

Interactive
Comment

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

Received and published: 25 February 2008

RESPONSE: Jimenez and DeCarlo provide an extensive comment on our ACPD paper by Moffet et al. We would like to thank Jimenez and DeCarlo for taking the time to put together such a thoughtful set of comments. Their comment makes a number of important points that we have addressed in our revised version of the paper.

The comment begins by stating that ATOFMS data disagree with the findings from "most other methods" based on presentations at the 2nd MILAGRO science meeting (Mexico City, May 2006). It is relevant to note that our paper was published in ACPD before that meeting took place. In addition, there are two other points that need to be made with regards to this statement:

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

1) There was no general consensus at the MILAGRO meeting as to the exact contribution of biomass/biofuel burning sources to the total observed aerosol. If anything, the heavily-expressed view was that biomass/biofuel emissions made a substantial contribution to the Mexico City aerosol in 2006, which is completely consistent with the ATOFMS findings presented in the original and now revised versions of the paper.

2) Jimenez and DeCarlo claim that ATOFMS data disagree with "most other methods", but most of the support for this argument is based on their own group's unpublished AMS data. At the time we wrote the ACPD paper, the AMS data were unavailable to us for comparison. It is of course not possible to cite, or make other use of, unpublished data of non-co-authors. The results presented in our paper are based on our own ATOFMS data and analyses and must be judged in this context. However, the results of a recently ACP published paper by Yokelson et al. (2007) do support one of the major findings of our paper that biomass/biofuel makes substantial contributions to the Mexico City aerosol. In the revised version of the paper, we compare our findings with previous findings from 2003, as well as published papers on the 2006 study.

The preliminary AMS analyses measured lower biomass/biofuel contributions to the ambient PM_1 at T0 during MILAGRO than the ATOFMS. In the comment by Jimenez and DeCarlo, no mention is made of any reasons for why the AMS may be underestimating the amount of biomass/biofuel. Instead, a number of issues with the ATOFMS measurements that could lead to the noted discrepancy are described. Based on the slant of this comment, the scientific community might conclude that the AMS has no detection biases and makes no assumptions that could contribute to the discrepancy. Certainly, there may be multiple reasons for the lack of agreement. AMS and ATOFMS are complementary techniques and measure different species in the aerosol. The AMS measures the mass concentrations of non-refractory species in PM_1 , whereas the ATOFMS measures both refractory and non-refractory elements of $PM_{2.5}$ and is primarily a number based technique. Certainly, the ATOFMS data could be biased for some of the reasons Jimenez and DeCarlo describe. The mass distri-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

bution was indeed shifted in the original manuscript due to an erroneous shift in the APS aerodynamic size distribution used to scale the ATOFMS data as discussed below. Another possibility is the AMS does not measure some of the refractory material in biomass/biofuel emissions. Refractory salts (KCl, NaCl, etc.), soot, and refractory organic carbon can make substantial contributions to biomass/biofuel burning aerosols depending on the burn conditions and fuel type. Furthermore, many studies have shown that in addition to photochemical processes, a number of primary sources of oxidized organic species exist. Thus, it is possible in previous studies, prior to the introduction of a wood burning organic factor that has been developed over the past year (i.e. BBOA), the AMS data analysis could have been assigning some of the biomass/biofuel ions (i.e. m/z 44) to SOA instead of biomass/biofuel. However, this response is not intended to be a review of the preliminary findings of the AMS, nor is it intended to be a criticism of the AMS technique. It is intended to respond to the comment by Jimenez and DeCarlo by further elucidating the key differences between these two aerosol mass spectrometry techniques (AMS and ATOFMS) in an effort to provide a better understanding for why such a discrepancy may exist. In future comparisons of the ATOFMS and AMS datasets and assumptions, along with data from other measurements made during the study (i.e. isotopes, filter data), we will be able to learn more and possibly arrive at a consensus conclusion as to the fraction of the Mexico City aerosol attributable to biomass/biofuel burning.

We respond to the relevant specific points below. Excerpts (in italics) are taken from the comment. Our responses (in roman) are given after each comment.

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

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

most places no caveats are given about the interpretation of that statement.

RESPONSE: Most of the concerns expressed by Jimenez and DeCarlo focus on the mass distribution presented in Figure 7 in the original paper. Initially, we used a standard scaling procedure developed by our group and published in the literature which uses size distributions from an aerodynamic particle sizer (APS) [Qin *et al.*, 2006]. In this previous paper, we showed ATOFMS number concentration data can be scaled with 1 hour time resolution APS data to obtain PM_{2.5} mass concentrations that were strongly correlated ($R^2 = 0.91$) with a reference method commonly used for measuring PM_{2.5} (a beta attenuation monitor). Note that this scaling procedure was developed in a biomass/biofuel impacted region as well [Qin and Prather, 2006]. For MILAGRO scaling, we used an APS from another group at T0 and after our paper was posted, we learned the APS was not detecting smaller sizes efficiently during the study. This strongly impacted the peak in the submicron mode shown in Figure 7, shifting it to larger sizes. Thus, in the revised paper we have dropped the APS scaling procedure and changed all size metrics to number fractions. This change eliminates most of Jimenez and DeCarlo's concerns regarding the mass fraction of biomass/biofuel particles in Mexico City and the assumptions that are necessary to convert between number and mass concentrations (even though we have published a paper showing this is feasible with a properly functioning APS). It is important to note that even with this change, biomass/biofuel burning-derived particles still represent a significant number fraction (at times up to 76%) of the 180-1000 nm size range of the Mexico City aerosol, as detailed below and in the revised version of the paper. The concentration metric of number fraction is clearly stated throughout the revised version of the manuscript. We also include a discussion of the estimated mass fraction of biomass particles based on measured ATOFMS size distributions of fresh and aged biomass particles in the revised version of the manuscript (discussed below and in the revised manuscript).

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



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.

RESPONSE: The AMS was the only instrument at T0 which provided direct *real-time* aerosol chemistry measurements that we could use for comparison. These data were not available to us at the time we wrote the original ACPD paper. Filter data, which should be used to verify all of the real-time measurements, were also not yet available. We look forward to making comparisons with real-time data showing the diurnal trends in biomass/biofuel burning aerosols and describing these findings in future publications.

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.

RESPONSE: de Gouw's measurements were made at T1, not T0 where the ATOFMS measurements were made. In another paper describing source apportionment of organic sources during MILAGRO, Schauer (Atmos. Chem. Phys. Discuss., 7, S5446–S5454, 2007, www.atmos-chem-phys-discuss.net/7/S5446/2007/) points out that the influence from levoglucosan and biomass combustion at T0 and T1 were isolated from one another and showed no correlations. Thus, de Gouw's measurements T1 are most likely not relevant to our findings at T0.

We have examined the initial acetonitrile data from T0 and the trends in acetonitrile are not nearly as consistent as implied here. When these data become available, we plan to make a comparison with the ATOFMS data. In a previous ATOFMS study (INDOEX),

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

we showed a strong correlation between K-biomass particles with similar mass spectral signatures to those shown in this paper and acetonitrile. A high correlation ($R^2 = 0.84$) was found between the number concentrations of K-biomass particles and gas-phase acetonitrile mixing ratios during INDOEX, providing additional confidence for the mass spectral signatures used for the MILAGRO study [Guazzotti *et al.*, 2003a]

*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.*);*

RESPONSE: A number of recent studies have stated that one should use caution when using levoglucosan as a quantitative tracer of biomass/biofuel burning as both the conditions and fuels drastically alter the proportion of levoglucosan in wood smoke particles [Hedberg and Johansson, 2006; Mazzoleni *et al.*, 2007]. As described in both our original and revised versions of the paper, there are many sources of biomass/biofuel in Mexico City: 1) wood smoke from regional fires, 2) cooking, 3) incineration 4) refuse burning, and 5) small brush fires (agricultural burns).

Before one can claim the AMS can be used for quantitative measurements of biomass/biofuel burning aerosols, there are major issues than need to be addressed in carefully documented calibration studies. In the major AMS paper apportioning the sources of the aerosol in Mexico City measured during the 2003 study, the AMS analyses did not identify biomass/biofuel burning aerosol as a major component of the organic aerosol (Salcedo, *et al.* 2006). Salcedo *et al.* (2006) state that "the organic diurnal pattern is a combination of traffic emissions in the morning (represented by fragment m/z 57) and photochemical production of secondary organic aerosol during sunlit hours (related to fragment m/z 44)." They stated that using MODIS fire count data, fires did not make significant contributions to the ambient aerosols until the end of the study. It is important to note that smaller fires that were shorter in duration such as the local brush fires were often missed by MODIS satellite passes and thus the hot spot data can often under-count the con-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

tributions from biomass/biofuel burning (Fast et al. 2007; Yokelson et al. 2007). Notably, there were more fires overall detected by satellite data in April 2003 (25,000 vs. 4,300) than in March 2006 (i.e. the months each study was performed) in Mexico (see <http://www.conabio.gob.mx/mapaservidor/incendios/tablas2003/2003.html>). At the time of the 2003 study, the AMS apportionment analysis did not include a biomass burning organic aerosol (BBOA) factor. A more recent paper on the 2003 study states that further examination of the contributions from fires in 2003 is underway [*Molina et al.*, 2007]. In the past year, another group reported using AMS and multiple factor analysis for the apportionment of organic aerosols beyond HOA and OOA for sources including wood burning aerosols [*Alfarra et al.*, 2007; *Lanz et al.*, 2007]. Lanz et al. (2007) caution against equating OOA- and HOA-like factors with SOA and POA in regions where "the direct emission of oxygenated aerosol species from sources like biomass burning, charbroiling, food cooking etc. cannot be ruled out."

There are a number of other questions that will need to be addressed before the AMS can be used for quantitative apportionment of biomass burning aerosols. The AMS is currently calibrated in the lab using pure ammonium nitrate aerosols [*Jimenez et al.*, 2003]. Given this, how will one determine the relative response factors (and electron impact ionization cross sections) for OC in the many different sources of biomass/biofuel burning aerosol in Mexico City (at least 4 major types)? How does one relate the vaporization ionization efficiencies of different sources of biomass/biofuel burning to ammonium nitrate? How does the response factor change with fuel type and burn conditions? How does it change with location? How will one correct for size transmission biases of fresh and aged particles that will be transmitted into the AMS with different efficiencies? Will matrix effects impact the AMS measurements? This may all be possible, but it will need to be proven and published before we can justify including a discussion of it in our revised manuscript. Again, for any instrument there are major issues to deal with before one can claim quantitative results for biomass aerosols.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

BB organic aerosol derived from the application of PMF to the HR-ToF-AMS data;

RESPONSE: These data were shown at the science meeting, but were not available to us at the time of writing the original publication. It is our understanding the data will be published during the next year.

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);

RESPONSE: This deals with a key part of the comparison issue. The AMS measures non-refractory compounds in the aerosol. The ATOFMS and other single particle mass spectrometers use a UV laser to desorb and ionize the aerosol and thus measures both refractory as well as non-refractory compounds and elements. There are a number of papers in the literature that indicate KCl (and other inorganic salts), that can represent up to 30% of the mass of biomass/biofuel particles, volatilizes above 700 degrees so it would be considered refractory and hence not be detectable by the AMS (heater T = 600 degrees). In addition, publications suggest there can be a significant fraction of refractory (high mass) organic carbon in biomass/biofuel, in addition to black carbon or soot, which are all refractory species [Novakov and Corrigan, 1995; Roden *et al.*, 2006] The amount depends on burn conditions, fuel type, and the level of atmospheric or aqueous phase processing. It has also been shown that organic species in biomass/biofuel aerosols can "char" upon heating; would these species volatilize and be detected by the AMS [Andreae and Gelencser, 2006; Subramanian *et al.*, 2007]? To address these issues, a paper detailing the species and fraction of material from biomass/biofuel burning the AMS can detect under different burn conditions and for different fuels would be quite interesting.

*- 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 concentrations 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).*

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

RESPONSE: We addressed the issues with the APS used to calculate Fig. 7 above and provide an estimate of the estimated mass fraction of biomass below. Stone et al. only report apportionment of wood burning as a biomass source. If we isolate just biomass burning (wood smoke) aerosols, our number fraction estimate represents 4–40% of PM_{10} which is quite close to the Stone et al. $PM_{2.5}$ mass fraction estimate of 5–30%. Notably, Stone et al. report on most days the contribution from "other" organic sources represents 40–50% of the measured organic mass. This large unapportioned fraction is not surprising given the large number of known primary organic sources in Mexico City. Some of the unapportioned organic mass may also be due to secondary organic aerosol. Stone et al. used WSOC correlations to conclude that the organic species at a peripheral site (not T0) were mainly secondary. No direct evidence is provided for the primary:secondary split for the "other" category at T0. In addition, a number of studies have shown that WSOC is produced by biomass burning aerosols and thus should not be used as a definitive marker for photochemically produced secondary organic aerosols [Hoffer et al., 2006; Lanz et al., 2007]

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.

RESPONSE: This discussion has been changed in the revised manuscript. Notably, the biomass burning aerosols were apportioned using source fingerprints acquired in previous source and ambient studies with the ATOFMS. The particle spectra contained more than just a simple K^+ ion at m/z 39, and included levoglucosan, organics, ammonium, sulfate, and nitrate. Any particles that contained just a K^+ were assigned to an unknown particle type. When ATOFMS detected mass spectral mixtures showing K associated with a large amount of OC, to make sure we didn't over-count biomass/biofuel particles, we classified those particles as OC in the revised manuscript. Thus the

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

estimate for the biomass/biofuel fraction does not include these mixed particles (i.e. agglomerates), and serves as a lower limit of the fraction of biomass/biofuel aerosols. It is interesting to note that during peak traffic periods (early mornings) many of the OC particles showed a significant ion peak at m/z 39 (K^+), suggesting the high levels of biomass/biofuel burning particles coagulated with particles from other sources. The mass fraction issue is addressed below.

To be continued in Part 2.

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper