

We thank the Reviewer for the detailed and constructive comments, which have greatly helped us to improve the quality of the manuscript. We have carefully considered these comments. The point-by-point responses are presented below.

This paper presents an analysis of single particle mass spectra collected using the LS-ToF-AMS, consisting of an improved light scattering module integrated with the Aerodyne ToF-AMS. The authors discuss hardware improvements, their impact on instrument performance, estimates of instrument collection efficiency, and identification/classification of particle types based on organic mass spectra. The technique and resulting dataset are novel and of great interest. However, some major issues exist within the data analysis and a number of conclusions are not well supported by the data. First, the collection efficiency analysis depends on correct identification of LS detected particles that produce/do not produce a detectable mass spectrum. The current method is not valid across the entire size range to which it is applied (see Comment 16). Second, there are a number of flaws in the identification of Clusters II and III with specific sources and processes, and especially in their relation with ensemble-derived factors (see Comments 19-25). These issues are fundamental to the conclusions of the paper and major revisions are required before this manuscript can be published. Detailed comments are provided below.

Major Comments

1. P3049 L14-16: “The single particle mode in the ToF-AMS operation is typically turned off during field measurements to conserve data storage and processing time.” The authors are referring to the so-called “brute force single particle (BFSP)” mode, where the AMS saves either (1) all MS extractions within a chopper cycle, with the fraction of cycles saved limited by the data transfer rate, or (2) all MS extractions within a chopper cycle, with the chopper cycles selected based on a user-set chemical profile (e.g. all particles with nitrate-containing peaks above a set threshold). This mode is distinct from the LS-based triggering discussed later in the paragraph, and the difference should be noted explicitly.

We have replaced the “single particle mode” with “BFSP mode” and clarified the differences between BFSP and LSSP modes.

P3049 L14-16: change “The single particle mode in the ToF-AMS operation is typically turned off during field measurements to conserve data storage and processing time.” to “In the brute force single particle (BFSP) mode of the ToF-AMS operation, mass spectrum extractions within a chopper cycle are saved, enabling acquisition of single-particle mass spectra. However, the BFSP mode is typically turned off during field measurements to conserve data storage and processing time.”

P3049, L22-23, replace “Particle light scattering signals triggered the saving of single-particle mass spectra, which considerably enhanced data-saving efficiency.” with “In LS-ToF-AMS, single-particle mass spectra are recorded during the operation of the light scattering single particle (LSSP) mode. The LSSP mode is similar to the BFSP mode,

except that particle light scattering signals trigger the saving of single-particle mass spectra, which considerably enhances the data transfer and saving efficiency compared to the BFSP mode operation, during which mass spectra in each chopper cycle are saved individually regardless of the existence of particles.”

2. P3051 L18-21: “The detection process is fast enough (100 us), compared to the traveling time (5 ms) of the particles in the particle-sizing chamber, to allow correlated measurements of single particle light scattering and chemical compositions.” This could be phrased more clearly. I am not sure what is meant by “detection process.” It appears to be the collection time for a single mass spectrum (i.e. single extraction), but it is not clear whether vaporization and ion flight times are included. I’m also not clear why the relationship between “detection process” and particle flight time determines whether correlated LS/chemical composition measurements are possible. Shouldn’t the chopper frequency also play a role, as the combination of chopper frequency and spread in particle flight times governs the probability of coincident particles at the LS unit?

We agree that chopper frequency also plays a role and we have clarified this sentence. We have made the following corrections:

P3051 L18-21, remove “The detection process is fast enough (100 μ s), compared to the traveling time (5 ms) of the particles in the particle-sizing chamber, to allow correlated measurements of single particle light scattering and chemical compositions.”

P3051 L22, after “particle flight”, add “The chopper was operated at 143 Hz. With this frequency, there is typically ~ 1 particle or less per chopper cycle on average (DeCarlo et al., 2006), allowing correlated measurements of single particle light scattering and chemical compositions.”

3. P3051 L23-26: “By measuring particle flight time between the mechanical chopper and the light scattering laser and thermal vaporizer, particle vacuum aerodynamic diameter (dva) can be determined from a calibration curve, which relates particle flight time to particle size for atomized ammonium nitrate particles of known sizes.” This are several issues with this statement. (1) The dva calibration relates particle velocity (i.e. flight time over a known distance; not simply flight time) to dva. This is a useful distinction to make, as it clarifies that dva can be extracted from flight time measurements of chopper-to-vaporizer, chopper-to-LS, or LS-to-vaporizer, which is slightly unclear in the original statement. (2) The dva calibration applies for ALL particles, not simply ammonium nitrate. I am not sure whether the authors intended to imply this, but the current phrasing is ambiguous. (3) Does the reference to ammonium nitrate indicate that the dva calibration was performed using DMA-selected ammonium nitrate? In this case, the method and accuracy of the DMA size calibration should be discussed. The calibrations must be somehow referenced to a primary size standard such as PSL spheres.

We used ammonium nitrate for calibration of the majority of the points and used PSL to check the sizing of particles. The calibration curve is shown as follows. The flight time was extracted from chopper to vaporizer. We have clarified this sentence to read:

“By measuring particle flight time between the mechanical chopper and the thermal vaporizer, particle vacuum aerodynamic diameter (d_{va}) can be determined from a calibration curve, which relates particle velocity (calculated using the known distance between the chopper and the vaporizer and the measured flight time) to particle size. The calibration curve was derived using polystyrene spheres (PSL of diameter 200 nm, 350 nm, 500 nm, and 600 nm) and ammonium nitrate particles that were size-selected by a Differential Mobility Analyzer (DMA). Comparison of nominal PSL size and mobility-selected size showed good agreement.”

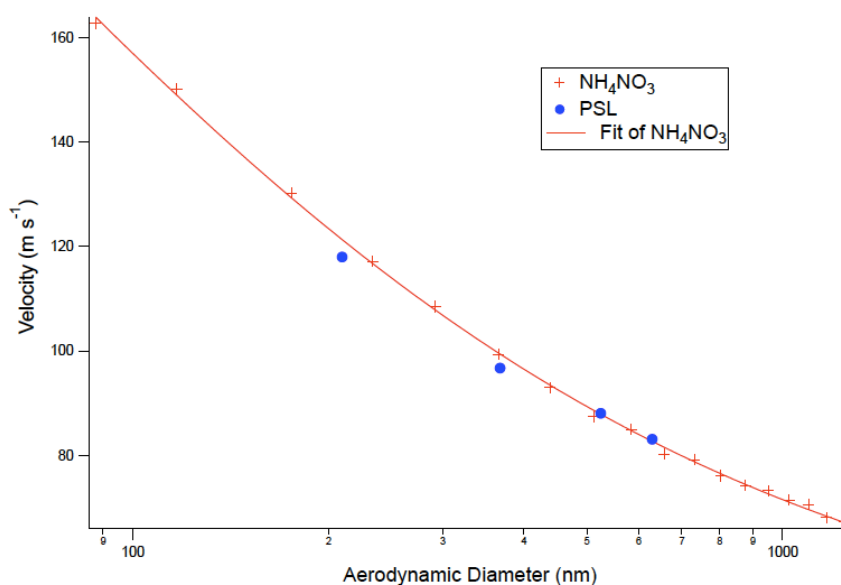


Figure 1. Particle size calibration curve.

4. P3051 L 27-30: “The density (1.4 g cm⁻³) was derived by comparing AMS-measured mass size distribution with DMA-measured volume size distribution detailed in Lars et al. (2012).” This seems an unnecessarily crude method of estimating d_g , and several parallel methods are possible using the system in this paper. Cross et al. (2007) demonstrated the LS-ToF-AMS to provide direct estimates of d_g from the optical scattering signal. This approach seems ideal for the current manuscript; why is it not used? The AMS ensemble measurements can also be used to estimate particle density based on the composition of the individual components and assumed densities for these components. Finally, it is not clear how much variation was observed in the analysis of Lars et al. or how this analysis was performed. Unfortunately, Lars et al. (2012) does not appear in the reference list. A minor point is that the DMA does not count particles; the instrument used for this should be reported.

The paper Lars et al. (2012) is a typo and it should be Ahlm et al. (2012), which is in the reference list. We are sorry for the error. The density was used to estimate the geometric

diameter as suggested by the Reviewer in the comments before publication on AMTD (the geometric diameters are given in the parentheses after each d_{va}). The calibration of R_{LS} vs. d_g is required to employ the particle density calculation shown in Cross et al. (2007); it relies on a particle population of uniform optical properties. The R_{LS} vs. d_g calibration was not performed for this study since optical property is not the central focus of this work, so the method of Cross et al. was not used.

We did not use the ensemble measurement (from the MS mode) to estimate density because it requires 1) assumption of density for organic components and 2) black carbon and dust measurements to calculate particle volume. Therefore, this method is likely associated with larger errors than the method used in Alhm et al. (2012). Alhm et al. (2012) calculated density for multiple days and found that the densities were nearly constant. Therefore, a constant density was used for this measurement.

We believe that the density calculation does not affect the main result of this work, which focuses on identifying single-particle types. In addition, the density of 1.4 g cm^{-3} is consistent with the density of $1.4\text{-}1.6 \text{ g cm}^{-3}$ (with accuracy of 10%) found in Cross et al. (2007) and within the range of typical submicron particle densities.

We have clarified that the instrument is an SMPS: Replace “DMA-measured” with “SMPS (scanning mobility particle sizer)-measured” on P3051 L29.

5. The advantages of the new comparator circuit are not clearly described (P3052 L10-17). The authors need to be careful with their terminology regarding data transfer vs. data saving. Without the comparator circuit, the LS data for every chopper cycle must be transferred to the computer where a software evaluation is conducted to determine whether a particle is present. This transfer process is longer than an individual chopper cycle, thereby reducing LS sampling efficiency. In the new system, this evaluation is conducted by the comparator circuit, removing the need for data transfer during blank chopper cycles. LS and MS data are now transferred to the computer and saved only for particle-containing chopper cycles, greatly increasing the instrument duty cycle. An additional improvement, which is not currently mentioned, is the implementation of the GZIP compression algorithm for the single particle data files. This reduces file size, thereby reducing data transfer time and improving the duty cycle.

We have made the following corrections to clarify:

P3052 L10-12, change “(2) using an external comparator circuit to test for the presences of a single particle in the scattered light signal, using a user set threshold level.” to “(2) using an external comparator circuit to test for the presence of a single particle in the scattered light signal, using a user set threshold level. This test is performed without transferring data to the computer for software evaluation, a process that takes longer time than an individual chopper cycle.”

P3052 L15-16, replace “data saving” with “data transfer.”

P3052 L17, at the end of the paragraph, add “In addition, the GZIP compression algorithm is applied to the single-particle files, thereby reducing the data transfer time and enhancing the sampling efficiency of LS-ToF-AMS.”

6. The “light scattering particle counter” (P3052 L18-26) is part of the comparator circuit discussed above, and I suggest these two discussions be combined.

We have moved the second paragraph on P3052 to after “using a user set threshold level” to combine the discussions of the light scattering counter and the comparator.

7. The authors note the dependence of the duty cycle on particle concentration (P3053 L2-7), which is very welcome. If the data are available, it would be very useful to provide a plot of this dependence in the supplement, given this is the first published characterization of the comparator circuit-based LS system.

We have investigated the dependence of duty cycle (data saving duty cycle calculated from the comparator circuit) on particle number concentration (from the SMPS measurement) for particles from 180 – 1000 nm d_{va} (as shown in the figure below). We found that the duty cycle is weakly or not dependent on particle number concentration.

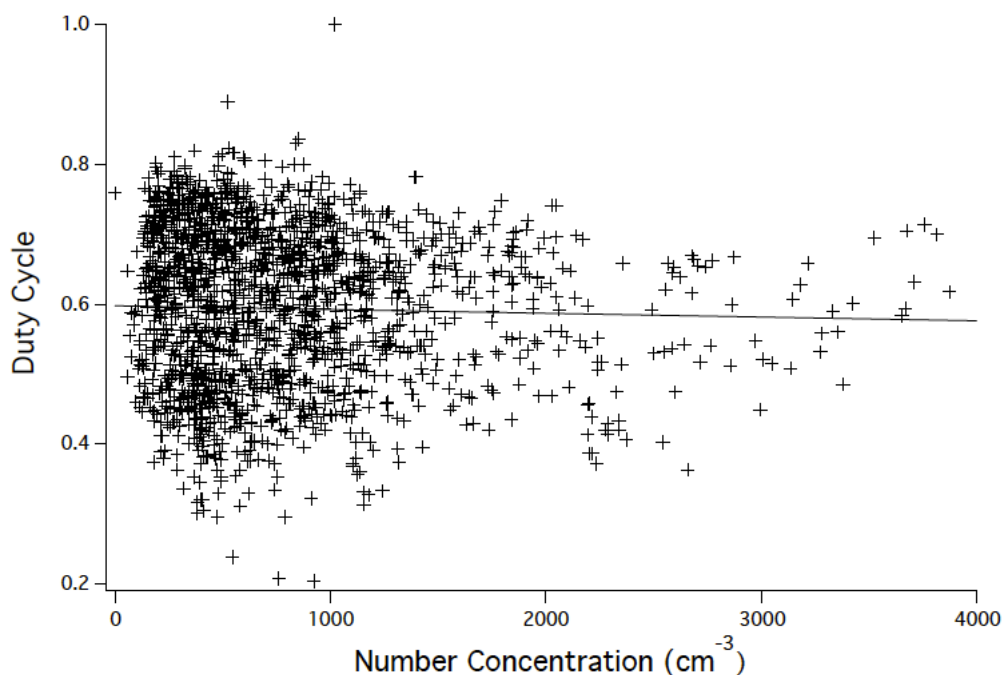


Figure 2. Data saving duty cycle (number of particles saved using LSSP over total number of LS-circuit counted particles) versus SMPS measured particle total number concentration (130 to 715 nm d_m). The line represents the linear fit of the points with a slope of -5.6×10^{-6} .

8. P3053 L21-22: What is meant by “summed light scattering signals” (also applies to Fig. 1). Is this the time-integrated light scattering signal?

We have changed “summed light scattering signals” to “time-integrated light scattering signals” for clarification on P3053 L21-22 and in Figure 1.

9. P3053 L23-25: Two separate criteria are given for determining the detection limit (optical signal and chemical ion signal). Which of these two is typically the limiting factor, or do they present similar restrictions?

The two criteria are 1) $S/N > 5$ for light scattering signals, and 2) MS signals > 6 ions. (Note that we have corrected the original threshold to be 6 ions not 100 ions, please refer to the uploaded document “Reply to the threshold issue” for details). These two criteria serve different purposes. Criterion 1) is used to determine the detection limit ($180 \text{ nm } d_{va}$) of the light scattering module, and criterion 2) is used to classify particle vaporization types, i.e., particles with MS signals < 6 ions are categorized as null type particles.

We have clarified this point by changing “The detection limit, defined as the size at which particles produce detectable optical signals ($S/N \geq 5$) and chemical signals (> 100 ions), was $180 \text{ nm } d_{va}$ ($130 \text{ nm } d_g$)” to “The optical detection limit, defined as the size at which particles produce detectable optical signals ($S/N \geq 5$), was $180 \text{ nm } d_{va}$ ($130 \text{ nm } d_g$).”

In Table 1, change “Smallest particles that produce significant optical ($S/N \geq 5$) and chemical signals (> 100 ions)” to “Smallest particles that produce significant optical signals ($S/N \geq 5$) (optical detection limit).”

10. Fig. 1a shows that the population of organic-dominated particles tends toward lower sizes relative to the total ensemble. It appears that these particles coincide predominantly with Cluster III (Fig. 1b). The authors suggest that this is a result of these particles being primary and nonspherical, with the nonspherical particles containing black carbon. The assumption of primary particles is plausible based on the mass spectrum (Fig. 3a-iii), as it resembles hydrocarbon-like and cooking OA spectra published in numerous other studies. However, the authors compare it to a mass weighted average of cooking OA, petroleum SOA, and traffic/biogenic nighttime OA, which would imply a strong secondary component. This contradicts the assertion of a primary aerosol. Regarding the suggestion of black carbon-containing nonspherical particles, the BC inclusion would have to be quite significant to affect the particle shape. It seems unlikely that such particles would occur so frequently in the $300\text{--}600 \text{ nm } d_{geo}$ range. Perhaps this could be explored by comparing the measured ion signal vs. the theoretical signal from a particle with this size (i.e. looking for discrepancies in mass balance due to the BC core). However, it is possible that current estimate of d_{geo} is too uncertain for this. Another possibility is simply that the authors’ assumption of a uniform density (see comment 4) is inadequate. It is quite likely that organic-dominated particles will have lower densities. Thus the estimate of d_{geo} (the quantity most closely related to LS signal) may be biased low for such particles. Finally, note that on P3054 L13, “diameter” should be “ d_{va} .” It

should also be noted here that, if the authors' assumption of non-spherical particles is correct (or the particle density is lower as suggested above), the estimate of d_{geo} will be biased low.

The O/C values for COA, petroleum SOA, and nighttime OA factors were in the range of 0.00-0.20 (P3060 L20-21). Although the petroleum SOA factor was termed as SOA (because the O/C of this factor was greater than 0.1—the typical O/C of primary emissions (Liu et al., submitted; posted at <http://aerosol.ucsd.edu/publications.html>), this factor likely represents an early generation of SOA components that may also contain substantial POA. Therefore, Cluster III particles are predominately primary.

Figure 1 shows a distinct population of organic-dominated single particles that are highly correlated with Cluster III and exhibit a lower d_{va} (pointed out by the Reviewer in Comment #10) and higher scatter light signal (pointed out by the Reviewer in Comment #11) than the other the single particles. Note that the conversion of d_{va} to d_g assumes that the particles are spherical and of uniform density; thus, the d_g axis does not apply to this subset of particle types. As noted above, these particles are linked chemically to primary organic components and exhibit a hydrocarbon-like composition. A similar externally mixed particle type was observed and reported by Cross et al. (2009).

The lower d_{va} suggests a lower effective density (where effective density is a function of the particle's material density and shape) compared with the other single particles. The higher integrated light scattering signal suggests a higher real refractive index. A potential explanation might be primary soot particles with an associated non-refractory organic component. For a large enough soot component, the combined particle real refractive index might be higher and the effective density (mainly due to shape) and, thus d_{va} , might be lower. That said, we currently have no other evidence that these particles contain a substantial nonspherical black carbon component, therefore we have rephrased as follows:

Revise the discussion of the split in Figure 1 (P3054 L7-13) to read: “A group of particles with relatively high organic mass fractions (~ 1) are distinct from the majority of the particles (Fig. 1a). This subset of particles are dominated by hydrocarbon-like organic aerosol (HOA) signals, have lower d_{va} 's and higher integrated scattering signals compared to the rest of the particles. As these particles are classified in Cluster III that may consist of substantial primary OM (Fig. 1b and Section 3.2), these particles may contain black carbon or other primary refractory components that modified the shape, density, or the combined real refractive index of the particles. A similar externally mixed, HOA-dominated particle type was observed in Mexico City and reported in Cross et al. (2009). However, more work needs to be done to fully characterize these particle types.”

11. Another curious feature of Fig. 1a is that the organic-dominated particles yield higher LS signals than the other particles. Y-axis values for organic-dominated particles with $d_{\text{geo}} > 325$ nm are almost universally > 5 , while the other particles virtually never cross this threshold. Do the authors have an explanation for this? As a follow-up to Comment 10, note that nonspherical particles will have a broader particle beam than spherical particles of the same d_{va} . This will tend to lead to lower-intensity LS signals, because a larger fraction of particles intersects the laser beam at lower laser intensities. This is contrary to the observed behavior, and further suggests nonsphericity/BC inclusion is unlikely.

Please refer to the response to Comment #10 above.

12. P3054 L14: This should be “overall duty cycle” not “overall chopper duty cycle.” The duty cycle under discussion contains but is not limited to the chopper duty cycle, as discussed correctly later in the paragraph. Is the saving duty cycle calculated as a function of time, or is the single value of 0.62 applied to the entire study? It seems to be the second, but it should be the first. The authors have previously noted the saving duty cycle dependence on particle concentrations, so a constant value is probably not warranted.

We have changed the “overall chopper duty cycle” to “overall duty cycle.” The overall duty cycle ranged from 0.2 – 1 with an average value of 0.62. We used the time-dependent overall duty cycle to calculate the time series of particle number concentration (Fig. S1) and the average duty cycle to calculate the average number concentration for the entire campaign (Fig. 2).

P3054 L16, change “duty cycle (0.62)” to “duty cycle (ranged from 0.2 – 1.0 with an average of 0.62).”

13. P3054 L23: It is not clear to me that the first two reasons for decreasing detection efficiencies for small particles are different (i.e. broadening of the particle beam beyond the particle/laser overlap vs. low intensities for small particles at the laser edges). Because the laser edges are not a step function, these two issues are linked and should probably be discussed together. Have the authors measured the relative importance of laser/particle overlap vs. laser size detection limit? This can be done easily by measuring LS detection efficiency as a function of aerodynamic lens position, with the lens walked across the laser (similar to the standard lens alignment procedure).

We have linked the two reasons together: Change “(i) widening of particle beam beyond the region of overlap of the particle and laser beams, (ii) low detection efficiency for small particles passing through the edges of the laser beam” to “(i) widening of particle beam beyond the region of overlap of the particle and laser beams or low detection efficiency for small particles passing through the edges of the laser beam.”

The relative importance of laser/particle overlap vs. laser size detection limit was not conducted in the field. Our AMS has been deployed for a field campaign and this test can be done in future projects.

14. The agreement between the LS-AMS and DMA-measured number concentrations for particles > 400 nm dva (P3054 L25-30) is strange in light of Fig. 2, which shows an LS detection efficiency of well below 50% for dva = 400 nm. While unit detection efficiency is seen for particles of 500-700 nm dva, Fig. 2 shows that the 400-500 nm region contains on the order of 50% of the total particle concentration. (Although it is a minor fraction of the total, LS detection efficiency also decreases for dva > 700 nm). Therefore the reported slope of 1.0 should not be obtained.

We are sorry that we failed to catch an error in our code. It turns out the lower limit 400 nm is not d_{va} but should be d_g . The scatter plot of the SMPS-measured and LS-ToF-AMS-measured number concentration is shown below. The reported slope of 1.0 was derived by forcing the linear fit through the origin. When intercept is allowed in the linear fit, we get a slope of 0.89 and an intercept of 6.25. We have made the following corrections to clarify:

P3054, L28-29 and P3055 L1-2, change “400- to 1000-nm dva (285- to 715-nm dg) particles agreed reasonably well (slope = 1.0 and $R = 0.7$; Supplement), while total concentration of 200- to 400-nm d_{va} (140- to 285-nm d_g) particles measured by LS-ToF-AMS was much lower.”

to

“560- to 1000-nm d_{va} (400- to 715-nm d_g) particles agreed reasonably well (Supplement)—the linear fit has a slope of 0.89 (the SMPS-measured concentration was 11% higher) and an intercept of 6.25, and the number concentrations correlated with an R of 0.7, Supplement), while total concentration of 200- to 560-nm d_{va} (140- to 400-nm d_g) particles measured by LS-ToF-AMS was much lower.” The same correction was made in the supplemental materials.

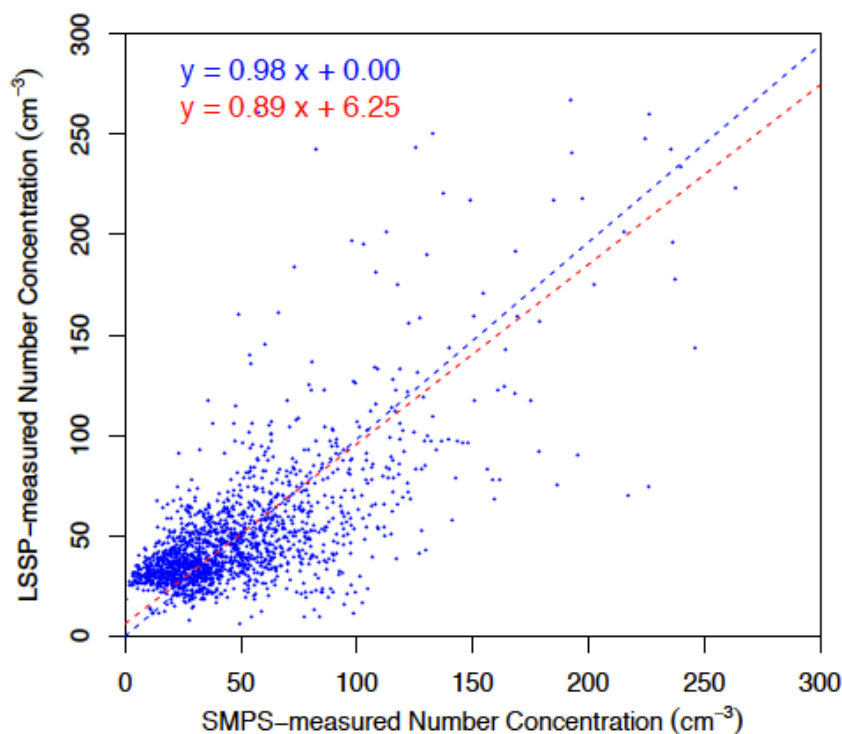


Figure 3. Correlation of the SMPS-measured and LS-ToF-AMS-measured number concentration for particles of 560- to 1000-nm d_{va} (400- to 715-nm d_g). The dashed line represents the best fit of the data by forcing the linear fit through the origin (blue) or by allowing a non-zero intercept (red).

15. P3055 L 24: “After comparing the physical signal identifying particle arrival (time to detector calculated from the time of light scattering, T_{LS}) to the chemical signal identifying particle arrival (time of mass spectrum, T_{MS}), each single particle was classified into one of three discrete particle types:” This is not clearly written. (1) “Arrival time” is ambiguous (this refers to T_{MS} , time from chopper opening (or midpoint of chopper opening?) to peak of the mass intensity profile, but is easily confused with particle arrival time at the vaporizer. (As a side note, is the ion transit time from vaporizer to detector estimated, or is this assumed to be negligible?) (2) There is no “physical signal” measured. Instead the predicted T_{MS} , calculated from particle velocity (chopper opening/midpoint to laser) and chopper-to-vaporizer distance (perhaps plus ion transit time) is compared to the measured T_{MS} . (3) Is T_{LS} the time from chopper opening/ midpoint to laser or the “predicted T_{MS} described in this comment? It seems the latter is meant, but the authors’ definition (“time to detector calculated from the time of light scattering, T_{LS} ”) is not clear, though somewhat suggesting the former.

We have re-written the sentences on P3055 L22-29 and P3056 L1-2 to make it clear: “Timing of the optical signals (T_{LS}) and chemical signals (T_{MS}) was retrieved by locating the maximum light scattering intensity and mass intensity from the light scattering (i.e., light scattering intensity as a function of particle time-of-flight) and mass intensity

profiles, respectively. T_{LS} and T_{MS} , respectively, represent the particle flight time from the midpoint of chopper opening to the laser and to the mass spectrometer (including the vaporization and ion transit time from the vaporizer to the time-of-flight mass spectrometer). Using the particle velocity (calculated from T_{LS} and the chopper-to-laser distance) and the chopper-to-vaporizer distance, the timing of particle chemical signals can be predicted (T_{MS_P}). By comparing timing of the predicted particle chemical signals (T_{MS_P}) with the timing of the measured chemical signals (T_{MS}), i.e., a scatter plot of T_{MS_P} versus T_{MS} , the vaporization and ion flight time (T_{MS_ION}) can be estimated by the y-axis offset. Using T_{MS} and the sum of $T_{MS_P}+T_{MS_ION}$, each single particle was classified into one of three discrete particle types: (1) “prompt,” for which the deviation of $T_{MS}/(T_{MS_P}+T_{MS_ION})$ from 1 was less than 20% (i.e., particles optically and chemically detected at the expected time offset); (2) “delayed,” for which the deviation of $T_{MS}/(T_{MS_P}+T_{MS_ION})$ from 1 was greater than 20% (i.e., T_{MS} significantly lagged $T_{MS_P}+T_{MS_ION}$); and (3) “null,” for which optical signals were detected, but no significant chemical signals were observed.”

16. There is a serious issue with the identification of null particle events (P3056). The 100-ion threshold used to distinguish null vs. prompt/delayed is greater than the expected number of ions for particles with d_{geo} extending well into the measured size range. Consider a 300 nm spherical particle with the effective density and molecular weight of ammonium nitrate, and the ionization efficiency of nitrate. Nitrate ionization efficiencies (IEs) for the HR-ToF-AMS are typically in the range of 10^{-8} to 10^{-7} ions/molecule. The 300 nm particle in question would yield 19, 93, and 185 ions, for IEs of 1×10^{-8} , 5×10^{-8} , and 1×10^{-7} , respectively. Put another way, for these IEs one would only expect to measure more than 100 ions for particles larger than 527, 308, or 245 nm (d_{geo}). The exact cutoff of course depends on the IE of the instrument used for this study, but it is very unlikely that this bias can be ignored. Note that the Cross et al. (2009) study to which the present results are compared utilized a C-ToF-AMS, which has a much higher IE and is therefore unlikely to be affected by this issue. Note that the estimated ions per particle discussed above assumed the molecular weight of nitrate. Particles dominated by higher molecular weight species (e.g. sulfate, organics) will contain fewer molecules, generate fewer ions, and be more strongly affected by this bias. Before the collection efficiency results can be evaluated, the authors must thoroughly address the implications of the 100-ion cutpoint.

We have corrected the threshold to be 6 ions not 100 ions, please refer to the uploaded document “Reply to the threshold issue” for details.

17. The differences in number vs. mass-based CE (P3056 L17) may also be due to the 100-ion cutpoint issue discussed above. It may also be due to problems in the AMS/DMA comparison, particularly if the constant density of 1.4 g cm^{-3} is used. See Ahlm et al. 2012. It also seems unlikely that there is sufficient mass below 180 nm d_{va} to account for the increase in mass-based CE (0.8) relative to number-based CE (0.5). Even if much of the mass is found in small particles, the decrease in AMS transmission efficiency for particles with $d_{va} < 100 \text{ nm}$ would prevent such an increase. The authors

can demonstrate that their hypothesis is plausible through analysis of AMS and DMA size distributions. Otherwise, this explanation should be removed.

The 100-ion cutpoint question is addressed in the uploaded document “Reply to the threshold issue”. We have calculated the mass fraction of particles smaller than 180 nm d_{va} from the AMS PToF mode measurements. The mass fraction of particles smaller than 180 nm d_{va} was 35% (the figure below shows size distribution of nonrefractory (NR)-PM₁ measured by the AMS). Assuming the CE values of particles smaller than 180 nm d_{va} (dominated by organics) and larger than 180 nm d_{va} were 1.0 and 0.5, respectively, the mass-weighted CE of NR-PM₁ was $0.35 \times 1.0 + 0.75 \times 0.5 = 0.725$, which is close to the mass-based CE of 0.8. We have made the following correction to make this point clear:

P3056, L15-16, change “smaller particles (<180 nm) may have had higher CE due to their near-zero sulfate content” to “smaller particles (<180 nm d_{va}), which accounted for 35% of submicron particle mass, may have had higher CE due to their low sulfate (15% of nonrefractory (NR)-PM₁) and high organic contents (75% of NR-PM₁).”

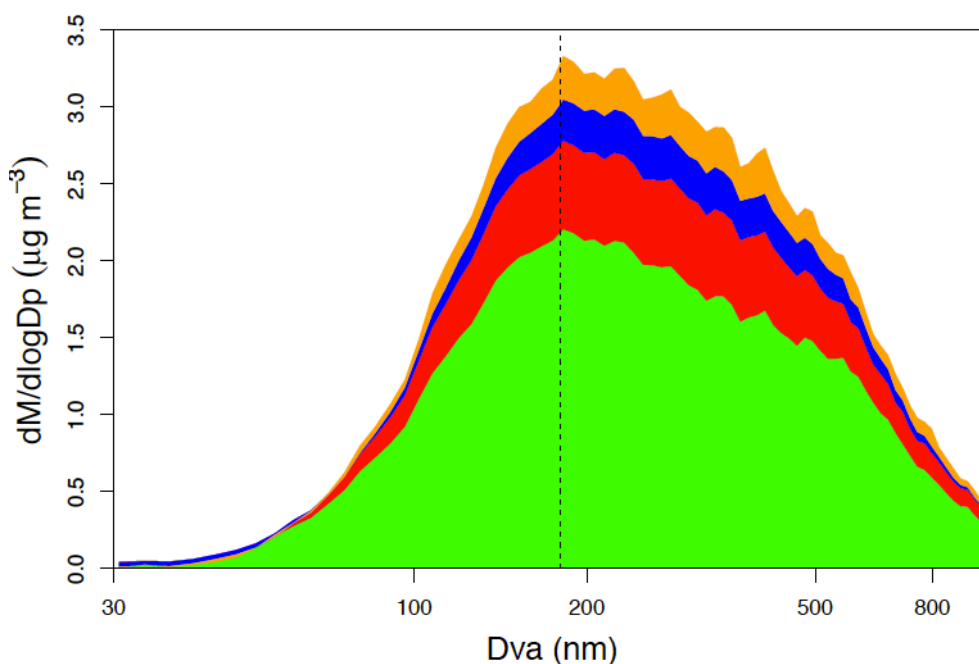


Figure 4. Size distribution of PM₁ measured by the AMS. The colors represent organics (green), sulfate (red), nitrate (blue), and ammonium (orange). The vertical line indicates 180 nm d_{va} .

18. The attribution of decreased CE in the 800-1000 nm d_{va} size range to dust (P3056 L22-24) seems quite speculative. It is possible that larger particles are inherently more difficult to vaporize. Have the authors tested this, e.g. with ammonium sulfate? Or perhaps there are size-dependent chemical differences (e.g. enhanced sulfate) that

contribute to a lower CE? This would be somewhat consistent with Fig. 1a, where the high-CE organic-dominated particles are not present at large sizes.

The Reviewer raised a good point. We have found an increase of sulfate mass fraction in large particles: the mass fraction of sulfate increased from 0.15 (in 700-800 nm particles) to 0.23 (in 800-1000 nm particles).

P3056, L22-24, change “Particles in 800- to 1000-nm d_{va} (570- to 715-nm d_g) had the lowest CE values, likely due to enriched dust components in this size range (Silva et al., 2000) that were not vaporized by the AMS.” to “Particles in 800- to 1000-nm d_{va} had the lowest CE values, likely due to enriched dust components in this size range (Silva et al., 2000) that were not vaporized by the AMS or because of the enhanced mass fraction of sulfate and decreased mass fraction of the organics (Fig. 1a).”

19. P3059 L 14-18: “The number concentration of Cluster II particles increased at night, likely resulting from temperature-driven condensation of this particle type under low-temperature conditions: :” It is likely that condensation of Cluster II-like material, rather than condensation of new Cluster II particles, is the driving factor (this is probably just a phrasing problem). But this also strongly suggests a gradient between Cluster II and the other clusters, despite the metrics for assessing gradients discussed on the previous page. It is worthwhile for the authors to take a closer look at the temperature dependent evolution of mixing state. How are particles classified in transitional periods when Cluster II-like material is partially condensed?

See response to the Comment #20 below.

20. Further to Comment 19, the identification of Cluster II as semivolatile material is questionable. The authors argue that the increase in number concentration of Cluster II particles overnight (i.e. lower temperature) implies semivolatile material. However, Fig. 7 indicates that all three clusters follow approximately the same diurnal pattern. It is possible there are differences in the time series that are not visible in this figure; in this case the actual number concentration time series diurnal patterns should be added. It would also be beneficial to show these time series for the entire campaign, and not just the diurnal patterns.

Responses to Comments #19 and #20:

We have taken a closer look at the relationship of the temperature and the three single-particle clusters. Since the differences in time series of the three clusters may not be visible in the average diurnal plot, as suggested by the Reviewer, we have shown the time series of the number fraction for the three clusters in the revised manuscript (replace the original Fig. 7 with the Fig. 5a below). Figure 5a shows that the number fraction of Cluster I particles co-varied with odd oxygen (and temperature, not shown), while both the number fraction of Cluster II and Cluster III particles anti-correlated with temperature, i.e., there were more Cluster II and III particles at night. Figure 5b shows that the number fraction of Cluster I, II, and III particles did not differ significantly at

different temperature ranges. Specifically, in the transition period (temperature 20-30 °C), the number fraction of Cluster II particles was nearly the same as the fraction under other temperatures. In addition, correlation of Cluster II particle number fraction with nitrate was poor, suggesting that there were likely other factors that affected the formation of Cluster II particles besides temperature, so the statement that Cluster II particles were semivolatile might not be justified. We have made the following revisions to clarify:

P3059 L9-10, change “which is consistent with the noon high particle number concentration for Cluster I (Fig. 7).” to “which is consistent with the correlation of the number fraction of Cluster I particles with odd oxygen (Fig. 7a).”

P3059 L14-18, change “The number concentration of Cluster II particles increased at night, likely resulting from temperature-driven condensation of this particle type under low-temperature conditions as suggested in previous studies (Huang et al., 2011; Lanz et al., 2007), given daily temperature fluctuations of 10–20 °C over the course of the measurements.”

to

“The number fraction of Cluster II particles increased at night and showed the opposite diurnal cycle to temperature (Fig. 7b), which is consistent with the previous findings that the less processed component accumulated and condensed onto preexisting particles during nighttime hours (Lanz et al., 2007). However, the correlation of Cluster II particle number fraction with particle-phase nitrate, whose formation is strongly dependent on temperature, was not found, suggesting that there might be other factors that affected the formation of Cluster II particles.”

P3059 L23-24, remove “The number concentration of Cluster III particles was high at night and continued until 1400 in the afternoon.”

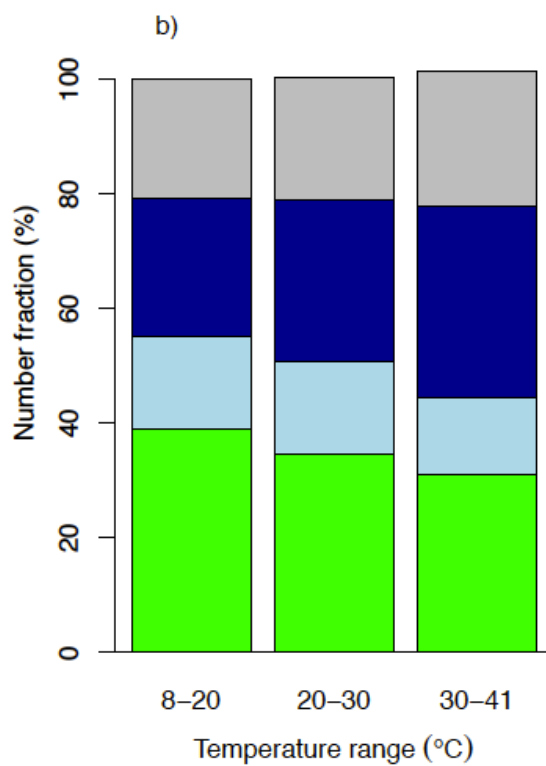
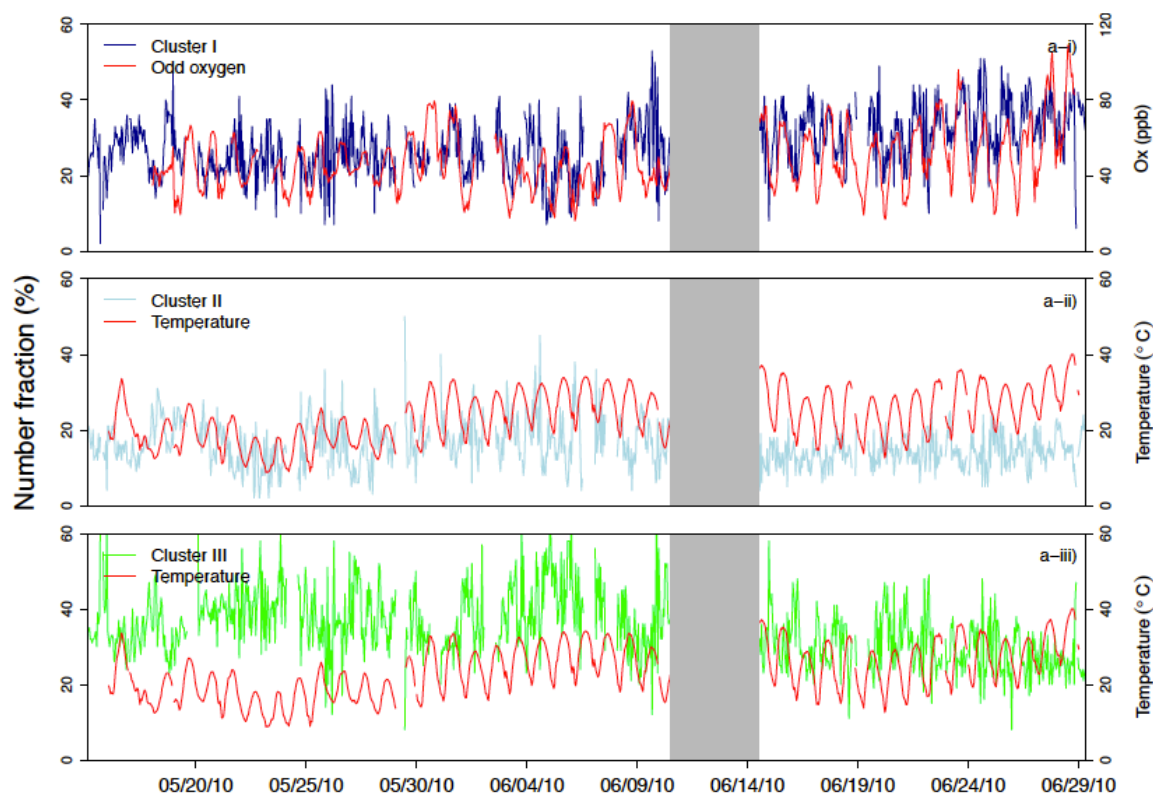


Figure 5. a) Time series of the number fraction for i) Cluster I (dark blue), ii) Cluster II (light blue), and Cluster III (green) particles. Time series of odd oxygen (panel i) and

temperature (panel ii and iii) are shown for comparison. b) Campaign-average number fraction of Cluster I (dark blue), Cluster II (light blue), Cluster III (green), and the minor cluster (grey) particles versus temperature ranges.

21. P3059 L18-20: “m/z 29 and 57 are markers for HOA and m/z 27, 41, 55, and 69 are cooking organic aerosol (COA) tracers.” This is overstated. As shown in a number of studies, these 6 peaks contribute strongly to both HOA and COA, although they trend in the direction stated. A characteristic time series and/or diurnal cycle is really required to identify the contribution of either. Given that both the suspected sources are primary, one would expect the particles to be externally mixed. Therefore it should be possible to distinguish HOA and COA through a more detailed analysis. One approach would be to investigate evolution of the frequency distribution of m/z 55/57 ratios for Cluster III particles as a function of time of day. If the particles are in fact an external HOA/COA mixture, then differences should be evident.

We agree with the Reviewer that the fragments m/z 27, 29, 44, 55, 57, and 69 contribute to both HOA and COA. We have investigated the ratio of m/z 55 to m/z 57 for Cluster III particles (Fig. 6 below). The m/z 55-to-m/z 57 ratio (the median ratio is ~1.5) did not show a clear diurnal cycle, suggesting that the HOA and COA components are not distinguishable. This is likely because of the similarity of the HOA and COA mass spectra (Mohr et al., 2009; 2012)—only the UMR spectra were reported for the single particles measured from the LSSP mode, while the HOA and COA components could be separated by different contributions of the oxygen-containing ions to m/z 55 in their HR spectra Mohr et al. (2012). We have made the following clarifications:

P3053 L20, after “software Sparrow 1.04A written in Igor” add “, which classifies the particles by their vaporization types and generates the physical (particle size in d_{va} , light scattering intensity) and chemical (unit-mass spectrum and mass concentrations of organics, sulfate, nitrate, and ammonium) data of single particles.”

P3059 L18-23, change “The average spectrum...and cooking oils” to “The average spectrum for Cluster III particles was characterized by m/z 27, 29, 41, 43, 55, 57, and 69, which are characteristic of both HOA and cooking organic aerosol (COA) components (He et al., 2010; Mohr et al., 2009; 2012). However, the HOA and COA components are not distinguishable due to the high similarity of their unit-mass spectra (Mohr et al., 2009; 2012), although both the HOA-influenced component (the nighttime OA factor) and the COA component were identified from the PMF analysis of the high-resolution ensemble mass spectra measured by the same LS-ToF-AMS during the CalNex campaign (Liu et al., submitted). The number fraction of Cluster III particles peaked at night, anti-correlating with temperature. Thus particles in Cluster III may be produced by a mixture of different sources, possibly including cooking oils and local unoxidized vehicular emissions at night.”

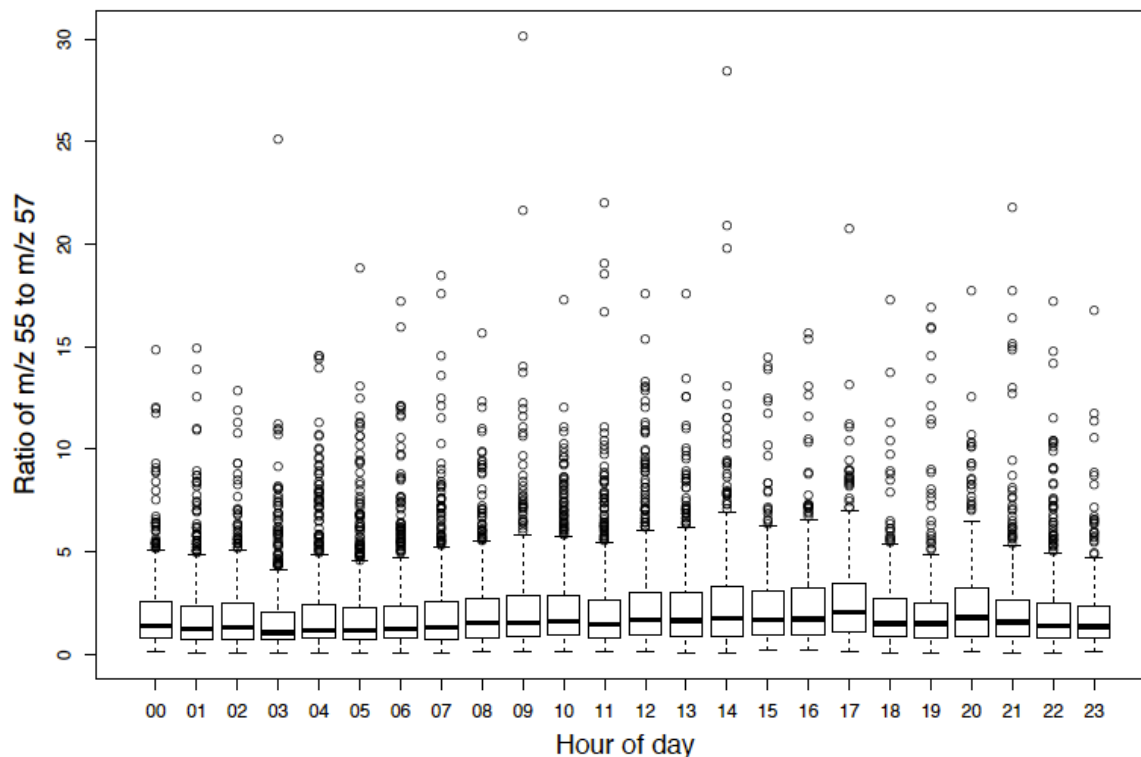


Figure 6. Box plot showing the diurnal cycle of m/z 55-to-m/z 57 ratio (from the LSSP mode measurements) for Cluster III particles.

22. P3059 L25 to P3060 L2: Correlation with $C_4H_9^+$ alone is insufficient to postulate HOA-dominated particles. At a minimum, m/z 55 and 57 should be compared within this subset to see if they are more HOA-like than the entire Cluster III. The argument for nonspherical particles is presently not convincing, as discussed in Comments 10 and 11.

We have re-considered this point. The subset of Cluster III particles (the organic-dominating particles) and the entire Cluster III particles had similar correlation with $C_4H_9^+$ and $C_4H_7^+$, so there is insufficient evidence to argue that the subset of Cluster III particles are more HOA-like than the rest of the Cluster III particles. We have removed the statement “The organic particles that had.....A similar result was observed in Cross et al. (2009).” on P3059 L25 to P3060 L2.

23. The identification of Cluster II with semivolatiles (see Comments 19 and 20) is made more questionable by Fig. 8. The mass fraction of this cluster does not increase during the night when temperatures are lower. If anything, the mass fraction is higher during the day. How does this fit with the interpretation of Cluster II?

Please refer to responses to Comments #19 and #20 for this question.

24. Section 3.3. The mass spectral comparison between ensemble and single particle factors supports the authors’ interpretation, although the Cluster II spectrum is quite interesting. The fraction of m/z 43 is extremely high; I cannot remember seeing a similar

SV-OOA spectrum. Do the authors have any thoughts on why this spectrum might be so unique?

We agree with the Reviewer that the Cluster II spectrum has a strong m/z 43 peak that does not often show up in ambient measurements. However, the Cluster II spectrum is highly similar to the spectrum of the low O/C alkane SOA factor identified from the ensemble PMF analysis, which also showed a strong peak at m/z 43 (Fig. 6 b-ii in the submitted manuscript), suggesting that the SOA formed from oxidation of alkane hydrocarbons might contribute largely to the Cluster II particles.

25. Section 3.3. In Fig. 8, the agreement between the cluster and the low O/C alkane SOA + low O/C aromatic SOA is quite poor as is the COA+PO SOA+NOA vs. Cluster III correlation. This figure does not provide evidence for a connection between the ensemble and single particle factors for either case. In fact, the agreement of Cluster II vs. COA+PO SOA+NOA and Cluster III vs. low O/C alkane SOA + low O/C aromatic SOA looks much better. Unless the cluster or ensemble traces are reversed in the figure, this very much calls into question the associations suggested by the authors. These contradictions should be addressed in Section 3.3. They must be resolved satisfactorily for Clusters II and III to be related to the ensemble factors. Otherwise this conclusion should be removed and the section rewritten accordingly.

Since the campaign-average diurnal cycle may mask differences and similarities in actual time series, we have modified Fig. 8 to show comparisons of single-particle cluster and ensemble-factor time series. The revised Fig. 8 is shown below. Although it seems that the single-particle Cluster II may compare well with COA + PO SOA + nighttime OA factors in the average diurnal cycle plot (the original Fig. 8), the mass fraction of COA + PO SOA + nighttime OA factors was 1.5-2 times higher than the mass fraction of Cluster II particles. In addition, the time series of COA + PO SOA + NOA factor mass fraction did not correlate with Cluster II particles ($r = -0.06$) but correlated with the mass fraction of Cluster III particles with $r = 0.63$. To clarify, we have added a table to the supplemental materials to show the cross-correlation between single-particle clusters and ensemble PMF factors (shown below). Therefore, Cluster III particles compare better with COA + PO SOA + nighttime OA factors than Cluster II particles both in time series and in mass spectrum. We admit that the comparison between Cluster II particles and the low O/C alkane or aromatic SOA factors was not good as shown in the revised Fig. 8. This discrepancy is likely due to 1) measurement and analysis uncertainties, 2) internally mixed particles that were split between more than one cluster or assigned to one of the minor clusters (IV, V, VI, etc.), or 3) the low detection of single particles that were smaller than 550 nm d_{va} (Fig. 2). We have noted the differences and made the following corrections in the text:

P3060 L26-28, change “The mass fraction of Cluster I particles had a similar magnitude and diurnal cycle to that of the high O/C alkane SOA component (Fig. 8), supporting the consistency of Cluster I particles with high O/C components.” to “The mass fraction of Cluster I particles had similar magnitude and time series to that of the sum of high O/C

alkane and aromatic SOA components (correlated in time with $r = 0.69$; Table S1), supporting the consistency of Cluster I particles with high O/C components.”

P3061 L5-7, change “The mass fraction of Cluster III particles and the sum of ensemble-derived Group III components co-varied, with low fractions during daytime and increased abundance at night.” to “The mass fraction of Cluster III particles and the sum of ensemble-derived Group III components co-varied ($r = 0.63$; Table S1), with low fractions during daytime and increased abundance at night.”

P3061 L7-13, change “There were some deviations ... and atmospheric processes.” To “There were some deviations in magnitude and time series for single-particle clusters and ensemble-derived components, especially for Cluster II particles that only poorly correlated with the low O/C alkane SOA factor ($r = 0.22$). The differences were likely due to 1) measurement and analysis (cluster, PMF, etc.) uncertainties, 2) internally mixed particles that were split between more than one cluster or assigned to one of the minor clusters (IV, V, VI, etc.), or 3) the low detection efficiency of single particles that were smaller than 550 nm d_{va} (Fig. 2). However, the broad match of single-particle clusters and ensemble factors confirmed that the factors reflected organic components of different origins and atmospheric processes.”

We have added a correlation table to the supplemental information to show the cross correlation between the three single-particle clusters and the ensemble factors:

Table S1. Cross correlation of the mass fraction time series for the three single-particle clusters (Clusters I, II, and III) and the ensemble-derived factors. Person’s correlation coefficients (r) are shown.

	High O/C alkane SOA + high O/C aromatic SOA	Low O/C alkane SOA	COA + PO SOA + Nighttime OA
Cluster I	0.69	-0.29	-0.62
Cluster II	0.02	0.22	-0.06
Cluster III	-0.67	0.18	0.63

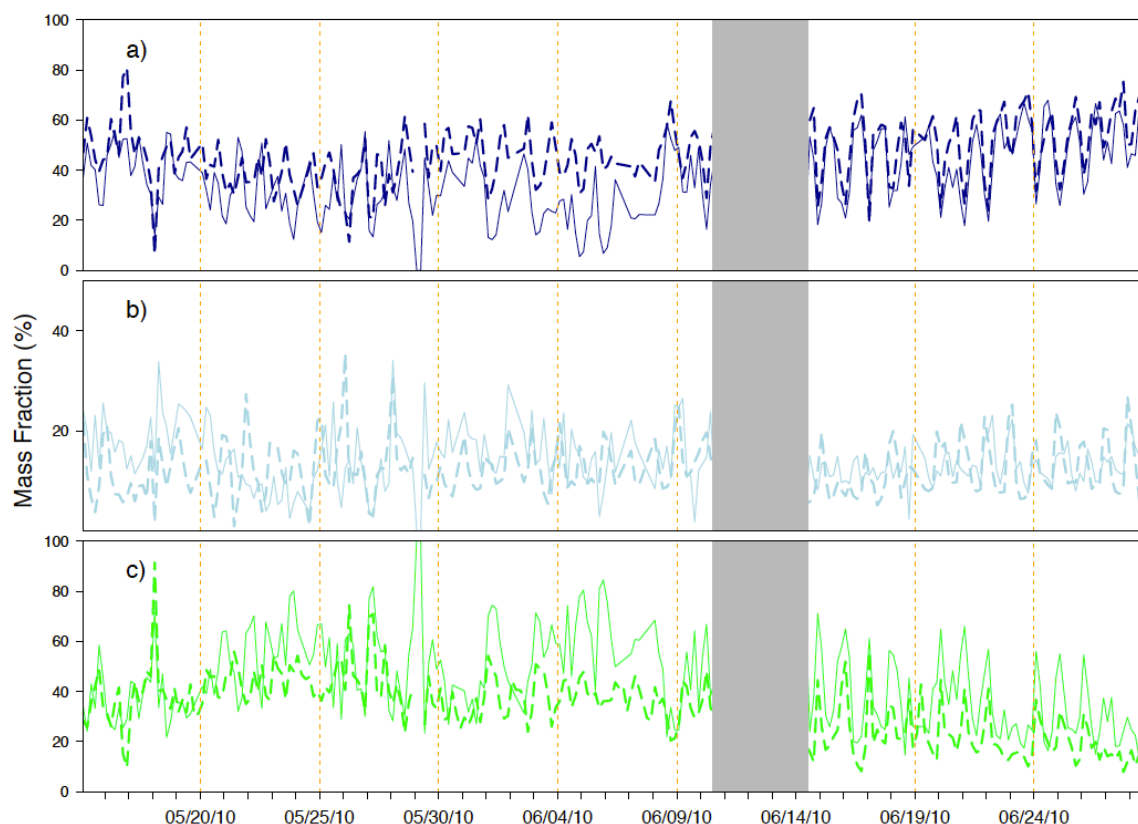


Figure 7. (new Fig. 8 in the revised manuscript) Solid lines show time series of the mass fraction for (a) Cluster I (dark blue), (b) Cluster II (light blue), and (c) Cluster III (green) particles. Dashed lines represent time series of the mass fraction for (a) the sum of high O/C alkane and aromatic SOA (dark blue), (b) the low O/C alkane SOA (light blue), and (c) the sum of COA, PO SOA, and nighttime OA factors (green) identified from ensemble measurements using PMF analysis (Liu et al., submitted). Measurements were averaged to 4-hour intervals.

26. Mass spectra and time series for the minor clusters (P3061 L10-11) should be shown, perhaps in the Supplement.

The mass spectra and time series of the number fraction for the minor clusters are now included in the supplemental materials. P3059 L3, after “the three major clusters are shown in Fig. 5a”, add “(The cluster centroids and time series for the minor clusters are shown in Fig. S3 and S4, respectively, in the supplemental information.)”

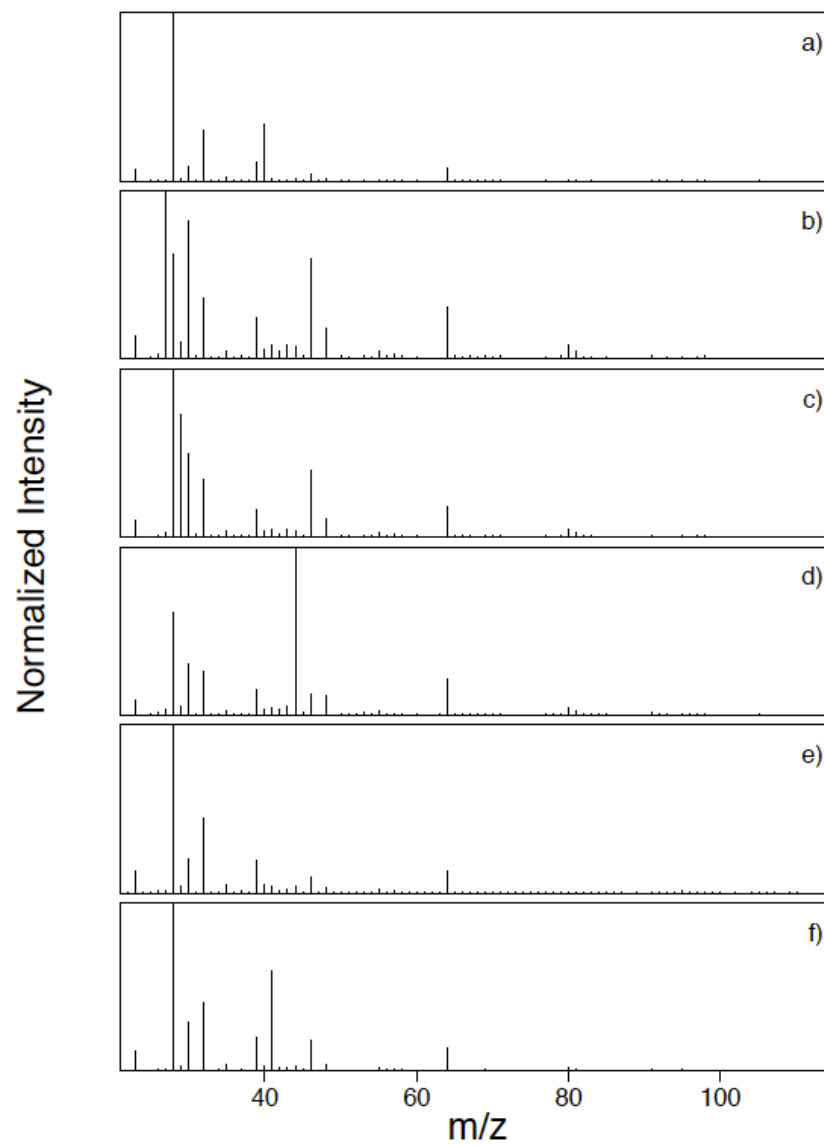


Figure 8 (Fig. S3 in the revised manuscript). Cluster centroids of the minor clusters in the 9-cluster solution, with panels a) to f) showing the centroids for clusters IV to IX, respectively.

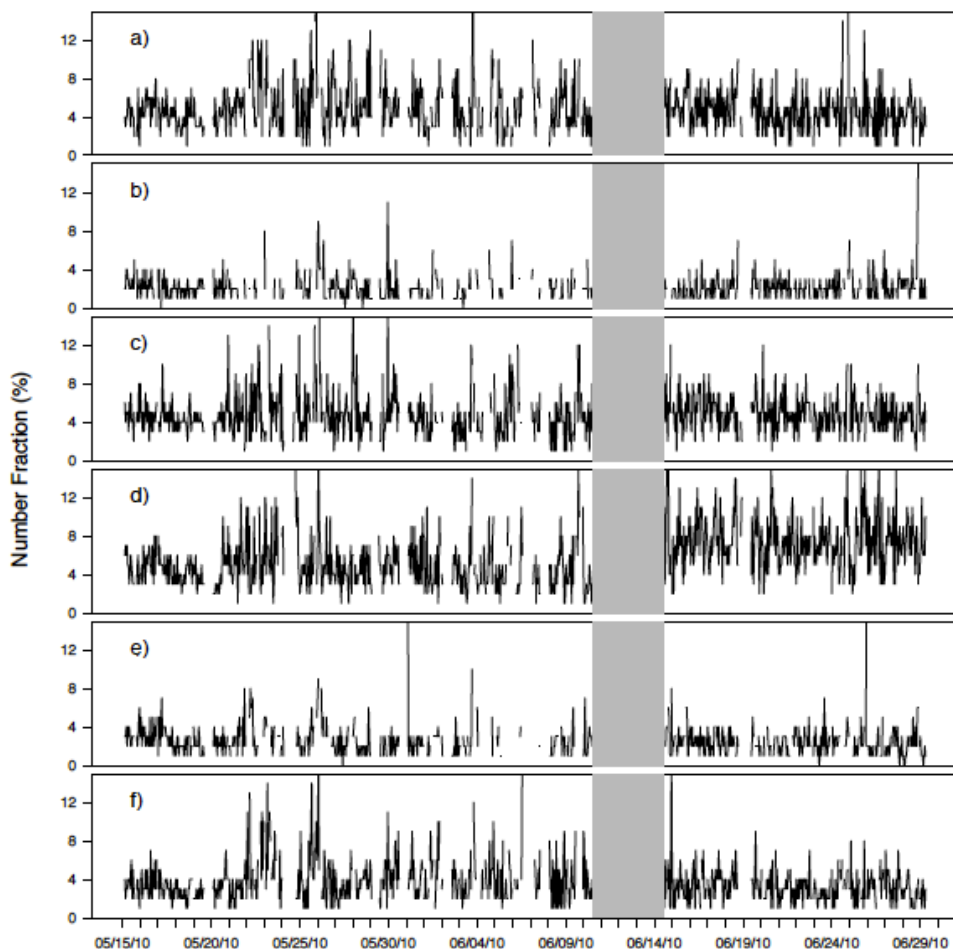


Figure 9 (Fig. S4 in the revised manuscript). Time series of the number fraction for the minor clusters in the 9-cluster solution, with panels a) to f) representing clusters IV to IX, respectively.

27. (Section 4: Concluding remarks): There are a number of issues with this section, related to the comments above. Specific issues are: (1) the prompt vs. null classification (P3061 L18-19, see Comment 16); (2) estimate of number-based CE for $d_{va} > 100$ nm (P3061 L23-24, see Comment 16); (3) explanation for discrepancies between mass- and number-based CE (P3061 L 24-26, see Comment 17); (4) identification of cluster sources (P3062 L5-7, see Comments 19-25); (5) agreement between ensemble and single particle factors (P3062 L10-12, see Comment 25).

We have made revisions in the main text according to the Reviewer's comments; please refer to the responses to the specific comments for details. We have made the following revisions to the Conclusion section:

Remove "This was lower than the overall mass-based CE of 0.8, likely due to higher CE for particles smaller than 180 nm d_{va} (130 nm d_g) (which typically had lower ammonium

sulfate and therefore bounced less in the vaporizer).”, since we do not have direct evidence for bounce rather than other factors causing this effect.

Change “Mass spectra and diurnal cycles of the three particle types” to “Mass spectra and time series of the three particle types.”

Minor Comments

P3049 L14: “chopper cycle (143-Hz frequency).” This frequency is set by the operator and can vary considerably. For the Introduction, it is better to note the typical range of values.

The chopper frequency ranges from 125-160 Hz. We have noted this range in the revised manuscript:

P3049 L14: remove “(143-Hz frequency)”.

P3052 L28-29, change “The chopper used during this study had a 0.02 duty cycle and operated at a frequency of 143 Hz.” to “The chopper used during this study had a 0.02 duty cycle and operated at 125 to 160 Hz frequency (set to 143 Hz) during the measurement.”

P3050 L13: Should give the version number and author for Sparrow (D. Sueper, U. of Colorado-Boulder). Version is given later (P3053 L19) but should be here instead.

P3053 L19, after “Sparrow 1.04A”, add “written by D. Sueper, Aerodyne Research Inc. and University of Colorado-Boulder.”

P3051 L7: Should this be 120, 120 and 60s? Otherwise the values don’t add up to 5 min.

We have changed “120, 120 and 80 s of every ~5 min” to “120, 120 and 80 s of approximately every 5 min.”

P3051 L12: “...are focused by a series of aerodynamic lenses: : :” Technically, this unit is a single aerodynamic lens that consists of a converging series of apertures.

We changed “are focused by a series of aerodynamic lenses” to “are focused by an aerodynamic lens system.”

P3051 L17: Suggest replacing “detector” with “mass spectrometer.” “Detector” is frequently taken to mean the MCP.

We changed “detector” to “mass spectrometer.”

P3051 L 29-30: “distribution” should be “distributions” (occurs twice).

This is corrected as suggested.

P3052 L9-10: “: : the chopper frequency is the fundamental clock for all ToF-AMS data acquisition.” This is true only in the PToF or LS modes.

We have changed “the chopper frequency is the fundamental clock for all ToF-AMS data acquisition” to “the chopper frequency is the fundamental clock for the PToF and LSSP mode ToF-AMS data acquisition.”

P3052 L11: “presences” should be “presence.”

This is corrected as suggested.

P3054 L11: “dominating” should be “dominated.”

This sentence has been re-written and “dominating” has not been used.

P3054 L27: “similar result” should be “a similar result.”

This is corrected as suggested.

P3055 L17: “nitrate and sulfate.” The m/z list would also include ammonium signals (m/z 15).

We have changed “nitrate and sulfate” to “nitrate, sulfate, and ammonium.”

P3055 L27: “into” should be “as.”

This is corrected as suggested.

P3059 L26: “mass concentration” should be “the mass concentration.”

This sentence has been removed (Comment #22 in this document).

P3059 L27: “correlated to” should be “correlated with.”

This sentence has been removed (Comment #22 in this document).

References:

Mohr, C., P. F. DeCarlo, et al. (2012). "Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data." *Atmospheric Chemistry and Physics* 12(4): 1649-1665.

Mohr, C., J. A. Huffman, et al. (2009). "Characterization of Primary Organic Aerosol Emissions from Meat Cooking, Trash Burning, and Motor Vehicles with High-Resolution

Aerosol Mass Spectrometry and Comparison with Ambient and Chamber Observations."
Environmental Science & Technology 43(7): 2443-2449.