically generated secondary aerosol. The observations of aerosol mass and optics are useful for models that couple meteorology, chemistry, and optics.

**14. Figure 9. The percentage difference between the two goes from +15% to -10%. This is really a change of -25% right?** On page 16963, put before "The OOA diurnal variation is also displayed..." The following was added at the indicated place, page 16963 line 19: "The percentage difference between PAS and aethalometer instruments has a daily variation of about 25% in total (from a maximum of about +15% to a minimum of about -10%)".

## 2nd Referee Comments

**1. The role of BL dilution. It is easy to understand how BL dilution -the entrainment of clean air into the polluted BL- will change Babs and Bsca. However, it is hard for me to understand (from this paper) how BL dilution will change the SSA, which is an intrinsic property of individual aerosol particles, as it does not depend on aerosol concentration. BL dilution is mentioned several times in the paper; for example, BL dilution is implied in altering the SSA on page 16959, line 13. Maybe I am reading too much into this section, but if I am not, then more clarification on the role of BL dilution is necessary. Also, see page 16958, line 24. I do not understand the statement that "the BL rise in the morning does not perturb the observations"; surely it must perturb Babs and Bsca.** As the referee points out, the SSA of an individual aerosol particle is an intrinsic property of it, and

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thus, it cannot change with BL dilution. However, BL dilution may change the proportion of the different kind of aerosols and as a consequence it may modify the average SSA. We are assuming that BL height development and ventilation dilutes aerosol from primary sources as well as photochemically generated secondary aerosols, since the latter are being produced at larger rates than BC is emitted once the BL starts to grow during daylight hours. It is likely that secondary aerosols are generated throughout the whole volume of the BL, while primary emissions are generated only at the surface by sources. Since black carbon is more a light absorber than a light scatterer and has its source only in primary emissions, these processes would lead to a rise in the average SSA.

**2. The paper only considers the fine mode aerosol. AERONET observations (e.g., Dubovik et al., 2002, Journal of the Atmospheric Sciences, 59, 590-608) taken at a site in Mexico City indicate a significant amount of the aerosol volume (mass) in the coarse mode (diameter > 2.5 um). My guess is that there will be too few particles in the coarse mode at the T0 site to influence the conclusions expressed in the paper. Is there anything the authors might do the reassure the reader that the coarse mode can be neglected? Maybe all that is possible is a flat statement that there is too little information about the coarse mode to consider it in this paper (and in any event, the S8201 effect of the coarse mode is probably small).** There can indeed be a significant concentration of coarse aerosols (between PM2.5 and PM10) during dry periods due to the presence of dust e.g. see (Querol et al. 2008) and (Aiken et al. 2008), but these particles are not sampled by any of our instruments due to the size cuts of the inlets used. This was already discussed in our ACPD version (P16957 L28-29 to P16958 L4) with the following text: "It was estimated that the sampling inlets on the instrumentation resulted in an effective size cut of PM1 (i.e. one micron). The fraction of the PM2.5 mass between PM1 and PM2.5 in Mexico City is typically small (Querol et al. 2008; Salcedo et al. 2006), so slight differences in the detailed size cuts of the different instruments should only lead to small differences on the aerosols sampled".

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**3. Eqn. (1). It seems to me that the numerator of Eqn. (3) is expressed exactly as Bsca(Bsca,p/Babs)*Babs, where Bsca,p is the scattering of the primary aerosol. I am concerned how well the expression SSAp/(1 - SSAp) approximates the Bscat,p/Babs (where SSAp is the SSA attributed to primary sources). In other words, to what extent is Eqn. (1) an approximation? I do not think this is a major issue but a little clarification would be useful.** The main approximation in equation (1) is that secondary aerosol has a very strong influence on aerosol scattering, and a comparatively small influence on aerosol light absorption (Recent data from the project MEGALOPI in China suggests this as well). The approximation in equation (1) is commensurate with the notion that aerosol mass concentration is closely tied to aerosol light scattering in Mexico City as illustrated in Fig 5.

**Technical comments:**

**1. Almost all papers dealing with the aethalometer seem to promote different spellings for this instrument. This paper is no exception, and in the paper "aethelometer" is spelled in three different ways. I think the correct spelling is "aethelometer", or so I hope...** "Aethalometer" is now exclusively used.

**2. Page 16953, line 5: I assume the emission values are daily values? Or monthly?** "...generated yearly" was added to the text on this line.

**3. The paper should spell out the time averaging interval for the optical properties. Maybe it is mentioned in the paper and I did not see it.** All the reported optical data are averages of the measured values over 20 days in order to average over typical meteorological events. The introduction (page 16953 line 27) was modified to make this clear: These flow patterns give rise to pollutant concentrations that can vary markedly from day to day; however, it is the purpose of this paper to seek an understanding of the average diurnal behavior of aerosol concentrations and optical properties during the month of March, 2006.

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 16951, 2008.