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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurement of ambient aerosols in northern Mexico City by single particle mass spectrometry" *by* R. C. Moffet et al.

R. Moffet

rmoffet@ucsd.edu

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Size distributions of primary BB particles typically show a peak around 200-400 nm (Clarke et al., 2007; Dubovik et al., 2002). Preliminary results from fire plumes around Mexico City sampled from the US Forest Service Twin Otter show a peak of the volume distribution at _230 nm (from optical counter data, Darin Toohey, U. Colorado, Pers. Comm.). If these particles grow a factor of _2 in size to the peak of _700 nm observed in the ATOFMS in this study, only _1/8 of their mass would be the original mass emitted from BB, and _7/8 would be the mass of other species that have condensed (or coagulated with) these particles. (Here we are neglecting the differences between the various diameters as they do not affect the main point). Some of the condensate may be secondary species from BB precursors but based on previous studies (e.g. the

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growth of PM/CO ratios downwind of BB) this is unlikely to increase the particle mass by more than a factor of 2.

RESPONSE: As mentioned and described in the revised manuscript, the ATOFMS distribution for the number fraction peaks at ∼300 nm. Also, the size of 230 nm referenced above is for aircraft *optical* size data of all ambient particles in a biomass/biofuel plume sampled at a different altitude and location. We question the relevance of this optical size distribution from Toohey et al. to our paper, but we look forward to seeing the published results with more pertinent information so we can better understand details regarding its acquisition. However, there are many published references in the literature that show that the peak of the biomass/biofuel mass median diameter (MMD) varies from 250-400 nm [*Reid et al.*, 2005; *Subramanian et al.*, 2007]

The revised version of the manuscript now segregates the aged versus fresh biomass particles based on the nitrate ion intensities which serve as a proxy for the degree of aging. These two particle types impacted T0 at different times of the day under different transport (meteorological) conditions. The size distribution of aged versus fresh biomass particles can be used to estimate a size shift for fresh versus aged biomass particles of 50 nm (300 vs. 350 nm). This shift corresponds to a volume increase of 1.6 which comes close to literature reports of a 1.8 volume increase for biomass/biofuel particles that have aged between 1-3 days by Reid, et al. [*Reid et al.*, 2005] Note that this size shift includes ammonium, nitrate, and water in addition to SOA. This is now described in the revised version of the manuscript.

If it is stated that "biomass particles dominate" most readers are going to understand that the mass of those particles indeed originated from BB, when a more accurate description would be "a large fraction of the particles detected contain at least a small mass fraction originating from BB" or something along these lines. Precision in the language and conclusions is important here and thus we encourage the authors to use more precise language throughout the paper in describing their results.

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RESPONSE: The revised manuscript clearly states that biomass/biofuel burning particles represent a larger number fraction of the submicron particles (180 to 1000 nm) in Mexico City than OC particles from other sources. As stated, the designation of number fraction is clear and consistent in the revised version of the manuscript. Also, as addressed above, the core size of fresh biomass/biofuel burning particles was large and thus biomass burning aerosols most likely represented a sizeable portion of the mass. It is not surprising the core size of biomass/biofuel burning particles is relatively large compared to other primary sources such as vehicles, given the inefficient combustion conditions (especially compared to vehicle engine emissions).

Alternatively, if data such as the "mixing matrix" in Fig. 4 can be used to separately quantify the mass of primary BB particles and of the secondary species that have condensed on them, this would be unique and very useful information.

RESPONSE: As discussed above, we now include an estimate of the fraction of the biomass core based on measured ATOFMS size distributions of fresh and aged biomass particles. More details on biomass aging will be included in a future paper focused on biomass/biofuel burning particles in Mexico City during MILAGRO. This paper will address the many forms of biomass/biofuel burning and how ATOFMS single particle signatures can be used to distinguish between refuse burning, cooking, incineration, and biomass/biofuel burning aerosols in Mexico City.

Another possibility is that perhaps some misclassification occurred with particles of other types being categorized as BB. E.g. perhaps C3H3+ was misidentified as K+ for some particles (as mentioned on page 6428). Or perhaps some dust types containing K were classified as BB (e.g. the concentration field analyses for "biomass" and "NaK" particle types in Fig. 10 and 11 are relatively similar). The authors may be able to rule out this hypothesis, but we suggest that this is addressed in more detail in the revised manuscript.

RESPONSE: We have published results from a number of ATOFMS studies, including

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lab studies of organic particle standards and biomass/biofuel burning source characterization studies. In these studies, we determined an intense mass spectral peak at m/z 39 is indicative of K^+ [*Guazzotti et al.*, 2003b; *Hughes et al.*, 1999; *Qin and Prather*, 2006] Misidentifying C_3H_3 as K is unlikely as there is no known organic molecule that will fragment to give a dominant organic ion peak at m/z 39 with the K^+ isotope at m/z 41 in the correct proportion. In other locations where biomass/biofuel burning was not a dominant source, the peak at m/z 39 is not as prominent in either the intensity or the overall number of particles detected. The peak at m/z 39 occurs in the majority of the submicron particles in the Mexico City dataset, further supporting biomass/biofuel burning as a significant source of aerosols at T0. We have also published a number of papers that show how single particle mass spectral signatures can be used to distinguish between K in dust and biomass/biofuel burning; it is highly unlikely dust particles were incorrectly classified as biomass/biofuel burning [*Arimoto et al.*, 2006; *Qin and Prather*, 2006; *Sullivan et al.*, 2007]

This comparison highlights the fact that the statements made from ATOFMS data in this paper concern mostly the upper end of the accumulation mode and that there is very little information in this paper for particles below 400 nm, where most of the submicron mass is. Thus it is possible that BB particles in the reported ATOFMS size range have a different diurnal cycle than over the total submicron size distribution.

RESPONSE: As stated, the reason for the size shift to larger sizes was due to the APS scaling and not the "ATOFMS data". We now use ATOFMS data directly in the revised version of the paper. In fact, ATOFMS detected particles down to 180 nm during MILAGRO (lower size limit added to revised version of paper). As shown in Fig. 6a and 7 in the revised manuscript, the time series for aged and fresh biomass/biofuel burning particles peak at different times. ATOFMS begins to detect less aged biomass/biofuel burning particles which begin to increase at 11 am, when the winds shift and begin to come from the south where the fires were located, peaking in the afternoons most days of the study. The nitrate/aged biomass/biofuel burning particles peak each day

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when nitrate mass concentrations (and ozone) peak (10-12 am), suggesting photochemical formation of HNO_3 followed by deposition of nitric acid and ammonium on the biomass/biofuel burning particle cores.

However it may also be due to the fact that the ATOFMS concentrations have been scaled to those from an APS instrument. The APS has very limited size resolution below 800 nm and also reduced counting efficiency. Also, our limited experience with the APS indicates that this instrument can, at times, be unreliable under field conditions.

RESPONSE: Yes, we encountered this in this study. However, it should be noted we have used APS data in many other studies (20+) and have never encountered this type of problem with one of our own APS instruments before.

Thus we suggest that the APS distributions are compared to those from the LASAIR (with appropriate assumptions about density etc., see below) to gain further confidence on this scaling. Comparing with SMPS distributions is also possible, although it is a trickier proposition due to the diverging influences of particle shape and density on mobility vs. aerodynamic diameters [DeCarlo et al., 2004].

RESPONSE: Since we changed the size distributions to percentages in the revised paper, this comment is no longer applicable.

In our opinion the complexities of the ATOFMS detection process and quantification procedures are not explained in sufficient detail in the paper, and the uncertainties in the mass concentrations and size distributions presented are not reported in the manuscript.

RESPONSE: This represents an opinion that was not expressed by either of the reviewers of the paper. As it stands, the current paper shows number fractions and thus does not include any "complexities" or major assumptions. Details are given on how the main particle types are derived using ART-2a. We have published many papers on these topics which are cited as appropriate in the revised manuscript. Given the

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current length (and focus) of the manuscript, we chose not to go into them again in this paper.

Thus the total distribution has to be scaled to some "true" ambient number concentration at that size measured by another instrument (the APS in this paper), with a scaling function that changes about three orders of magnitude over a decade of particle size (Fig. 2 of Allen et al., 2000).

RESPONSE: In fact, the ATOFMS size distribution does not "have to be scaled". The revised version of the manuscript shows size and time series data as the fraction of number/percentage and thus requires no assumptions or scaling.

An important subpoint concerns the implicit assumption that particles of different types and compositions are detected with the same efficiency with the ATOFMS. An important effect which is not mentioned in this paper is the possibility that particles with non-spherical shapes may have lower detection efficiencies. Since physical shape and particle source are likely correlated (especially for primary particles), this could lead to systematic underestimation of non-spherical particle types. This effect is due to the poorer focusing experienced by non-spherical particles in aerodynamic devices, compared to spherical particles of the same size, and has been documented theoretically and experimentally [Liu et al., 1995a, 1995b; Jayne et al., 2000; Huffman et al., 2005; Murphy, 2007; Zelenyuk et al., 2006].

RESPONSE: The references cited above all use an aerodynamic lens inlet. As stated, this inlet has been shown to dehydrate the particles, increasing the shape factor bias. In fact, during MILAGRO, the AMS used this inlet, but the ATOFMS used a different inlet, a standard converging nozzle that has been described in detail in many previous publications. The key point is the ATOFMS inlet used in this study does not remove water and other secondary species from the particles. When more water and secondary species are left on the particles, the particles tend to be more spherical. The issues of particles diverging in the beam from this inlet are discussed in another paper by our

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group [*Moffet et al.*, 2007]. This divergence mainly affects the detection of soot (which comes from diesels, cars, and biomass) in the smallest ($<$0.5 micron) sizes, and larger super-micron irregularly shaped dust particles.

The latter paper, which describes a laser-ablation instrument states: "Just to serve as an example, we observed that overall detection efficiency of ammonium nitrate particles decreases by a factor of 10 upon crystallization, a decrease entirely due to particle shape change."

RESPONSE: This paper describes a different laser ablation instrument which uses a different (aerodynamic focusing) inlet.

Based on that potential effect, one possibility is that perhaps some fresh BB particles are non-spherical [e.g. Schneider et al., 2006] and their detection efficiency increases during the day as they are coated by secondary species and they become more spherical and better focused aerodynamically. This could partially explain the increased detection of BB particles by the ATOFMS in the afternoons.

RESPONSE: As described above, and in the revised version of the paper, ATOFMS detects and distinguishes between both fresh and aged biomass/biofuel burning particles. Notably during MILAGRO, ATOFMS detected (by *number*) more fresh (i.e. non-spherical) than aged biomass/biofuel burning particles at all times of the day and night, but represented the largest *fraction* in the afternoon. The fraction of the aged biomass/biofuel types tracked the nitrate and ammonium mass concentrations, implying a chemical, not a physical, process is dictating the relative abundance of this particle type. We describe the optical properties of biomass/biofuel burning particles detected in Mexico City in another paper [*Moffet et al.*, 2007].

The recent review by Dan Murphy [2007] entitled "The Design of Single Particle Laser Mass Spectrometers" states in its abstract that "Systematic bias against non-spherical particles probably exceeds a factor of 2 for all instruments."

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RESPONSE: The use of the word "probably" indicates this is speculation based, most likely, on results from aerodynamic inlets which differ significantly from the inlet used this study. This bias would occur for all mass spectrometers including the AMS so it is doubtful this would explain the discrepancy between the AMS and ATOFMS alluded to by Jimenez/DeCarlo.

Finally, in the past several studies have documented or discussed possible "chemical matrix effects" in laser ablation instruments in general and the ATOFMS in particular [e.g. Gross et al., 2000; Wenzel et al., 2003; Murphy, 2007; Hinz and Spengler 2007]. For example particles containing sulfate are detected with much reduced efficiency in some instruments, and species such as Na and K are detected with very high efficiency. It is stated here (page 6418) that the fact that the percentages of detected particles were relatively constant indicates that chemical matrix effects did not play a major role in this study. In our opinion these overall statistics only provide weak evidence on the absence of matrix effects, given the complexity of the size and composition distributions of ambient particles in MC. Matrix effects may indeed not be important here, especially for very complex and internally mixed particles, but additional evidence would be useful.

RESPONSE: The subject of matrix effects has been addressed by our own group as well as others. Matrix effects exist for all mass spectrometers (including the AMS), but have been discussed in the literature mostly by the single particle mass spectrometry community. As discussed, AMS calibration studies involving ammonium nitrate are done in the lab, but careful studies of how ionization efficiencies and response factors change in the AMS for different species in real ambient aerosols have not been reported to our knowledge. The lack of literature reports does not mean the mean these effects do not exist for the AMS. Previous studies by our group (i.e. Wenzel et al. cited by the commenter as well as in our APCD paper) have identified periods where matrix effects are playing a role by a marked decrease (or increase) in hit percentage. Such instances are well documented in the published literature. The hit % remained relatively constant during MILAGRO, providing strong evidence that matrix

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effects did not play a significant role in Mexico City. This is most likely because the complexity of the aerosol led to a relatively uniform absorption of the LDI laser for all particle types. Single particle LDI tends to have more issues with matrix effects in simplistic aerosols such as those made in the laboratory (i.e. pure ammonium sulfate) which are rarely detected in ground based ambient aerosols. Most of the time, ground based sub-micron tropospheric particles are complex mixtures containing absorbing carbonaceous species.

The ATOFMS mass reported here is obtained after scaling with the densities reported in page 6424. The reported density of 1.9 g/cm3 for carbonaceous particles appears quite high.

RESPONSE: As mentioned above, we no longer use densities to scale our data in the revised manuscript

Most of the mass in the submicron mode in MC is constituted of organics, ammonium sulfate (or bisulfate), and ammonium nitrate, with smaller amounts of black carbon and crustal species (Salcedo et al., 2006).

RESPONSE: Salcedo et al. reported results from a study in MC for a different year (2003) and sampling location (Cenica), using submicron non-refractory AMS data combined with other measurements (i.e. aethalometer, Dustrak, PIXE) to deduce the overall chemical composition of $PM_{2.5}$. The AMS does not detect refractory species such as those from industrial sources (soot, metals, salts), which, as measured by the ATOFMS during MILAGRO, can constitute a significant fraction of the submicron particle mode during short time periods mainly at night and in the early morning hours. It is possible that in 2003 industrial ash particles could in fact have been apportioned as "soil". During 2003, “soil” contributions were estimated from elemental concentrations from PIXE analysis, using an ad-hoc formula with assumptions developed for the western U.S. that is routinely applied to the IMPROVE network data. Hence, there is most likely uncertainty in the apportionment of some of the inorganic material in 2003. This is an

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area where new measurements in 2006 such as the ATOFMS can hopefully provide complementary data to the AMS by measuring the refractory components directly and the associated variations in mixing state of the major particle types over the course of a day; refractory and other particle types are discussed in our revised paper.

Again it appears unlikely that such mixtures could have a density of 2.0 g/cm3.

RESPONSE: Since we are not using the scaling procedure in the revised manuscript, this comment has been addressed.

- P6416, line 5: we suggest also citing the recently published MCMA-2003 overview paper by Molina et al. (2007), which summarizes the observations from that campaign. This paper discusses BB in some detail as a potentially important source of fine PM in MC.

RESPONSE: Good suggestion–this has been added with more discussion on this topic in the revised manuscript. We had not seen this paper when writing our original paper as the ACP version of the Molina (2007) paper didn't come out on-line until after we submitted our original ACPD manuscript. Thus, our statements regarding the relatively low contribution from biomass burning aerosols in 2003 were based on the Salcedo (2006) publication.

To be continued in Part 3.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 6413, 2007.