**Atmospheric
Chemistry
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Discussions**

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Comment

Interactive comment on "Single particle characterization using a light scattering module coupled to a time-of-flight aerosol mass spectrometer" *by* E. S. Cross et al.

E. S. Cross et al.

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Comment E2-2: p. 21332. For the range of refractive indices expected in the MCMA (real refractive indices of 1.4-1.6, Seinfeld and Pandis, 2006), the uncertainty in do is +/-10% (Cross et al., 2007).

- It isn't clear why the authors have to estimate these values when they have been measured in the MCMA area. It would be much more appropriate to use the measured refractive index values reported in Moffet et al. (JGR, 2008) for Milagro. The reported range is significantly larger than this which would lead to a larger uncertainty in Do.

Response: The range of refractive indices used corresponds to the range expected for nonrefractory submicron ambient aerosol particles (corresponding with the particles

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with prompt vaporization within the AMS). The text (located in Appendix B) has been altered to clarify this as follows:

In the absence of black carbon, most nonrefractory sub-micron aerosol particles have a real refractive index between 1.4 - 1.6 (Seinfeld and Pandis, 2006). Across this range, the uncertainty in do is ˜ 10% (Cross et al., 2007). The majority of particles with prompt vaporization within the LS-ToF-AMS most likely fall within this refractive index range.

Comment F: p. 21335: This agreement is shown quantitatively in Fig. 6b which displays the correlation between the LSSP and PTOF signals for arrival times between 3.1-5.5 ms (data between arrows in Fig. 6a). The correlation is linear with a slope of 0.85, indicating that the LSSP mode collected 85% of the PTOF signal. We note from Fig. 6a and 6b that the LSSP signal is about 15% smaller than the than the signal obtained in the PTOF mode. The missing 15% is likely due to delayed vaporization of particles smaller than the optical size detection limit and therefore are not detected in the LSSP mode. This interpretation is further supported by the fact that at longer times-of-flight ($>$4.8 ms in Fig. 6a), the average LSSP and PTOF modes agree fully.

- The statements regarding Figure 6 are quite confusing. There needs to be a better bridge between Figures 2 and 3 which shows a minor fraction of the smallest particles were detected and Figure 6 which is used to state that the LSSP mode collected 85% of the PTOF signal. There is a serious inconsistency in these results as they are explained.

Response: The reviewer misunderstands the data displayed in Figure 6 (Figure 3a and 3b in the revised manuscript). This is most likely due to some lack of clarity on our part. We have re-structured section 3 of the revised manuscript in order to clarify the points discussed by the reviewer as follows: As stated in the text, the correlation between the LSSP and PTOF signals is drawn across the particle time-of-flight window from 3.1 - 5.5 ms. This corresponds with particles with diameters above the optical size detection limit allowing a comparison between the total ion signal measured in both

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the single particle mode and ensemble PTOF acquisition mode (after correcting for the difference in their respective sampling duty cycles). The total ion signal measured in the LSSP mode is the combination of mass contributions from prompt, delayed, and null particles. All aspects of collection efficiency (dependence on size, phase or composition) will apply equally to the PTOF and LSSP modes. The comparison between the PTOF and LSSP modes is meant to provide an internal consistency check between the ensemble and single particle measurements made with the LS-ToF-AMS. The details of this comparison are provided in Section 3.3 of the revised manuscript.

Comment G: p. 21336: The observation of two distinct particle types within the same chopper cycle indicates that the ambient ensemble was externally mixed during this sampling period. Are the authors actually stating that two particles are used to determine the entire ambient ensemble was externally mixed? Out of how many? Statistically, this is a weak statement based on only 2 particles. How do the authors know these 2 particles were representative of the entire atmospheric aerosol?

Comment I2: p. 21338: The simultaneous observation of these two externally mixed particles illustrates the capabilities of the LS-ToF-AMS technique to provide a measure of the mixing state and atmospheric processing of ambient submicron aerosol particles.

This is an over-statement and should be removed. Showing the data for two particles is not really demonstrating the full potential of the technique. Higher statistics than just 2 particles would be far more appropriate.

Response to Comments G and I2: The two distinct particles measured within the same chopper cycle do not describe the entire atmospheric aerosol, but rather provide a clear example of two chemically distinct particle types co-existing within the ambient ensemble at the time they were sampled. We believe that the coincidence example demonstrates the capabilities of the LS-ToF-AMS technique. We certainly agree with the reviewer that higher counting statistics are necessary before characterizing the entire ambient aerosol ensemble as externally mixed. We have altered the statement

in the text as follows:

The simultaneous observation of these two chemically distinct particles illustrates the capabilities of the LS-ToF-AMS technique to provide information about the mixing state of submicron aerosol particles.

Additionally we have shortened the section describing the coincident particles and have placed the measured and calculated properties in table 1 rather than describe these values at length in the text.

Comment H: p. 21336: They use 3 different methods to calculate mass. Depending on which method is used, they get a range of sizes ranging from 211 to 446 nm for the same particle. Which method is most trustworthy and has the least error and required assumptions? This is a wide range for mass estimates and seriously calls to question the ability to be "quantitative". If this is the error for 1 particle, then it will be multiplicative for many particles.

Response: There is a misunderstanding within this comment. As listed in Table 1, particle #2 has a measured dva = 446 nm, doptical = 263 nm, and a calculated physical diameter (from the sum of the measured ion signals) = 211 nm. Each diameter measurement has an associated uncertainty. The dva is a function of the particle density, physical diameter, and shape hence the larger value for this diameter compared with the optical and chemical diameters. For the dva value, the uncertainty is derived from the slit width of the spinning chopper wheel that is used to define the start time of the particle time of flight. The LS-ToF-AMS had a 1% slit width chopper which corresponds to a maximum uncertainty in dva of +/-13%. The optical diameter has an uncertainty that depends on the particle shape and refractive index as described in Cross et al., 2007. The calculated particle mass (used as the x-axis in Figures 4a and 4b of the revised manuscript) uses the combination of the optical and aerodynamic diameters along with a chemically-derived density for each of the single particles.

It is now stressed in the text that this is not the range of physical diameters obtained

for the same particle, but rather the vacuum aerodynamic and optical diameters.

Comment I: p. 21337: The mass of particles 1 and 2, as measured by the calibrated mass spectrometer, is 18.2 fg, and 13.0 fg, respectively. How is the mass spectrometer calibrated for this experiment using ammonium nitrate? If so, how will this affect the absolute magnitude of the mass of each particle if they contain completely different components with different densities (and shapes)? Also, should read "masses" and "are" 18.2.

Response: Yes the ionization efficiency of the LS-TOF-AMS deployed during MILA-GRO was calibrated using ammonium nitrate. Relative ionization efficiencies were used to obtain mass loadings of the other nonrefractory components of the particles.

Comment J: p. 21338: A unique feature of the LS-ToF-AMS is that it provides ensemble as well as single particle measurements. Unique compared to which other method? This statement is true for any single particle method one can always get an average from multiple particles, and in fact can do so on a selective basis. However, it is true that one cannot go in the reverse direction (i.e from an ensemble to single particle data)

Response: We have not made our point clearly. We think that we have clarified this by re-writing this part of the text as follows:

However, a unique feature of the LS-ToF-AMS is that it provides an interleaved dataset of ensemble average as well as single particle measurements. Thus, information gathered from the analysis of the prompt single particles measured can be compared and combined with the observations of the ensemble aerosol to provide a more complete description of the mixing state and atmospheric transformations of the ambient submicron aerosol.

Comment K: p. 21341: In order to limit any potential effects of particle bounce, prior to full vaporization of the non-refractory component of single particles, we have chosen to analyze only the prompt vaporization single particle events (refer to Sect. 3.1).

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Comparing the single particle mass measured by chemical ion signals with the mass derived from dva and do measurements indicates that approximately 88% of the single particle mass is accounted for by the chemical ion signals (Fig. 3a). The remaining 12% may be due to refractory material (dust, metals, black carbon, etc.) that the AMS does not measure.

This is a critical point in the paper that could be lost on the general reader. So, for clarification, for all analyses from this point until the end of the paper (i.e. all of Section 4), are you using only 23% of the particles to draw conclusions about the entire ambient aerosol? It is unclear how the conclusions are realistic for such a limited subset of particles. One of the conclusions is the reported measurements are accounting for 88% of the single particle mass. There is a serious disconnect here. As stated, the AMS analysis excludes non-spherical and refractory particles. It excludes most of the larger more massive particles, as well. They have stated they are analyzing 23% of the signal and thus not using 77% of the mass yet they claim they are only missing 12%.

This is a discrepancy that needs to be addressed.

Also, the authors need to be clear throughout the rest of the paper when making broad generalizations about the ambient aerosols from which they are drawing their conclusions. The reader is left pondering what the other 77% of the non-detected aerosols were composed of. Since the paper is very long, the authors may want to think about eliminating Section 4 since it is the weakest part of the paper.

Response: The points made by the reviewer are correct, that is, we use only 23% of the single particles (those with prompt vaporization) for the analysis of particle composition during the 75-hours of single particle sampling. For these particles, ion-determined mass is 88% of the single particle mass calculated from the optical and vacuum aerodynamic diameter measurements. It is not clear that the 12% difference is due to refractory material in this subset of particles or whether this is a measurement accuracy issue. We thought that we had made this point clear but obviously we have not.

We have now prefaced our discussion of section 4 by more clearly stating the following:

We note that by focusing on the data obtained from the prompt vaporization particles only, we restrict the interpretation of the submicron ambient aerosol particles to only a subset of ambient aerosol particles (i.e. those that readily vaporize at 600 C and are in the optical size range) Therefore, the single particle results are not meant to describe the entire atmospheric submicron aerosol particle population in the MCMA, but rather to illustrate the capabilities of the AMS instrument equipped with a light scattering module and operated as a single particle detector in the field.

Comment L: p. 21341: Typically, dust and soil particles fall into the super-micron size range, which is not detected with the AMS due to transmission efficiency losses for larger particles (Lui et al., 2007). Should be noted, the AMS also doesn't detect any size of dust (salts) because they are refractory and thus not volatilized at 600 degrees. Industrial dust/salts were detected down into the submicron size range.

Response: We have added the following sentence in the revised manuscript to incorporate this additional note:

We note that the AMS chemical detection would not be sensitive to submicron dust particles due to their refractory characteristics.

Comment M: p. 21342: Levoglucosan (1,6-anhydro-_-D-glucopyranose), the pyrolysis product of cellulose, is a well-established marker for the combustion of biomass materials (Simoneit, 2002). Once partitioned into the particle phase, levoglucosan does not degrade, making it a useful tracer for long-range transport of biomass burning aerosol (Fraser and Lakshmanan, 2000).

There are many other more recent papers in the literature which call into question the use of levoglucosan as a robust tracer of biomass burning. The authors need to give a balanced (and up to date) perspective different fuels, aging processes, etc. are shown to change the relative amount of levoglucosan in biomass burning aerosols. Others

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have shown levoglocosan decreases in intensity in aged biomass burning aerosols detected with the AMS (Coe, JGR, 2008). The Carnegie Mellon group has also shown levoglucosan decays away in recently conducted chamber experiments. So, it is highly likely this 5% is a serious under-estimate and missed fresher (less spherical) or larger (more aged) biomass burning aerosols. The amount was also smaller during this period as the region had many rain events, as pointed out in the paper. Finally as shown recently by electron microscopy results, the majority of the Mexico City particles contained potassium and were non-spherical biomass particles due to shape issues, would most of these irregularly shaped biomass/biofuel particles bounce and not be detected like ammonium sulfate?

Thus it is questionable with all of these caveats to make any major claims as to an estimate of BBOA at T1 for the study. Yet, at the bottom of p. 21342, they state: "While the absolute magnitude of biomass burning sources may not be adequately represented in the current data set, our single particle measurements indicate that biomass burning was a relatively minor source for particulate matter at T1 during the sampling period under discussion."

Response: We once again need to point out, although we have not pointed this out in the ACPD manuscript, that the main purpose of our paper is not to present a definitive characterization of the aerosol particles in Mexico City, but rather it is to demonstrate the capabilities of this new instrument combination. Accordingly, the quoted sentence by the reviewer is simply meant to indicate that we have detected some mass spectral signatures that are characteristic of biomass combustion. However, we agree with the reviewer that identification of biomass burning aerosol is a complex and extensively studied process. Accordingly, we have modified the sentence to say: Levoglucosan is one of the suggested markers for the combustion of biomass materials.

We have removed the statement about levoglucosan not degrading. We agree with the reviewer that there are components of biomass burning aerosol particles that the AMS is not chemically sensitive to.

Comment N: p. 21343: They state: With these particles removed, the reconstructed organic (HOA+OOA) accounted for 93% (R2=0.84) of the measured single particle organic mass, suggesting that HOA and OOA give a reasonable, but not complete, description of the organics at T1. Again, this general conclusion is based only on the 23% of the particles producing prompt ion signals? This needs to be clarified.

Response: We have clarified the issue raised by the reviewer by re-stating that the analysis is conducted on the subset of promptly vaporized single particles only as follows:

With these particles removed, the reconstructed organic (HOA+OOA) for the promptly vaporized particles accounted for 93% (R2=0.84) of the measured single particle organic mass, suggesting that HOA and OOA give a reasonable, but not complete, description of the non-refractory organics measured with the AMS at T1.

Comment O: p. 21344, they state: Based on this observation and on mass balance, we will assume that the inorganics were in the form of NH4NO3, (NH4)2SO4, and NH4Cl.

These are the forms of nitrate, chloride, and sulfate the AMS can detect. The other forms such as NaNO3, NaCl, KCl, metal-chlorides and metal nitrates may not be detectable in the AMS. The vaporization temps of the Na and K inorganic salts are above 800 degrees and thus these are refractory species in the AMS.

Response: We have modified the sentence to indicate that we are talking about the nonrefractory inorganic components.

Based on this observation and on mass balance, we will assume that the nonrefractory inorganic species measured with the AMS were in the form of NH4NO3, (NH4)2SO4, and NH4Cl.

Comment P: p. 21344: They state: The single particle data directly confirm assumptions that are typically drawn from ambient, ensemble sampling of size-resolved aerosol chemistry where the average chemical compositions of particles appear to be relatively

constant as a function of particle size (Salcedo et al., 2006) -This is a strong statement and not really appropriate considering they are analyzing a narrow size range at the smallest sizes of the total aerosol as shown in Figure 2. The MILAGRO paper by Moffet et al. cited throughout this paper shows a very strong size dependence on chemical mixing state in Mexico City. Also, as the particles grow in size, they show more signs of aging. External mixtures are far more prevalent at the smallest sizes (and above 1 microns). These may be out of the size range of the AMS used in this study and thus an ensemble average may be representative of the very narrow (small) size range the AMS seems to be detecting with prompt vaporization signals. In other words, this is more of a conclusion regarding the specific aerosol the AMS can efficiently detect versus the aerosol that is actually present in the atmosphere.

Response: We agree with the reviewer in that we are only sampling a limited portion of the accumulation mode aerosol particles with the single particle technique and we have removed the sentence from the text.

Comment Q: p. 21344: they state For example, Fig. 10 shows that most of the ambient particles measured at T1 contained ammonium nitrate.

This should be re-worded to state more accurately: most of the ambient non-refractory particles with a prompt ion signal (23% of the total) measured at T1 contained ammonium nitrate.

Response: The sentence has been revised as suggested by the reviewer. It now reads:

most of the promptly vaporized ambient particles measured with the LS-ToF-AMS at T1 contained ammonium nitrate.

Comment R: p. 21345: they state: This observation is strongly supported by the single particle mass spectra reported by Moffet et al. (2008a) for ATOFMS results obtained at the T0 site. Nearly all classified single particle types reported exhibit both NO2 and NO3 ions (see Fig. 2 in Moffet et al., 2008a).

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Importantly, many of these nitrate-containing particles detected with the ATOFMS by Moffet et al. contained NaNO3 and not just ammonium nitrate which the AMS claims is most of the nitrate mass. One must exercise caution when interpreting the nitrate concentrations detected by the AMS when it is stated most of the nitrate is in the form of ammonium nitrate, the authors mean most of the non-refractory nitrate that produces a prompt ion signal is in the form of ammonium nitrate which makes sense since this is the most common non-refractory form of nitrate. However, the AMS is not detecting sodium nitrate which was significant during certain periods in Mexico City, even in the submicron particles.

Response: The sentence has been removed from the revised manuscript. Where comparisons are made between the ATOFMS and LS-TOF-AMS response, an effort is made to clearly state that the ATOFMS measurements include refractory and nonrefractory components of the single particles.

Comment S: p. 21353: In such cases, the Pb signal was approximately 100 times smaller than the chloride signal. Care must be taken when interpreting AMS measurements of heavy metals and further characterization of the ionization efficiency of metal species must be done before quantitative information is reported. Nevertheless, on a qualitative basis, these observations suggest that only some of the chloride events at T1 were correlated with Pb, and that when present, lead constituted a relatively minor component of the total particle mass. Lower concentrations of Pb containing particles were also measured at the T1 site relative to the T0 site by Moreno et al. (2008). -If the AMS cannot measure most of the Pb mass (what is the volatilization temp and limit of detection of the AMS for the different Pb salts?), it isn't appropriate it represents a small % of the mass. The AMS did detect Pb with Cl in almost 1/2 of the events the question arises, since it is not easily detectable with the AMS, what % of the Pb events were below the AMS detection limits? It would be worthwhile to report the AMS detection limits for Pb. How high a % would have to exist in a single PbCl3 particle for the AMS to detect lead? Also, most of the Pb particles were highly nonspherical. Wouldn't these

be missed due to particle bounce issues such as reported for ammonium sulfate?

Response: We agree with the criticism of the reviewer. The quoted sentence has been revised as follows:

In such cases, the lead signal was approximately 100 times smaller than the chloride signal. However, the AMS is not well characterized for the detection of heavy metal compounds. Further characterization of the ionization efficiency of such heavy metal species must be completed before quantitative information is reported. Accordingly, we cannot draw quantitative conclusions of the observed results for lead.

Comment T: p. 21354: "Murphy emphasizes the importance of understanding the chemical detection sensitivity of single particle mass spectrometers. Calibration experiments indicate that the PALMS and ATOFMS instruments are 12 times more sensitive to metal species than detection of NH4NO3 or HNO3. Therefore, when measuring single particles with any Pb content, it is possible to over-estimate the mass contribution of the metal species to the total particle composition with laser-ablation single particle mass spectrometers."

Provide the reference which shows this factor of 12. It is likely the PALMS and ATOFMS have different detection efficiencies since they use different LDI wavelengths. There is no paper that shows the detection efficiency for both instruments for metals vs. NH4NO3 and HNO3. Most/all single particle mass spec reports of Pb have reported # fractions and not attempted to report mass contributions as this final sentence implies. Without knowing the mass fraction of Pb in a single particle, it would be difficult to do this. For that matter, it is unclear if the AMS can provide such info given the fact that many forms of Pb could be refractory. What is the sensitivity of the AMS towards Pb in the various salt forms?

Response: We have removed the section discussing the sensitivity of laser-based SPMS instruments toward heavy metals because at the current time a fair comparison cannot be drawn due to the fact that the characterization of the LS-ToF-AMS ionization

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efficiency for heavy metals is highly uncertain.

Comments U-1 and U-2: p. 21354: Our single particle measurements at T1 suggest that the predominant form of chloride in the single particles was ammonium chloride

-Can the authors estimate the fraction of the total chloride the AMS detects? Have they derived calibration curves for Cl in various salt forms? The chloride signals shown in Figure 8-10 are extremely small. It is likely the AMS only detects a small fraction of the total Cl since most of the Cl in the form of NaCl, KCl, PbCl, and ZnCl would not be vaporized in the AMS. -Also, because the shape of the metal-chloride particles were needle-like (Moffet, ES&T, 2008), it is likely the AMS didn't detect these particles as part of the 23% for which they acquired a prompt ion signal. Again, it would be more appropriate to state "the predominant form of non-refractory chloride in the 23% of particles which underwent prompt vaporization (23%) was ammonium chloride".

Response: We agree with the reviewer that the chloride mass concentrations reported by the AMS are for non-refractory, promptly vaporized chloride only. Accordingly we have revised the manuscript by adding the following sentence on p.43.

We note that the chloride signal measured with the LS-ToF-AMS is only for nonrefractory species and, in the present case, for particles that are promptly vaporized. Accordingly, refractory forms of the chloride are excluded from chemical detection. Our single particle measurements at T1 suggest that the predominant form of nonrefractory chloride in the single particles plotted in Figure 10 was ammonium chloride.

We have not derived calibration curves for the various salt forms of chloride.

Comment U-3: Also, on p. 21354: Examination of all single particles measured during the high chloride particle events show that no particles had effective densities greater than 1.8 g/cm3. -This must be re-worded. No particles that produced prompt ion signals in the AMS had effective densities greater than 1.8. It is highly likely given the non-spherical nature (see Moffet ES&T, 2008) of these metal-chloride particles, that

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they were not detected in the AMS as part of the 23% analyzed. However, they could have been part of the other 77% that were not analyzed.

Response: We understand the confusion resulting from our lack of clarity in the manuscript. Effective densities were calculated for all the single particles measured, independent of their chemical ion signal response based on the combination of vacuum aerodynamic and optical diameters. Therefore, no single particles measured (including the 77% that were delayed and null) had effective densities greater than 1.8 g/cm3. The issue of non-spherical, needle-like metal chloride particles complicates the interpretation of the single particle effective densities measured with the LS-ToF-AMS.

Comment V-1: p. 21355: The mass spectrum shows that this particle was predominately NH4Cl combined with some NH4NO3 and very little organic. Based on these observations, we conclude that a significant fraction of the particulate chloride measured with the LS-ToF-AMS at T1 was in the form of NH4Cl. - It would be appropriate to add the caveat that it is possible these NH4NO3/NH4Cl particles contained other refractory metal and salt species (NaCl and KCl); with the AMS alone, you cannot tell. Such mixtures are actually shown in the Moffet Milagro paper for T0 chloride-containing particles. Since the AMS is only detecting ammonium chloride particles, they should explicitly mention for the non-mass spectrometry expert that this is a chemical bias of the AMS and they would miss detecting the NaNO3, KCl, NaCl, and Pb and Zn-chloride-nitrate particles detected by other instruments (i.e. single particle mass spectrometry, electron microscopy and STXM). It is likely the AMS missed these other types because they were dry and irregularly shaped (i.e. needles) as well as refractory at 600 degrees. Also, was this period an appropriate one (i.e. proper transport conditions) where the ATOFMS T0 results should be compared with the AMS T1 results? This should be discussed. It would be interesting to use the light scattering signal to more fully explore the densities of these inorganic particles that are detectable.

Response: We have revised section 4.1.3 (in the updated manuscript) on the high-chloride content single particles to state more clearly that the LS-ToF-AMS is only

sensitive to nonrefractory forms of the chloride.

Comment V-2: Also, since the PILS was sampling during this same period, it would be interesting to see if they also conclude most of the chloride was in the form of ammonium chloride. How much of the chloride detected by the PILS-IC does the AMS detect? This gets back to the question of what is the detection limit for chloride by the AMS when it is in the form of NaCl, KCl, or metal-chlorides vs. NH4Cl?

Response: Using a co-located measurement of particulate chloride to understand the detection efficiency of the AMS is a good idea however with the limited sampling period and relatively low sampling duty cycle of the LSSP mode as deployed in this prototype instrument configuration, such comparison are beyond the scope of this manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 21313, 2008.