**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

Interactive comment on "Mexico City aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0) – Part 1: Fine particle composition and organic source apportionment" *by* A. C. Aiken et al.

A. C. Aiken et al.

allison.aiken@colorado.edu

Received and published: 7 August 2009

We thank Referee #1 for his/her support for publication in ACP and useful comments which helped us improve the manuscript.

(R1.1) General Comments:

Page 8384, lines 21-24: The authors state that a CE of 0.5 was used for the non-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

refractory data obtained with the AMS and that this is verified with the intercomparisons presented later in the paper. The AMS CE is not explicitly addressed in the text describing the inter-comparison plots (Fig. S3) and is only mentioned later in the manuscript on p. 8402 in connection with the CMB-OMM, PMF-AMS comparison. Obviously inter-comparing measurements in a complex urban environment like Mexico City is extremely challenging. The authors do a good job describing the various considerations necessary (mainly differences in size cut-offs) to effectively compare measurements obtained from different instruments but fail to tie the observations directly back to a verification of the AMS CE. The authors are correct to point out the fact that none of the instruments are a 'true' PM1 mass measurement. One striking feature in Fig. S3 is the difference between the SMPS mass and AMS (with CE of 0.5 applied to NR) + refractory mass as displayed in (b), (f), and (g). The plots show that the AMS+refractory is _ 32% higher than the SMPS mass. As stated by the authors, the maximum size cut of the SMPS (as operated at T0) was 436 nm (mobility diameter) or _ 654 nm dva [assuming a sphere with a density of 1.5 (Fig. S2)]. In Figure S11, the dm axis for the SMPS measurement is converted to dva using a bulk composition density and assuming spherical particles. In this plot the 'missing' mass is more clearly illustrated, but Figure S11 is not used for this purpose, instead it is only used to compare 2003 and 2006 size distributions. I think that a more detailed discussion of Figure S3 (b) is warranted in connection with the application/confirmation of the 0.5 CE used across the NR AMS data. For example, the authors could color S3 (b) by hour of day to show that, when the size distribution of particles is smaller (early morning rush hour) the mass measurements compare more favorably. This is shown on average in Fig S3 (f) with relatively higher SMPS/AMS+R ratios in the overnight and early morning. Overall, I think that the manuscript would benefit from a more explicit 'verification' of the 0.5 CE in the section describing Fig S3.

We agree with the reviewer that the wording concerning "verification" of CE (or more properly Eb, the bounce-related fraction of the collection efficiency, see Huffman et al., AS&T 2005) was perhaps too strong in the ACPD manuscript. In response to this

comment we have changed the text on P8384 L21-24 to:

"A collection efficiency (CE) of 0.5 was used for all data, based on the observed composition and the composition-CE relationships observed in previous campaigns (Canagaratna et al., 2007 and references therein), consistent with other recent studies in Mexico City and during MILAGRO (Salcedo et al., 2006, 2007; DeCarlo et al., 2008; Kleinman et al., 2008), and also consistent with the intercomparisons presented below."

Unfortunately the collocated measurements available at T0 do not allow for a more detailed analysis of CE than what is already included in the ACPD manuscript. Especially the lack of PM1 speciated measurements of sulfate, nitrate, ammonium, and chloride (e.g. from a PILS-IC system) and of OC (from e.g. a 1-hr Sunset EC/OC analyzer) limits the information which can be extracted from the intercomparisons for this dataset. As already described in the ACPD manuscript, none of the instruments available for intercomparison covers the same size range of the AMS, or is a true mass measurement.

The reviewer seems to favor the SMPS over other instruments. On that topic, we note that the average density is Fig. S-2 is ∼1.42 g cm-3, which translates the 436 nm (dm) of the SMPS into 619 nm (and not 654 nm as estimated by the reviewer). We also note that we are not comparing the SMPS with the AMS only, but with the AMS + refractory components (BC, soil, metals) and thus the comparison will also be affected by inaccuracies in the refractory species measurements and not just the AMS. The soil and metal contributions are only available with 6 hr time resolution which degrades the scatter plots to some extent. This is one reason why speciated comparisons of the species that the AMS can measure are generally preferred for verifying CE. The AMS has ∼100% transmission until 700 nm dva and some transmission up to slightly above a micron, the BC measurement extends to 2 microns, and the soil measurement extends to 1.15 microns, so the fact that the mass estimated from the SMPS is lower than the AMS + refractory mass is to be expected. We already performed some of

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

the time-dependent comparisons suggested by the reviewer, but they did not provide additional information over what we already discuss in the manuscript, so we decided not to include them so as to not make the paper even longer. We note that during the early morning the primary particles are indeed smaller in dva space, but they are actually larger than their volume-equivalent diameter in the mobility diameter space measured by the SMPS (DeCarlo et al., AS&T 2004; Slowik et al., AS&T 2004), and thus even some of those particles may spill out of the size range of the SMPS.

We also compare the AMS with the PM1 estimated from a Grimm OPC-based instrument, which unlike the SMPS, was calibrated daily with a real PM1 mass measurement. The Grimm data shows better agreement with the AMS + refractory mass. The difference in the SMPS vs Grimm diurnal cycles and the fact that the other measurements do not correlate among themselves any better than with the AMS (as already described in the ACPD paper and now also shown graphically on the new Figure S-3(h)) also limits the trust that we can put into any one of them.

Finally, it has been our repeated experience that when two or more SMPSs are operated at the same site, they rarely agree better than 20% for the estimated particle volume due to various instrumental reasons, and thus we are hesitant to derive too strong conclusions from comparisons with a single SMPS. This is consistent with literature reports from groups specialized in SMPS measurements, e.g. Birmilli et al. (AS&T 2007) from the Wiedensohler group which is supplying research-grade SMPSs to many researchers around the world state: "The intercomparison experiments revealed deviations between the two SMPS systems by approximately 30% in total particle number concentration, and by ca. 5% in mobility mean diameter. These differences were relatively stable over the entire 23 days of all experiments, and were assumed to be caused by systematic differences in the DMA transfer functions, CPC counting efficiencies, and DMA high voltages. Following our experience made during several extensive SMPS intercomparison workshops, such differences are not unusual, even between nominally identical SMPS systems. Con-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

sequently, we monitored these effects throughout all experiments and accounted for them during the evaluation of the final mobility distributions." Intercomparisons of SMPS systems are still an active area of research precisely for this reason (see e.g. http://venda.uku.fi/research/aerosol/bacci/2nd_meeting/PDF/Massling.pdf). We note that errors in sizing are cubed when converting to particle volume, and an error of 5% in sizing such as that described by Birmilli would result in an error of $1.05^3 - 1 = 16\%$ in apparent volume. Reported uncertainties for instruments that estimate particle volume from measurements of number distributions are rarely below 30% (C. Brock, NOAA, pers. comm.).

Given these considerations, we have added the following text to the intercomparison section to address the reviewer's comments (including moving Figure S-11 to S-4):

"In Fig S-3, we show that the AMS CE of 0.5 estimated from the measured composition results in consistent comparisons with all other $\sim$PM1 measurements. The largest discrepancy is with the SMPS and is most likely due to the lower size cut of that instrument, as is mentioned above. Fig S-4 shows the comparison of the measured size distributions from the AMS and SMPS. To explore the possible causes of the observed differences, different CEs were applied sequentially for each organic PMF-AMS component and also the inorganic components. There was not a clear improvement in the comparison with the other co-located $\sim$PM1 measurements for the various perturbations of CE."

Regarding the comments about p. 8402, RIEs are individually applied for each AMS species and are not part of CE (i.e. they are accounted for separately in the quantification procedure, see e.g. Jimenez et al., JGR, 2003). A single RIE of 1.4 was used for all organic species based on laboratory calibrations with different types of organic species (Alfarra et al., Atm. Env. 2004).

On the other hand Eb is included in the CE, and an average Eb is thought to dominate CE. We stated:

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

"Finally, it is possible that the different PMF-AMS OA components could have slightly different relative ionization efficiencies (RIEs), and/or bounce-related collection efficiencies (Eb) to the extent that they are present in externally mixed particles. Both of these effects would lead to a positive bias of the chemically-reduced and more volatile components (HOA, BBOA, LOA) and a negative bias against OOA (Jimenez et al., 2003; Huffman et al., 2005, 2009; Zhang et al., 2005b)."

We have added the following text to clarify these issues:

"We experimented with different Eb*RIE for the different OA components retrieved by PMF, but the comparisons with other measurements (Table S-1 and Fig. S-2, S-3, and S-11) were not significantly improved. Thus, any variations in the product Eb*RIE for the different organic species are estimated to be small and not the main reason for the differences observed in some of the intercomparisons. This is consistent with the analysis by Docherty et al. (2009) for an AMS dataset in Riverside, CA, who estimate that the differences in Eb*RIE between different PMF-AMS OA components are less than 15%."

Minor Comments:

(R1.2) page. 8381, lines. 19-26: The authors indicate 6 references that show the importance of SOA as a fraction of total PM and then provide examples of how 5 of the 6 references apply. Either include an example of how the DeCarlo reference applies or don't include the DeCarlo reference in the list.

In fact two of the references were not described further in the remainder of the paragraph (Stone et al. 2008 and DeCarlo et al. 2008). We have added the following to the text to address this point:

"DeCarlo et al. (2008) report an OA/ΔCO for urban air that is much greater than that of primary emissions and a rapid increase in the O/C ratio of OA with photochemical age, both indicating strong SOA formation from MCMA emissions. Based on comparisons

with water-soluble OC, Stone et al. (2008) attribute the unapportioned OC from CMB-OMM as secondary OC for MCMA, resulting in 39% on average of the OC (and thus a larger fraction of the OA) being secondary at T0."

(R1.3) Page 8384, line 1: Including the residence time (16s) in the drier seems unnecessarily complicated and is confusing. Is the 0.6 Lpm that goes through the drier then sent to your instruments? Perhaps you could reformulate the sentence to clarify this.

This was a misunderstanding by the reviewer. The residence time mentioned is the total residence time within the sampling lines prior to the instrument, which includes a nafion drier. The sentence is needed to document the inlet used and indicate that the residence time is short enough to not result in any large loss of particles. The sentence has been rewritten for clarification as follows:

"The total inlet residence time was 16s under laminar flow. A nafion drier (Perma-Pure, Toms River, NJ) was used to dry the air prior to sampling with the AMS."

(R1.4) Page 8390, line 26-27: "when nitrate is also higher at the ground (Fig.2)" I believe that the authors meant to say when nitrate is 'lower' at the ground given the temporal trend in nitrate that they are referencing in comparison to the nitrate measured aloft.

The sentence is correct as written, as the flights were conducted in the afternoon (noon-6 pm) and the average nitrate during that period was higher (4.5 ug am-3 vs 3.5 ug am-3; see also Fig. 2d). To clarify this point we have rewritten this text as: "when nitrate is also higher at the ground compared to the 24-hr average (Fig.2)"

(R1.5) Page 8392, line 15-16: The sentence - "2/3 of organic oxygen is part of the OOA component and 1/3 of the nitrogen from the LOA component." Is confusing and needs to be re-written. You should try and avoid starting sentences with numbers as well.

We have changed the sentence (and also the previous one that started with a number too) to read:

"On average, 61% of the OA mass is from carbon, 29% from oxygen, 9% from hydrogen, and 1% from nitrogen. Of the organic oxygen, 2/3 of it is found within the OOA component, while 1/3 of the organic nitrogen is within the LOA component."

(R1.6) Page 8393, line 3-4: ". . ... and possibly also some of lightly oxidized SOA. . .." Get rid of the 'of'

This has been fixed.

References:

Alfarra, M.R., H. Coe, J.D. Allan, K.N. Bower, H. Boudries, M.R. Canagaratna, J.L. Jimenez, J.T. Jayne, A. Garforth, S.M. Li, and D.R. Worsnop, Characterization of Urban and Rural Organic Aerosols In the Lower Fraser Valley Using Two Aerodyne Particulate Mass Spectrometers, Atmospheric Environment, 38: 5745–5758, 2004.

Birmili, W., K. Stophkuchen, M. Hermann, A. Wiedensohler, and J. Heintzernberg. Particle Penetration Through a 300 m Inlet Pipe for Sampling Atmospheric Aerosols from a Tall Meteorological Tower. Aerosol Science and Technology, 41, 811-817, 2007.

DeCarlo, P., Slowik, J.G., Worsnop, D.R., Davidovits, P., and Jimenez, J.L. Particle Morphology and Density Characterization by Combined Mobility and Aerodynamic Diameter Measurements. Part 1: Theory. Aerosol Science and Technology, 38: 1185–1205, 2004. DOI: 10.1080/027868290903907.

P.F. DeCarlo, E.J. Dunlea, J.R. Kimmel, A.C. Aiken, D. Sueper, J. Crounse, P.O. Wennberg, L. Emmons, Y. Shinozuka, A. Clarke, J. Zhou, J. Tomlinson, D. Collins, D. Knapp, A. Weinheimer, T. Campos, and J.L. Jimenez. Fast airborne aerosol size and chemistry measurements above Mexico City and Central Mexico during the MILAGRO campaign. Atmospheric Chemistry and Physics, 8, 4027-4048, 2008.

K.D. Docherty, A.C. Aiken, J.H. Huffman et al., Fine Particle Composition in the Inland Los Angeles Basin during the 2005 Study of Organic Aerosols in Riverside (SOAR-1), ACPD, in prep., 2009.

J. Alex Huffman, John T. Jayne, Frank Drewnick, Allison C. Aiken, Timothy Onasch, Douglas R. Worsnop, and Jose L. Jimenez. Design, Modeling, Optimization, and Experimental Tests of a Particle Beam Width Probe for the Aerodyne Aerosol Mass Spectrometer. Aerosol Science and Technology, 39(12): 1143-1163, 2005, doi: 10.1080/02786820500423782.

J.A. Huffman, K.S. Docherty, C. Mohr, M.J. Cubison, I.M. Ulbrich, P.J. Ziemann, T.B. Onasch, and J.L. Jimenez. Chemically-Resolved Volatility Measurements of Organic Aerosol from Different Sources. Environmental Science and Technology, 43, 5351–5357, 2009. doi: 10.1021/es803539d.

Jimenez, J.L., Jayne, J.T., Shi, Q., Kolb, C.E., Worsnop, D.R., Yourshaw, I., Seinfeld, J.H., Flagan, R.C., Zhang, X., Smith, K.A., Morris, J., and Davidovits, P. Ambient Aerosol Sampling with an Aerosol Mass Spectrometer. Journal of Geophysical Research - Atmospheres,108(D7), 8425, doi:10.1029/2001JD001213, 2003.

Kleinman, L. I., Springston, S. R., Daum, P. H., Lee, Y.-N., Nunnermacker, L. J., Senum, G. I., Wang, J., Weinstein-Lloyd, J., Alexander, M. L., Hubbe, J., Ortega, J., Canagaratna, M. R., and Jayne, J.: The time evolution of aerosol composition over the Mexico City plateau, Atmos. Chem. Phys., 8, 1559-1575, 2008.

D. Salcedo, T. B. Onasch, K. Dzepina, M. R. Canagaratna, Q. Zhang, J.A. Huffman, P. F. DeCarlo, J. T. Jayne, P. Mortimer, D. R. Worsnop, C. E. Kolb, K. S. Johnson, B. Zuberi, L. C. Marr, R. Volkamer, L. T. Molina, M. J. Molina, B. Cardenas, R. M. Bernabé, C. Márquez, J. S. Gaffney, N. A. Marley, A. Laskin, V. Shutthanandan, Y. Xie, W. Brune, R. Lesher, T. Shirley, and J. L. Jimenez. Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass Spectrometry: results from the CENICA Supersite. Atmospheric Chemistry and Physics, 6, 925-946, 2006.

D. Salcedo, T. B. Onasch, M. R. Canagaratna, K. Dzepina, J. A. Huffman, J. T. Jayne, D. R. Worsnop, C. E. Kolb, S. Weimer, F. Drewnick, J. D. Allan, A. E. Delia and J. L. Jimenez. Technical note: use of a beam width probe in an Aerosol Mass Spectrometer

to monitor particle collection efficiency in the field. Atmospheric Chemistry and Physics, 7, 549-556, 2007.

Slowik, J.G., Stainken, K., Davidovits, P., Williams, L.R., Jayne, J.T., Kolb, C.E., Worsnop, D.R., Rudich, Y., DeCarlo, P., and Jimenez, J.L. Particle Morphology and Density Characterization by Combined Mobility and Aerodynamic Diameter Measurements. Part 2: Application to Combustion Generated Soot Particles as a Function of Fuel Equivalence Ratio. Aerosol Science and Technology, 38: 1206–1222, 2004. DOI: 10.1080/027868290903916.

Stone, E. A., Snyder, D. C., Sheesley, R. J., Sullivan, A. P., Weber, R. J., and Schauer, J. J.: Source apportionment of fine organic aerosol in Mexico City during the MILAGRO experiment 2006, Atmos. Chem. Phys., 8, 1249-1259, 2008.

Zhang, Q., Worsnop, D. R., Canagaratna, M. R., and Jimenez, J. L.: Hydrocarbon-like and oxygenated organic aerosols in Pittsburgh: insights into sources and processes of organic aerosols, Atmos. Chem. Phys., 5, 3289-3311, 2005c.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 8377, 2009.