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Atmospheric
Chemistry
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Discussions

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

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Referee #1

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.

- The authors thank the referee for the thoughtful, valuable comments and suggestions. All comments have been carefully considered in the revised manuscript.

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 ïňĄrst 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.

- We have organized the abstract to clarify the findings of the study.

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

- More relevant references were added (i.e., Middlebrook et al., 2003; Beddows et al., 2004; Guazzotti et al., 2001; Sullivan et al., 2007; Zhang et al., 2009; Healy et al., 2010; Kamphus et al., 2010).

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

- Several references (Hinz et al., 2005; Tolocka et al., 2006; Bein et al., 2006; Reinard et al., 2007) for non-ATOFMS were added and the previous results were summarized.

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

- Added

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.

- These references were added in the revised manuscript.

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.

- Added

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.

- These sentences were deleted. The review section in Page 1221 was revised to clarify these previous works.

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.).

- Inserted in the line and Table 4

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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.).

- We modified the sentence as follows: "The particle detection efficiency of the ATOFMS depends on the ability of the instrument to transport particles though the sizing region as well as to detect the particles with two sizing lasers (the transmission efficiency) and the capacity of the particle to then absorb ablation laser photons in order to produce a measurable mass spectrum (the hit efficiency)."

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, justiïňĄcation for the use of 1.6 g/cm3 should be provided.

- In this study FMPS number concentrations in 9 size bins between 0.1 and 0.3 μm (mobility diameter) were combined as one number concentration to obtain a scaling factor for ATOFMS particle counts below 0.5 μm. The objective of the study was to quantify chemical composition using individual peak intensities from ATOFMS without conducting any pre-processes, such as particle clustering analysis (i.e., ART-2a, K-means). To avoid determining chemically-resolved density for individual particles, we assumed the density of typical ambient particles suggested by previous studies (e.g.,Hand and Kreidenweis, 2002; Khlystov et al., 2004; Pitz et al., 2008). Hand and Kreidenweis (2002) reported that an effective density of 1.6 g/cm3 in in a remote region. In an urban area ambient particles was found to have an effective density of 1.6 g/cm3 (Khlystov et al., 2004). Pitz et al. (2009) also reported a similar average density of 1.6 g/cm3 for cities in Germany. These references were added in the revised manuscript.

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- While theoretical possible, incorporating particle densities estimated based on particle-types (e.g., aged OC-Nitrate, EC-OC-Nitrate) would have added another level of complexity to quantification process. Perhaps this could be pursued by others to see if any resulting improvement would justify these extra computational steps. Care would be needed as particle density tends to be varied spatially and temporally due to changes of particle physical chemical properties as well as meteorological parameters (e.g., relative humidity). Spencer et al. (2007, Environ. Sci. Technol.) reported that effective density during the summer varied from 1.0 to 1.5 g/cm3. Moffet et al. (2008, JGR) also observed a wide range of particle density (1.1-3.4 g/m3) for ambient particle types in Mexico City. Even within a particle type Moffet et al. (2008) found particle densities for the particle type were different at different sites (0.9 in Riverside vs. 1.1 in Mexico City). In summary, it would have been difficult to estimate chemically-resolved particle density every hour for converting FMPS mobility diameters to aerodynamic diameter. While this may have yield improvements, it was not clear that this would have outweighed the uncertainties that would have thereby been introduced.

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.

- Due to poor detection efficiency of ATOFMS measurements for particles smaller than 0.5 um, number concentrations of particles smaller than 0.5 μm were combined into one size bin as mentioned earlier. Further the FMPS number concentrations of ambient particles in the size range of 0.1 to 0.5 um sharply decrease as particle size increases, decreasing for example from 1700±1300 cm-3 for smaller particle (0.1-0.3 μm) to 90±90 cm-3 for larger particles (0.3-0.5 μm) in this study. Higher particle number concentrations by the FMPS and poorer detection efficiencies of the ATOFMS in the smaller size range (0.1-0.3 μm) introduced uncertainty in the scaling when FMPS number concentrations are directly compared with ATOFMS counts in the size range.

The largest scaling factors were applied to the ATOFMS data with the greatest uncertainty, that for the smallest particles. Perhaps as a result, using the scaling factor based on number concentrations resulted in much poorer correlations between the scale ATOFMS data and collocated chemical component measurements. Thus, the ATOFMS combined number concentrations were converted into volume concentrations as a way to weight the summation of the smallest particles towards mass. Furthermore, the volumetric scaling value for quantitative ATOFMS data showed the best agreement with collocated monitors when utilizing a diameter of 0.3 μm as an average ATOFMS particle diameter for this smallest size range. There were no differences in scaling factors for the larger particle sizes (> 0.5μm) between number and volume concentrations measured by the ATOFMS and APS. We used the volume concentrations for consistency.

- Qin et al. (2006) used APS number data (neither SMPS nor FMPS) in a narrow size range (0.3-0.5 um) for the ATOFMS count scaling, and Reinard et al. (2007) compared size segregated RSMS numbers (0.05, 0.11, 0.22, 0.44, and 0.77 um) with corresponding SMPS number concentrations.

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

- These implicit assumptions were not presented as being defendable. Our intent in explicitly stating them was to remind readers of limitations identified earlier in the manuscript and recognize the biases that they could potentially introduce. To clarify, we modified the sentence as follows: “Note that this approach may have potential biases when the aerosol is heterogeneous and only partially ablated by the laser.”

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.

- We added these sentences as follows: “A further bias can occur with the assumption that the particles are composed of only sulphate, nitrate, ammonium, OC, and

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EC. However, in terms of mass fractions of PM2.5 these five species are predominant in terms of chemical composition. In multiple Canadian urban and rural areas these five chemical species accounted for 66-85% of total PM2.5 mass concentrations determined by a TEOM, whereas most of metals contributed only 4~7% of the fine mass concentrations (Jeong et al., 2011)."

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

- These sentences were revised as follows: "Gross et al. (2000) reported that variations in relative peak areas of the ATOFMS ion intensity were smaller than absolute peak area variations for particles of identical composition. However, RPA values of positive and negative ions may also be affected by inherent variances of particle compositions due to matrix effects within particles and chemical specific ionization efficiencies (Reilly et al., 2000; Reinard and Johnston, 2008). The ionization efficiencies of alkali metals such as sodium and potassium are higher than any other measureable species because of their low ionization energies. The presence of these species may result in different ion formation processes than if they were absent, and as a result they may introduce systematic biases in measuring relative ion intensities (Reinard and Johnston, 2008)."

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 conïňĄdence 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.

- We have already explored the clustering results with a variety of vigilance factors. More details on the clustering analysis in this study are presented by McGuire et al. (2011). The mass spectra were clustered based on their log-transform to allow for less intense, yet important peaks to inform the clustering. Using a typical vigilance factor of 0.8 the ART-2a clustering algorithm produced 606 particle-types, which was not only far too many for interpretation, but each one also contained an insignificant number of particles. A lower vigilance factor of 0.3 was ultimately chosen to ensure that an interpretable number of particle types (33 particle types) was obtained, and that enough of these contained a significant amount of signal (i.e., >95% of particles captured in particle types with >500 particles).

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 3.1 was revised. Figures 3 and 5 were moved to Supplementary material. Figure 4 and corresponding discussions were removed from the manuscript.

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

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ion peaks, rather than just one; this should be considered and discussed. Possible other explanations are provided but are not properly supported.

- The unscaled results are shown in the manuscript to emphasize the importance of correcting for the ATOFMS detection efficiency.

- The section was revised to highlight the good agreement between scaled ATOFMS data with the GPIC and AMS. We also added the sentence to discuss possible uncertainties with the method as follows: “The variability in the quantitative ATOFMS methods using RPA and PA reflects that temporally and spatially inhomogeneous particle compositions may influence the sensitivity of the quantification method using single particle mass spectrometry.”

- The uncertainties associated with the Sunset OCEC analyser using the NIOSH’s thermal-optical transmission (TOT) method were accounted for.

- We have compared the estimation of EC and OC using multiple ions and found no improvement. Possible explanations for poor correlations of carbonaceous material determined by ATOFMS are suggested in more detail as follows: “Ferge et al. (2006) found that ATOFMS derived EC and OC values of tunnel dust samples deviated more from the concentrations determined by thermal-optical methods, as compared to EC and OC quantifications for laboratory generated particles. To account for this deviation, they suggested that the increasing fractions of inorganic content in particles increased the uncertainty in the determination of EC and OC concentrations. Suppression effects of low ionization energy alkali metals (e.g., Na+ and K+) on the ion intensities of organic materials have been previously reported by Reilly et al. (2000). Crustal compounds may be more prevalent in ambient particulate matter from rural areas than from a road tunnel. As a result, the estimation of carbonaceous material in ambient particles from the ATOFMS single particle mass spectrum data may be biased by the presence of inorganic components.”

Page 1233, Lines 12-14: This suggested result could, and should, be confirmed by

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examination of the data from this study!

- The sentence was removed from the revised manuscript as it could not be confirmed.

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.)?

- We agree with the reviewer's point. The lower hit efficiencies are mostly corrected by the ATOFMS scaling. We observed that the hit efficiencies were inversely proportional to the scaling factors (r = -0.78 for Toronto, r = -0.46 for Harrow) in this study. The figure (Figure 3 in the revised paper) and corresponding discussions were moved into Section 3.1 to explain the detection sensitivities of the ATOFMS. We added some explanation for the discrepancies in Section 3.2 as follows: "However, discrepancies between the measurements occurred for sulphate and ammonium on days with elevated levels of ammonium sulphate and nitrate (23 January and 1 February) in Toronto. There was no discernable association of relative humidity with these discrepancies. As discussed in Fig 3, relatively poorer hit efficiencies of ATOFMS on these days were already compensated by the scaling factors. During the SPORT campaign in Toronto, Godri et al. (2009) found that the GPIC sulphate on 23 January and the GPIC nitrate on 1 February were slightly higher than the AMS sulphate and R&P 8400N nitrate measurements, respectively, suggesting possible biases on the GPIC measurements on those days."

- The efficiency of the scaling procedure during periods of low hit efficiencies was further discussed in Section 3.3 in the revised text.

- Sulphuric acid was not measured in this study. The discussion with respect to Zhang et al.(2008)'s study was removed from the revised manuscript.

- We did investigate the influence of relative humidity (RH) as well as temperature on the hit efficiency to evaluate the effect of water condensed on particles on the laser desorption ionization mass spectra of single particles (Neubauer et al., 1997; Neubauer et al., 1998). There were no statistically significant correlations between ATOFMS hit efficiency and RH at the both sites. However, the ATOFMS hit efficiency was negatively correlated to ambient temperature. The correlation was particularly strong for particles smaller than <0.54 μm (r= -0.69 in Toronto, -0.36 in Harrow). It is likely that the increase of photochemical formation of secondary sulphate during the period of high temperature resulted in the decreased hit efficiency during these episodes. This might possibly be due to particle coating related to changes of particle physical chemical properties. We thought that these results would not add much since we have already indicated in the previous paragraph that coating was the likely cause. In the revised manuscript the comparison of RH and temperature with the hit efficiency was discussed in Sections 3.1 and 3.2.

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

- The reference was removed from the manuscript as mentioned above.

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.

- Direct conversion of the scaled ATOFMS RPA to mass using the density would neglect the differences in ionization efficiency of different components within the particles. We focused on finding the best marker ions (i.e., m/z -97, -62, 18) that were highly correlated with corresponding chemical species measurements. Instead of using the

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direct conversion, the mass calibration factors shown in Table 3 were obtained by examining the correlation between the ATOFMS volume intensities and corresponding AMS/GPIC/Sunset mass measurements (μg m-3). These ATOFMS volume intensities were converted into mass concentrations using the mass calibration factors for chemical species as shown in Figure 6 in the revised manuscript. The mass calibration factors accounted empirically for the differences in the ionization efficiencies.

- As suggested by Turpin and Lim (2001), organic matter (OM) concentrations were estimated from measured OC concentrations by multiplying by a factor of 1.4 to account for the additional mass of associated oxygen and hydrogen present in particles. However, the conversion factor of the mass of OC to that of OM may vary temporally and spatially ranging from 1.2 to 2.2 (Turpin et al., 2000; Zhang et al., 2005; Aiken et al. 2008).

- We did not estimate the mass concentrations of dust species. For clarity, we added the sentence as follows: “Note that the elemental composition of dust was a part of the unaccounted particulate matter mass in this mass reconstruction analysis.”

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).

- The potential for volatilization losses depends on the temperature difference between outside and the TEOM. To avoid confusion, the discussion was revised as follows: “Due to a strong winter-high seasonality of nitrate formation, the heated TEOM monitor volatilizes a significant portion of the PM mass (i.e., ammonium nitrate and semi-volatile organics) in wintertime (Schwab et al., 2004; Schwab et al., 2006).”

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?

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- We added several possible explanations for the discrepancy in the revised manuscript. In brief, the presence of large dust particles would result in the differences between the reconstructed ATOFMS sulphate, nitrate, ammonium, OE, and EC measurements and the DustTrak PM2.5 mass concentrations. The AMS sulphate, nitrate, ammonium, and organic measurements were also lower than the DustTrak measurements during the same period. This strongly suggests that the difference may stem from the presence of refractory materials that the AMS cannot detect. In addition, many dust related particles were observed by ATOFMS. During the dust event wind speeds were higher than the average during the entire period, supporting increase of large dust particles. The high relative humidity over the night would be another factor that introduces the maximum differences at night. Significant amount of water on the particle surface may lead to decreasing ion intensities of sulphate and nitrate due to the deliquescence of ammonium nitrate/ammonium sulphate (Ge et al., 1998). Moreover, the high RH during the nighttime can cause PM2.5 readings of DustTrak using a light scattering technology to be biased high from actual concentrations.

- We added two new plots in the Supplementary Material showing the comparison of AMS and scaled ATOFMS measurements with DustTrak readings as well as the temporal variations of hourly average relative peak areas of dust related ions (i.e., Na, Ca, Fe)

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).

- The beginning of the section was revised and the reference for fireworks components was compared in the manuscript. “Previous studies also found K, Al, Mg, Ba, and Sr are key elements of fireworks (e.g., Liu et al., 1997; Moreno et al., 2007).”

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- We discussed the similar findings of EC particles from other studies as follows: “The EC (I) type was observed in other ATOFMS studies at different locations (Dall’Osto et al., 2005; Moffet et al., 2008). These single particle analysis studies found that the early morning peak of an EC particle type with high intensities of Na+ was associated with freshly emitted vehicle particles.”

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

- We revised the sentence as follows: “However, not all particle components detected by the ATOFMS were used for the mass closure, thus Fig. 8 does not necessarily represent a complete mass reconstruction.”

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.

- As discussed previously, the contribution of trace elements (i.e., Al, As, Ba, Br, Ca, Cd, Cl, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Si, Sr, Ti, V, Zn) on the total PM2.5 mass concentration is much lower than the contribution of the major species (sulphate, nitrate, ammonium, OC, EC). For example, a study for the source apportionment of PM2.5 measured for nearly five years in five urban areas in Canada showed that these metal components accounted for 4∼7% of the total PM2.5 mass concentrations. We revised the paragraph as follows: “Most of the particle-types contain at least some of all five components, indicating a high degree of internal mixing of these components. This is not surprising given that four of the five components were presumably secondary in nature, with EC representing the only primary component. In terms of these five components, the particle-types differed mostly in their relative ratios of sulphate or nitrate to ammonium, and organic to elemental carbon. The degree of external mixing of the minor components, not shown here, was greater.”

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

- It makes no difference is mass or % mass is used. In the spreadsheet we actually used mass rather than % mass so we have revised the sentence to indicate that we used mass concentration to obtain the acidity ratio. The sentence was corrected.

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

- We added the reference, Ziemba et al., 2007. “A previous aerosol acidity study using 5-year data from filter samples reported that the aerosol molar ratio ranged from 0.75 to 0.98 during summer months while more than 97% of samples had a ratio between 0.5 and 1.0 at a rural site in the northeastern United States (Ziemba et al., 2007).”

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

- The reference was added as follows; “Previously, Angelino et al. (2001) found that amine particles characterized by m/z 86 increased with increasing RH and decreasing temperature in urban areas.”

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!

- We agreed that there have been great efforts to develop quantification methods for single particle analysis. However, in our study ion intensities for major PM2.5 compositions were directly scaled using two particle size spectrometers in the size of 0.1 μm – 2.5 μm without conducting particle clustering procedures. More importantly, the quantitative ATOFMS results were comparable to high time resolution measurements detected by AMS and GPIC during two intensive field campaigns. The good agreement with high time resolution instruments encourages using ATOFMS single particle data

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as alternative measurements of PM chemical species. For clarity, the sentence in this section was removed and modified in the abstract in the revised manuscript as follows: “This is the first study to estimate hourly quantitative data of sulphate, nitrate, ammonium, OC and EC in ambient particles from scaled ATOFMS single particle analysis; these were closely comparable with collocated high time resolution data of sulphate, nitrate and ammonium detected by AMS and GPIC.”

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?

- We do not agree with the reviewer’s point. The comparison will help readers to appreciate the significance of transmission biases in raw ATOMFS measurements and the degree to which these biases can be accounted for the scaling methods.

- The Pearson r correlation has been used in inter-comparison studies of PM speciation monitors which has been referenced.

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

- Other major cities (i.e., Detroit, Cleveland, and Columbus) in the US were marked in Figure 1.

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.

- As suggested by the reviewer, Figures 3 and 5 were moved to supplemental material and we deleted Figure 2 in the revised manuscript.

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?

- The correlation plots for chemical species at two sites were included in these figures.

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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.

- This is already discussed in the previous comment.

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.

- The reviewer seems to misunderstand the quantification of particle types in Figure 11(Figure 8 in the revised manuscript). The dust particle types are mostly governed by the mass concentration of nitrate (not sulphate). This quantification approaches for particle types was only applied to the five major PM compositions (sulphate, nitrate, ammonium, OC and EC) as described in Page 1235 Line 1-6. Thus, dust related metal components are not able to be shown in Figure 11. To avoid confusion, we modified the paragraph as follows: “Other compounds not quantified from the ATOFMS data, such as mineral oxides, likely also contributed. The contribution of these compounds in not reflected in Figure 11.”

- To indicate uncertainties in estimated mass concentrations of the five major PM components in particle types, the 95% confidence interval for the estimated mean as a function of particle types was depicted in Figure S5 (Supplementary material), showing statistically significant variations among these particle types (i.e., Oc-S, OC-S-N, OC). Again, more details on mass spectra of particle types and clustering analysis are presented in McGuire et al. (2011).

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

- The sentence was modified for clarity as follows: "There have been deviations between the strength of the association identified by these studies, reflecting that the use of PM mass concentration is insensitive to heterogeneities in physical and chemical PM characteristics (Künzli et al., 2006)."

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.

- This sentence was deleted.

Page 1222, Lines 4-5: ". . .collocated high time resolution measurements" of what?

- We revised as follows: "One of the objectives of these field campaigns was to compare the chemical components measured by the ATOFMS with collocated high time resolution measurements of sulphate, nitrate, and ammonium detected by an Aerodyne Aerosol Mass Spectrometer (AMS) and a Dionex Gas-Particle Ion Chromatography (GPIC)."

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.

- The sampling flow rates (150 L/min in Toronto and 30 L/min in Harrow) were provided in the revised manuscript.

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.

- The sentence was corrected as follows: "In this particle sampling region the aerosols are accelerated to their terminal velocities depending on their aerodynamic diameters which are then determined by measuring the transit time between two 50 mW Nd:YAG lasers (532 nm) in the sizing region."

Page 1224, Line 1: The phrase "dual detecting plates" suggests that one MCP detects both positive and negative ion mass spectra; please rephrase.

- We revised as follows: "These ions are accelerated and dual-polarity mass spectra for individual particles are measured."

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

- The sentence was revised as follows: "The GPIC measured water soluble particulate components (SO42-, NO3-, NO2-, NH4, Cl-) and gaseous precursors (SO2, HNO3, HNO2, NH3, HCl) every 15 minutes,"

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

- Corrected.

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

- Modified.

Page 1229, Line 13: Fix grammar.

- Corrected ". . .where Sdai,k is the hourly scaling factor for each single particle corresponding to chemical species (k)."

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

- The sentence was revised as follows: "Instead of using RPA, the hourly ATOFMS peak area (PA), as given in Eq. (6), was used to quantify chemical components."

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

- We found that more than 80% of total positive ion spectra contained potassium. However, the sentence was deleted from the manuscript as discussed previously.

Page 1234, Line 22: Fix grammar.

- The section was removed.

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

- Replaced with “components”

Page 1239, Line 8: Fix grammar.

- The sentence was corrected. “The acidity ratios for the OC-S-N and OC-S particle-types were 0.91 and 1.42, respectively,. . .”

Page 1239, Line 20: Fix typo.

- Corrected: “The OC-rich particles had an acidity ratio of 0.87 and thus were more acidic than the other OC particle-types.”

Page 1240, Lines 13-14: Fix grammar.

- Corrected: “The presence of amine was identified by a peak at m/z 59 [C3H9N]. OC fragments and low negative ion peaks were also observed in the mass spectra. While the amine particle-type accounted for 7% of the total mass measured by the ATOFMS,. . .”

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

- We reduced the number of significant figures in the table.

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

- We modified the figure with a higher resolution and a different color scheme.

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