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Interactive comment on "Quantification of aerosol chemical composition using continuous single particle measurements" *by* C.-H. Jeong et al.

Anonymous Referee #1

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General Comments: Jeong et al. describe the calculation of scaled sulphate, nitrate, ammonium, organic carbon, and elemental carbon mass concentrations within individual particles, as measured by aerosol time-of-flight mass spectrometry. The quantification of chemical species within individual particles is a very important, yet challenging, task, which the authors are commended for tackling. Given the many uncertainties and assumptions associated with these calculations, further discussion and justification should be provided in describing the method and comparisons with collocated instrumentation; specific questions and comments are detailed below. Major consideration should be taken with respect to the method of species mass concentration; specific comments and suggestions are noted below. In addition, the authors should complete a more thorough literature search of single-particle mass spectrometry studies, as this should help with discussions within the manuscript. The good correlations

between scaled ATOFMS sulfate, nitrate, and ammonium mass correlations with GPIC and AMS measurements suggest that this method may be useful for future ATOFMS studies. This result should be highlighted and associated uncertainties should be discussed in detail. There are major concerns with respect to the assumptions made in the calculations of the species mass fractions, as well as the method used. However, this manuscript is an important step forward in the quantification of species within individual particles.

Specific Comments: Abstract: The abstract is difficult to follow; reorganization should be considered to make the main points clearer. Please also clarify the following: To what were the ion peak intensities scaled? Correlation coefficients are noted for nitrate; however, what instruments are being compared here? What was the method of total PM mass measurement? The first sentence mentions urban and rural sites; however, no results of this comparison are noted here. In addition, the science learned during this study is not summarized here in the abstract.

Page 1221, Lines 8-10: Why are Greece and Mexico highlighted for non-US field sites? There have been many other international ATOFMS deployments.

Page 1221, Lines 12-29: It would seem appropriate to summarize other single-particle mass spec (non-ATOFMS) quantification work.

Page 1221, Lines 16-19: ATOFMS-MOUDI scaling was also completed by Qin et al. (2006, Analytical Chemistry).

Page 1221, Lines 21-23: This has been completed by other studies as well. For example, ATOFMS scaling by APS was also recently completed by Ault et al. (2009, Environ. Sci. Technol.) and was found to compare well with PM2.5 mass concentrations. Pratt and Prather (2009, Environ. Sci. Technol.) completed SMPS-ATOFMS scaling.

Page 1221, Lines 24-27: Note that Ferge et al. (2006, Environ. Sci. Technol.) also examined EC/TC values measured by ATOFMS and compared them to thermal standard techniques.

Page 1221, Lines 27-28: The statement “These studies used time averaging of several hours or more” is incorrect. Hourly resolution has been utilized in several studies.

Page 1225, Line 19: Note that m/z +43 can often correspond to $C_2H_3O^+$ and $CHNO^+$ (eg. Silva et al. 2000, Analytical Chem., Denkenberger et al. 2007, Environ. Sci. Technol.).

Page 1225, Line 26: Technically, the transmission efficiency, as measured, actually described transmission through the sizing region (i.e., further divergence could occur during transport to the source region of the mass spectrometer), as well as optical detection by the sizing lasers (hence the reduced detection of smaller particles; eg. see Liu et al. 2007, Aerosol Sci. Technol. and Su et al. 2004, Analytical Chem.).

Page 1227, Lines 3-4: Given the ability of the ATOFMS to differentiate particle chemistry on an individual particle basis and previous studies of chemically-resolved particle density (eg. Moffet et al. 2008, J. Geophys. Res., Spencer et al 2007, Environ. Sci. Technol.), why was only one effective density chosen? Applying estimated effective densities based on particle chemistry would be expected to provide a more accurate result. Further, justification for the use of 1.6 g/cm3 should be provided.

Page 1227, Lines 23-25: It is unclear why conversion from number concentration to volume concentration was necessary, given that both methods measure size-resolved number. This scaling method is also in contrast to that completed by Qin et al. (2006, Analytical Chem.) and Reinard et al. (2007, Atmos. Environ.), for example.

Page 1229, Lines 4-7: Justification for these large assumptions should be provided.

Page 1229, Lines 7-8: Implicit in this assumption is that the particles are composed of only sulphate, nitrate, ammonium, OC, and EC. The uncertainties associated with this are not, and should be, discussed.

Page 1229, Lines 14-20: Different atoms and molecules have different ionization ener-

gies, resulting in different ionization efficiencies when using laser desorption/ionization. This reflects species other than potassium, as well. The authors should consult the manuscript by Reinard and Johnston (2008, J. Am. Soc. Mass Spectrom.), which discusses ion formation mechanisms in laser desorption/ionization with respect to atmospheric aerosols.

Page 1230, Line 8: With such a low vigilance factor, what was the variance within one general particle type? According to Rebotier and Prather (2007, Analytica Chimica Acta), large variances in peak areas would be expected for this low vigilance factor, and particularly after hand re-grouping. Since peak areas are important to this study, were confidence intervals for individual m/z calculated for each particle type? This is important with respect to that the calculated mass fractions and comparison between particle types.

Section 3.1: This section should be condensed, as it discusses topics covered in many previous single-particle mass spec and aerodynamic lens system manuscripts. See, for example, Pratt et al. (2009, Analytical Chem.), who compared modeled and measured transmission efficiencies for an aerodynamic lens system used within an ATOFMS. Discussions within this section are also vague and poorly supported.

Section 3.2: This section could be more concise as well. Discussion of comparisons of unscaled values is not relevant given the known transmission biases with size. This can be removed. Good agreement between the ATOFMS scaled nitrate, sulfate, and ammonium with the GPIC and AMS is an important result that should be highlighted! This has important implications for future ATOFMS studies! Uncertainties should be discussed with respect to the application of this method to future studies. The OC/EC paragraph would benefit from discussions of the uncertainties associated with the Sunset OCEC analyzer. Further, Ferge et al. (2006, Environ. Sci. Technol.) and Spencer and Prather (2006, Aerosol Sci. Technol.) found good agreement, but used additional ion peaks, rather than just one; this should be considered and discussed. Possible other explanations are provided but are not properly supported.

Page 1233, Lines 12-14: This suggested result could, and should, be confirmed by examination of the data from this study!

Section 3.4 and Figure 8: Previously, pure ammonium sulfate particles were postulated to be present during periods of low hit rates in the 0.35-0.54 um size range (eg., Wenzel et al. 2003, J. Geophys. Res.); these particles were considered in scaling the ATOFMS data in the Wenzel et al study. This should be investigated here. In addition, was there similar variance in the ATOFMS hit efficiency of larger particles? Was sulfuric acid observed more readily during these periods (to support this claim)? Was there any correlation with relative humidity (e.g. Neubauer et al. 1998, Atmos. Environ.; see also Spencer et al. 2008, J. Geophys. Res.)?

Page 1235, Lines 2-4: Note that Zhang et al. also observed absorption to be enhanced.

Section 3.4: Why were the scaled ATOFMS RPA values not converted to mass using the assumed density? Wouldn't this be more straightforward that scaling again by the GPIC and Sunset OCEC data, which adds even more uncertainties and assumptions? How is the OM to OC conversion completed? This is not clear. Dust (and species other than OC, EC, sulfate, nitrate, and ammonium) is not accounted for in the calculated estimate of PM2.5; this should be discussed.

Page 1236, Lines 12-13: The volatilization of semivolatile organics and ammonium nitrate is based on the temperature used by the TEOM, not the season (the presence of those species would vary by season).

Page 1236, Lines 25-27: Since single-particle chemistry is available from the ATOFMS data, the chemistry during these periods should be investigated! Are more dust particles present during these periods? What are the characteristics of these periods? Was RH higher?

Section 3.5: Much of the beginning of this section repeats other sections of the manuscript. The mass spectra of the fireworks particles should be compared to Liu

et al. (1997, Analytical Chem.). Were potassium nitrate ion peaks observed? Several ATOFMS manuscripts exist that show the mass spectra associated with fresh vehicle emissions; the discussion of the EC particles could benefit from comparisons (and would strengthen the stated arguments).

Page 1238, Lines 6-8: What particles are not detected by ATOFMS? This is confusing given that the data has been scaled.

Page 1238, Lines 12-14: The particle types were only compared based on these species! Also, how can inorganic components of dust (such as Na, etc) be considered minor components by mass? This assumption does not seem appropriate.

Page 1238, Lines 15-17: Why was percent composition, rather than mass concentration, used for this calculation?

Page 1238, Lines 20-21: Provide a reference for the acidity range noted.

Page 1240, Lines 13-14: Another reference for the correlation between amine particles and high RH is Angelino et al. (2001, Environ. Sci. Technol.).

Page 1241, Lines 11-12: The authors may want to consider Fergenson et al. (2001, Analytical Chem.), for example, and reconsider this statement. In addition, several single-particle mass spectrometry manuscripts have recently quantified individual species in particles (eg. Froyd et al. 2010, PNAS; Pratt et al. 2009, Environ. Sci. Technol.). This said, this manuscript is still an important step forward!

Table 2: Why are unscaled values compared? This does not seem useful given the known transmission bias with size. Would be more appropriate and clear to report r2 values rather than r values?

Figure 1: It would be useful to label other major cities, such as Detroit, for example.

Figures 3-5: In my opinion, these figures are superfluous and could be removed from the manuscript, or included as supplemental material. Similar plots have been shown in several other single-particle mass spec manuscripts.

Figures 6-7: These figures are extremely important. It would be useful to show correlation plots next to the temporal plots. Under what conditions are good/poor observed?

Figure 9: The conditions of the underestimated times (primarily in Harrow) should be discussed. Can it be understood by the presence of certain particle types, for which the chemical species were not considered? A temporal plot of the scaled number concentration of particle types would be useful.

Figure 11: What is the variance (due to peak area, for example) within one particle type? How can the dust particle type be primarily sulphate by mass? For example, “Dust-Na” contains Na (Table 4); however, it is not listed as a component by mass. Further, on a mass basis, it seems like the OC-S, OC-S-N, and OC types are nearly identical; please comment and consider uncertainties in the calculations. This should also help give insight into the ATOFMS mass spectra.

Technical Corrections:

Page 1220, Lines 24-27: Confusing sentence – please clarify.

Page 1221, Lines 11-12: As the reader does not yet know that this field work was completed in Canada, this sentence seems out of place here.

Page 1222, Lines 4-5: “…collocated high time resolution measurements” of what?

Page 1223, Lines 5-6 and 8: The residence time of the air within the inlet, or at least the sampling flow rate, should be provided in addition so that the inlet dimensions are useful to the reader.

Page 1223, Line 25: Technically, the particles are accelerated to their terminal velocities prior to the sizing region, rather than within the sizing region; please correct phrasing.

Page 1224, Line 1: The phrase “dual detecting plates” suggests that one MCP detects

both positive and negative ion mass spectra; please rephrase.

Page 1224, Line 14: What are “…gaseous and ambient particles…”? Rephrase for clarity.

Page 1224, Line 7: “data was” should be “data were”.

Page 1225, Paragraph 1: For clarity, the beginning of this paragraph should note that it is referring to ATOFMS data.

Page 1229, Line 13: Fix grammar.

Page 1229, Lines 21-22: Examined in what way? Please clarify.

Page 1234, Lines 6-7: What fraction of the spectra contained potassium?

Page 1234, Line 22: Fix grammar.

Page 1238, Line 11-12: “Compound” usually refers to one type of molecule, rather than a class of chemical species.

Page 1239, Line 8: Fix grammar.

Page 1239, Line 20: Fix typo.

Page 1240, Lines 13-14: Fix grammar.

Table 5: What are the associated errors? It would seem that they are higher than reported by significant figures.

Figure 10: Several of the particle types listed have similar color shades in the figure and are difficult to differentiate.

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