Atmos. Chem. Phys. Discuss., 7, S3737–S3746, 2007
www.atmos-chem-phys-discuss.net/7/S3737/2007/

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.

J. Jimenez

jose.jimenez@colorado.edu

Received and published: 6 August 2007

Comment by J.L. Jimenez and P.F. DeCarlo on Moffet et al., ACPD 2007

This paper by Moffet et al. describes results from the deployment of an ATOFMS instrument at the T0 site in Mexico City (MC) during the MILAGRO 2006 field campaign. This is the first deployment of a single particle mass spectrometer to MC, which has resulted in a wealth of information not attainable with other techniques. Novel results include very rapid and size-resolved information on the mixing state of various species (including refractory species), and the identification of several industrial particle sources and dust types. Clearly, this is a very interesting paper and a very rich dataset that can probably continue to be analyzed for several years, by itself and in combination with data from other instruments.

Contribution of Biomass Burning to Fine PM during MILAGRO

Our comment mainly concerns some of the results reported here about the contribution of biomass burning (BB) to particle concentrations in MC, that appear to be in direct conflict with preliminary results of most other methods also deployed at T0 and at other sites around MC during MILAGRO. The abstract states that "biomass became the largest contributor to the accumulation mode mass from the late morning until early evening." This is repeated in the conclusions and in several places in the text, and in most places no caveats are given about the interpretation of that statement.

At the recent MILAGRO meeting in MC multiple pieces of evidence concerning the impact of BB to fine PM in the ground were presented. Most point towards a smaller impact than stated here, and with a different diurnal cycle with a peak in the morning and actually a minimum (rather than a maximum) in the afternoon. Although most of these results are not yet published, many are available from the authors and they will be published over the next year and thus we suggest that the authors take them into account while revising their paper.

A summary of some important evidence discussed at the meeting is:

- Acetonitrile is a VOC that is generally considered to be a good BB tracer. Preliminary results from acetonitrile measurements at several sites (e.g. J. de Gouw, NOAA, pers. comm.) indicate a maximum of acetonitrile in the morning around 6-8 am and a broad minimum in the afternoon between 11 am and 6 pm. Similar diurnal profiles are observed in; (a) m/z 60 (from levoglucosan and similar species) from the High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) from our group at T0 (Aiken, Ulbrich et al.); (b) BB organic aerosol derived from the application of PMF to the HR-ToF-AMS data; (c) K+ in PM1 from the HR-ToF-AMS (which is likely sensitive to the less refractory forms of K in BB PM, and not to the more refractory K in dust).

- In addition source apportionment results from the HR-ToF-AMS using PMF (Aiken, Ulbrich et al.) and from organic molecular markers (Stone et al., 2007) report con-

ACPD

7, S3737–S3746, 2007

centrations for BB PM which are significantly lower than those in Fig 7 (even after accounting for OM/OC and typical fractions of inorganics in BB PM). Finally a hybrid method (J. de Gouw, pers. comm..) at T1 also indicates that BB is not the largest contributor to fine organic PM at that location.

Most of the above measurements are still being analyzed and it is possible that the interpretation of the final data in publications by their respective groups may differ somewhat from that presented at the MILAGRO meeting. However we think it is unlikely that the conclusions of (a) maximum BB impact to fine PM in the morning, and (b) BB being a lower contributor at the ground than reported here, will change. For example traffic may make some contribution to acetonitrile, but according to the several VOC experts at the MILAGRO meeting this should be a small contribution and traffic is unlikely to dominate the diurnal cycle of this species in MC.

It is useful to note that a separate ACPD review which we did not have prior knowledge of (regarding another paper in this special issue which also discusses BB PM), basically summarizes the same evidence described above and draws the same conclusions (Comment on Yokelson et al. (2007) at http://www.cosis.net/copernicus/EGU/acpd/7/S2681/acpd-7-S2681.pdf).

There are several possibilities for the apparent discrepancy in the quantification of the contribution of BB discussed above. The discrepancy may be "apparent" in that all of the statements made are correct, but e.g. they apply to different particle size ranges. It is also possible that there are two different types of BB PM with very different compositions and diurnal cycles, but it would be useful if the authors could identify other non-ATOFMS tracers that support this hypothesis.

Below we list several possible reasons for the discrepancies between the biomass burning contributions deduced by this and other studies, that the authors may wish to discuss and clarify in the revision of their paper.

1. Methodology for identifying "BB particles" from ATOFMS data, and descrip-

ACPD
7, S3737–S3746, 2007

tion of the results

Due to the discrepancies mentioned above and to the importance of this topic, we suggest that the methodology for identifying BB particles is clarified. At present, this is described very briefly in 7 lines at the end of page 6420. The ATOFMS is very sensitive to K, and may classify as "BB particles" many for which only a small fraction of the mass is actually BB. 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 $\sim$230 nm (from optical counter data, Darin Toohey, U. Colorado, Pers. Comm.). If these particles grow a factor of $\sim$2 in size to the peak of $\sim$700 nm observed in the ATOFMS in this study, only $\sim$1/8 of their mass would be the original mass emitted from BB, and $\sim$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 growth of PM/CO ratios downwind of BB) this is unlikely to increase the particle mass by more than a factor of 2.

The possibility of classifying as "BB" particles which contain mass from other sources is mentioned in one paragraph of the present paper (page 6430). However, the potential magnitude of this correction is not given, and this caveat is not repeated in the abstract, conclusions, or other places in the paper where the conclusion about BB dominance is stated. It would be hard for a reader to miss the statements in the abstract and conclusions about this BB dominance, but it would be much easier to miss this one paragraph with the caveats. We suggest the authors include reference to this caveat in all places when the apparent dominance of BB is stated so that the reader is given all relevant information.

More fundamentally, these comments are related to the **explanation of the results of this study to a general scientific audience** which is not familiar with the complexities

ACPD

7, S3737–S3746, 2007

of the ATOFMS data. *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.

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.

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.

2. Differences in particle size ranges sampled by ATOFMS and other instruments

Some of the inconsistencies between the results of this and other studies may be due to the different sensitivities of different instruments to different particle size ranges. To make this point clear, we have posted a comparison of the size distribution measured during MCMA-2003 (Salcedo et al., 2006; which is very similar to those from 2006 at T0) at http://cires.colorado.edu/jimenez-group/SI/Moffet_Comment_Fig.pdf (Figure C-1; unfortunately ACPD does not allow the posting of figures in comments; note that the URL is case sensitive). Note that the relative size distribution from Salcedo et al. compared well with the relative size distribution from a collocated LASAIR optical particle counter (see Fig. 3 in that paper and associated discussion). The X-axes in

ACPD
7, S3737–S3746, 2007

EGU

Figure C-1 have been scaled so that particles of the same physical size would be at the same horizontal location in the slide (see below for details on aerodynamic diameters). 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 $\sim$ 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.

It is quite surprising to note, however, that even though the ATOFMS appears to be missing the majority of the submicron mode mass (Figure C-1), its average scaled mass concentration is larger than that at the nearby RAMA site (p. 6424). (Note that an instrument with a PM2.5 inlet such as in the RAMA network would sample particles between 1 and 2.5 microns with reduced efficiency due to the transmission curve of the impactor or cyclone. It is not clear whether this has been taken into account in the calculation of the ATOFMS PM2.5 scaled mass in this paper, and if not this could partially explain the surprisingly high ATOFMS average mass concentration).

To avoid confusion, we suggest that the definition of aerodynamic diameter used here is shown, as it affects the interpretation of the size distribution given here, as well as the distinction between 'submicron' and 'supermicron' particles. We assume that the diameter reported here is transition aerodynamic diameter (Dta) near atmospheric pressure, and not vacuum aerodynamic diameter (Dva) as in aerosol MS instruments that use low-pressure aerodynamic lenses [see DeCarlo et al., 2004 for details]. Dta near 1 micron will be almost the same as the continuum regime Da (Dca) and thus proportional to the square root of the particle density and not to the density. For the range of densities given on page 6424 of this paper, Dva is larger than Dca by 35-65% (approximating Dta as Dca in the continuum regime, and assuming spherical particles). For the average density of 1.4 g/cm3 calculated from the average PM2.5 composition (Table 2 of Salcedo et al., 2006), Dva is 18% larger than Dca.

Finally, one interesting detail is that the valley between the submicron and the super-

ACPD

7, S3737–S3746, 2007

micron mode is much deeper in the data of Salcedo et al. from either the LASAIR instrument or the AMS + BC + Dust (Figure C-1, and also Fig. 3 of Salcedo et al.) than in the Moffet et al. data. This may be a real difference, e.g. due to the higher prevalence of dust in the North of MC vs. the CENICA location in the South East. 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. A LASAIR OPC was operated by Laskin et al. at T0 during 2006, with a diluter to limit saturation of the instrument. 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].

3. Quantification of total mass concentrations from ATOFMS data

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. The ATOFMS detection process is *fundamentally* particle number-based. It sizes individual particles aerodynamically and determines their composition by bipolar mass spectrometry. As such the native data of the instrument are number distributions vs. aerodynamic diameter. These particles can be classified into different groups by mass spectral analysis methods to produce size-resolved number distributions for each particle type (per unit volume of air sampled). These distributions are for *counted*, rather than *actual* numbers of particles per unit volume of air. 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.,

ACPD
7, S3737–S3746, 2007

EGU

2000). Then the physical diameter is estimated from the aerodynamic diameter (using an estimated density and assuming spherical particles), the physical diameter is cubed to estimate the particle volume, and the volume is multiplied by an estimated density to derive mass concentrations. This scaling procedure implicitly assumes that all particles types at the same size are detected with the same efficiency, which may not be true in some cases (see below). Overall the ATOFMS "data matrix" is being scaled in several ways by some very large factors (orders of magnitude in some cases) and with several assumptions, and there is clearly significant room for uncertainty in this conversion procedure. It would perhaps be better to report the ATOFMS results as number distributions, which are much closer to its native data. If however the authors choose to report mass concentrations, these uncertainties need to be *much* more clearly stated. A rigorous uncertainty propagation analysis including all these effects would be very useful. Otherwise a reader looking at Figs 3 and 7 could take them at face value as measured mass concentrations with no indication of their relatively large uncertainties.

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]. 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." Although the instrument details are different to those used here, this result illustrates that the effect on detection efficiency may indeed be large even for mildly non-spherical particles. The

ACPD
7, S3737–S3746, 2007

EGU

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.” To our knowledge this effect has not been characterized for nozzle-type inlets such as in the ATOFMS used here. It may be smaller, or it may be larger than for lens-based instruments, but we strongly suggest that its potential influence and effect on relative uncertainties are described here.

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.

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.

4. Potential overestimation of some particle densities

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. Most of the mass in the submicron mode in MC is constituted of organics,

ACPD
7, S3737–S3746, 2007

ammonium sulfate (or bisulfate), and ammonium nitrate, with smaller amounts of black carbon and crustal species (Salcedo et al., 2006). Ammonium sulfate and ammonium nitrate have densities around 1.78 and 1.72 respectively, the density of oxidized organics is ∼1.27 (Cross et al., 2007), the density of hydrocarbons is ∼1.0, and the density of black carbon ∼1.77 (Park et al., 2004). It doesn't appear possible to create a mixture density of 1.9 by mixing species which have lower densities (and as dust is not present in most carbonaceous submicron particles). Indeed as mentioned above the average density of the submicron mode calculated from the data of Salcedo et al. (2006) is 1.4 g/cm3 (including dust).

Similarly a density of 2.0 g/cm3 for biomass burning particles appears high. BB particles are composed mostly of OC, with smaller amounts of EC and inorganic species. The density of organic species is correlated with the oxygen content (Pang et al., 2006) and organic species from biomass burning are more oxygenated than POA but less oxygenated than SOA, so a density around 1.1-1.2 would be expected. Inorganic species are also part of BB particles, but e.g. the density of KCl (one of important species in BB particles) is 1.99 g/cm3. Again it appears unlikely that such mixtures could have a density of 2.0 g/cm3.

Perhaps the overestimation of these densities may partially explain some of the discrepancies discussed above, since the densities are used to calculate the physical diameter, which is then cubed to calculate the volume.

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