We thank the Reviewer for the constructive comments and questions, 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.

The paper presenting the results of single particle analysis from ambient data taken with an LS-TOF-AMS during the CalNex campaign is an important study, and certainly has some unique analysis that links bulk AMS measurements to the single particle measurements. Unfortunately, there are some major issues with the discussion of the paper as detailed below, mostly revolving around the ion counting issues, and the signal to noise in the mass spectra due to those ion values. With the current discussion in the paper, and the fundamental issue with ion signal and the associated uncertainty with low ion counts in a mass spectrum, the paper cannot be accepted and must undergo significant reanalysis before it can be considered for publication.

Major Issues

1. Details on single mass spectra

More detail is needed on how single particle mass spectra were generated including number of MS added together (i.e. was it the full chopper cycle, or only a subset of the chopper cycle). How were the Hz units calculated for Figure 5. If the Hz units were calculated using the chopper cycle time as the base time unit, then ion Hz signals need to be divided by chopper frequency (143 Hz) to obtain actual ions counted. Applying this calculation to Figure 5 it becomes unclear how there are 100 ions (stated as the detection limit for the procedure) in the average mass spectrum in parts a-c. The largest signals are approximately 280 Hz which when divided by 140 yield 2 ions measured in the mass spectrum, summing across the mass spectrum from 20 to 100 m/z, it is clear that there cannot be 100 total ions in the mass spectrum. If instead of the entire chopper cycle only a subset of the mass spectra for each chopper cycle were co-added for a 100 microsecond particle vaporization, then the Hz value in Figure 5 should be divided by 1000 (assuming 100 microseconds of data was added together) to get the number of ions at each m/z.

To start with, please note that the correct units for single particle mass spectra are ions (bits*ns/single ion) and not Hz (i.e., ions per second). The unit shown in Fig. 5 (submitted manuscript) was bits*ns, and we have converted the y-axis values in Fig. 5 to be ions (divide bits*ns by single ion) in the revised manuscript. We apologize for our error on this in the originally submitted manuscript. Please refer to the uploaded document "Reply to the threshold issue."

The LSSP (as well as the PToF and BFSP) mode records full mass spectra as a function of time during each chopper cycle. Depending upon the specific operating conditions (i.e., chopper and pulser frequencies), approximately several hundred mass spectra are collected per chopper cycle. In the current configuration, there are 319 mass spectra obtained per chopper cycle. Each mass spectrum is baseline corrected to account for background signal (refer to Comment #3 of Reviewer 2) at each m/z, using the average of two user selected "DC" regions at the start and end of the chopper cycle. Single particle spectra are obtained by adding together a subset (~5 spectra) of the total number of baseline corrected mass spectra collected during a single chopper cycle.

We have added more details on how single-particle mass spectra are generated:

P3052, before the last paragraph, add "The LSSP mode records full mass spectra as a function of time during each chopper cycle. In the current configuration, there are 319 mass spectra obtained per chopper cycle. Each mass spectrum is baseline corrected to account for background signal at each m/z, using the average of two user selected "DC" regions at the start and end of the chopper cycle. Single particle spectra are obtained by adding together a subset (~5 spectra) of the total number of baseline corrected mass spectra collected during a single chopper cycle."

2. Ion counting issue

The following 3 excerpts from the paper reiterate the use of the 100 ion detection limit for analysis, which seems clearly at odds with the simple back of the envelope calculation of ions used for ionization efficiency calibrations included following the discussion.

page 3053 line 23-25 The detection limit, defined as the size at which particles produce detectable optical signals (S/N > 5) and chemical signals (>100 ions), was 180 nm dva (130 nm dg)

Page 3056 lines 2-4 The criteria of insignificant chemical signals includes a minimum sum of chemical signals for the mass intensity profile of 100 ions.

Page 3058 lines 14-18 The number of organic ions detected for each single particle is a function of the organic mass fraction (for a given threshold of 100 ions described in Sect. 3.1) and particle size (larger particles produce more ions). Sulfate and nitrate, the major inorganic ions, were found to be independent of organic cluster types (Fig. 5), i.e., sulfate and nitrate, respectively, accounted for 16 percent and 4 percent of single-particle mass for each cluster (on average).

This calculation comes from the standard Ionization Efficiency calibration calculations. Details on this can be found in Allan et al. (2003) and Jimenez et al. (2003) Calculation of ions from a 108 nm (physical diameter) - Assuming ammonium nitrate:

Volume of particle: pi/6*d^3 = 6.59584e-22 m3 Molecules in particle (assuming density of AN at 1720 kg/m3 and Jayne shape factor of 0.8): 7.2e6 molecules of Ammonium Nitrate

Given an Ammonium Nitrate ionization efficiency of 2e-7 or 2 ions per 1e7 molecules (approximate for V-ToF-AMS), the number of nitrate ions one would expect from a particle 108 nm in diameter is: 1.4 ions of nitrate

Ammonium has a relative ionization efficiency that is roughly 4 times higher, but the ratio of NH4 to NO3 would reduce that by a factor of 3.4 so one would expect approximately 1.2x the ions for ammonium: 1.7 ions of ammonium

Total of roughly 3 ions or ~30x lower than the assumed 100 ions for the lower detection limit.

One can easily calculate that the minimum diameter needed for 100 ions is quite a bit larger at: 343nm geometric diameter (keep in mind that ~50 percent of these ions will be associated with ammonium (lower than 20 m/z) and not nitrate which will have 45 or so ions associated with it). Organic molecules have a lower density, and hence a lower mass per volume, and a lower ion generation rate, although their RIE is slightly higher. This means for an organic particle or one with significant organic material, the lower diameter limit for 100 ions will likely be higher than the 343nm needed for ammonium nitrate.

Further, it is important to note that many of these particles are mixtures and are not pure components. This will further reduce the number of ions at a particular m/z especially if the material in the particle is organic which will spread the resulting signal over many more peaks in the mass spectrum (although a few key peaks will likely receive significantly signal).

Null calculations: If the threshold for a particle event is 100 ions, then how are null events determined? If a particle produces 50 ions that are clearly seen in the chopper cycle, is this deemed a null event and counted against the particle collection efficiency?

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.

3. How many ions are typically found at the “non-background” ions used in the mass intensity profile when there is not a particle present? All ions have backgrounds (look at the closed spectra of the MS mode), and a more complete analysis is needed here on the “average” non-particle ion count (Hz or absolute number of ions). This requires the saving of data from chopper cycles that do not have particles, and could also be compared to “null” particle events in terms of background ion signal.

As noted in the response to Comment #1 of Reviewer 2, all mass spectra collected during the LSSP mode for a given chopper cycle are background corrected at each m/z using the average of two user selected “DC” regions at the start and end of the chopper cycle. This approach accounts for ion backgrounds (such as observed in the closed spectra of the MS mode) on an m/z-by-m/z basis, which is important as each m/z has a different background level. The following analysis, done after this background correction, shows how well our approach works and underscores how null events are indistinguishable from non-particle events.

For the non-particle and null-particle events, there are typically 2-4 ions (Fig. 1 below), which are below the 6-ion detection limit. We have compared the ions associated with prompt and delayed, null, and non-particle events, using (a) the sum of non-background ions (i.e., m/z 15, 27, 30, 41, 43, 44, 46, 48, 55, 57, and 64) and (b) all the ions in the mass spectra (Fig. 1 below). In both cases, prompt and delayed particles have significantly higher number of ions than in null- and non-particle events, suggesting that null type particles have ions that are comparable to background ion signals.

We have added the above discussion. On P3056 L2-4, replace “The criteria…100 ions.” with “The criteria of insignificant chemical signals includes a minimum sum of chemical signals for the mass intensity profile of 6 ions. Using this criterion, the null particles had typically 2-4 ions (Fig. S2) that are comparable to the number of ions generated in the nonparticle events (chopper cycles that have no particles).”

Figure 1 (below) has been added to the supporting information as Fig. S2.

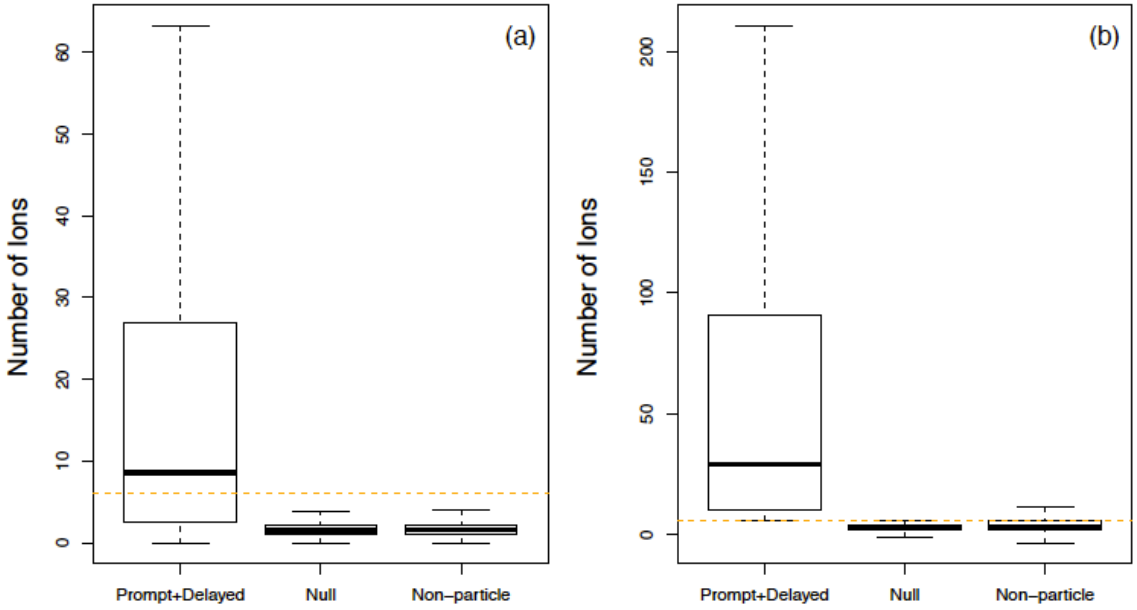

Figure 1. Comparison of number of ions associated with prompt and delayed, null, and non-particle events by using (a) the major ions including m/z 15, 27, 30, 41, 43, 44, 46, 48, 55, 57, and 64 and (b) using all ions (m/z 1 to m/z 111). Horizontal lines indicate the threshold of 6 ions.

4. Issue of particle coincidence: Have the authors considered the potential confounding issue of particle coincidence? If there is a 10 percent chance per chopper cycle that you sample a particle and save the MS data, then there is a 10 percent chance you will have coincident particles in those saved mass spectra. Do the authors have information on the number of chopper cycles saved vs number of total chopper cycles (as a function of time would be a bonus). This will give the reader an idea of the potential for coincidence.

As noted in Comment #2 of Reviewer 1, coincidence is not a significant issue, especially for particles of a given size. One can estimate the level of coincidence by calculating the average number of particles expected per chopper cycle. Figure 2 in the response of Reviewer 1 (see Comment #7 of Reviewer 1) shows that there were < 4000 particles/cm^3 (SMPS measurements for ~130-715 nm d_g, which approximates the size range that the LS-TOF-AMS samples) during the current study. This number concentration, along with a chopper frequency of 143 Hz, a chopper duty cycle of 0.02, and a sample flow rate of 1.4 cm^3/sec, indicates that on average 0.8 particles are sampled per chopper cycle (DeCarlo et al., 2006).

It is worth noting that for most of the time during this study the sampled number concentration was <= 1000 particles/cm^3 (see Figure 2 in Comment #7 of Reviewer 1), such that less than 0.2 particles were sampled per chopper cycle. Furthermore, Figure 2 (submitted manuscript) shows that the LS-TOF-AMS was not sensitive to most of the particles over this size range, such that there were significantly fewer particles per chopper cycle than even the 0.2 estimate. For example, 0.2 particles per chopper cycle is very close to 0.14 (i.e., 1/7), which represents the fastest sampling rate achievable with the current system, where there is a measureable particle in each chopper cycle sampled and the data saving and transfer process requires 6 further chopper cycles to complete (i.e., 7 chopper cycles per particle event). Thus, if the LS-ToF-AMS was sensitive to all of these particles, the ratio of the number of analyzed chopper cycles to number of total chopper cycles should be close to 0.2. As shown below (and expected), this is not the case.

Time series of the ratio of the number of analyzed chopper cycles to the number of total chopper cycles is shown in Fig. 2 below. This ratio ranges from 0 to 1, with an average and standard deviation of 0.62 and 0.14, respectively.

We have examined the light scattering (LS) profile (i.e., light scattering intensity as a function particle time-of-flight) for each LS event to identify potential particle coincidence. Particle coincidence is identified as multiple crossing of thresholds, which are defined as 5 times the standard deviation of the baseline of the light scattering profile. Using this criterion, the number of particle coincidence events is 0.3% of the sum of the prompt, delayed, and null particle events, suggesting that particle coincidence events are negligible.

We have added the discussion of coincidence before the last paragraph on P3052:

"Potential particle coincidence events were investigated by examining the light scattering (LS) profile (i.e., light scattering intensity as a function particle time-of-flight) for each LS event. Particle coincidence is identified as multiple crossing of thresholds, which are defined as 5 times the standard deviation of the baseline of the light scattering profile. Using this criterion, the number of particle coincidence events was 0.3% of the total particle events, suggesting that particle coincidence events are negligible. Particles in the coincidence events were excluded in the analysis."

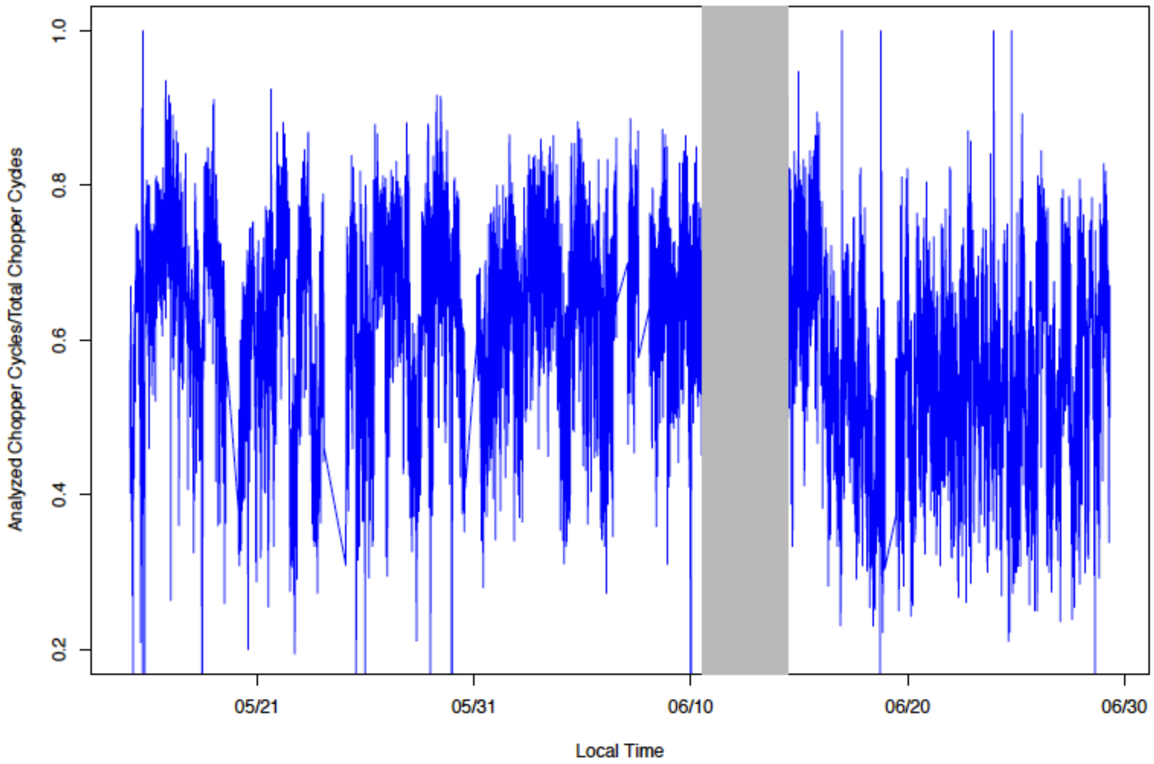

Figure 2. Time series of the ratio of the number of analyzed chopper cycles to the number of total chopper cycles.

5. Comparison to MS/PToF data (non-SP data): The comparison of the PMF results to the clustering results is certainly interesting, and appears to have some good correlations, but the paper would benefit from more comparison with the MS and PToF mode data. Specifically, on Page 3058 lines 14-18 (quoted above), were the values obtained for sulfate and nitrate, 16 and 4 percent respectively similar to the MS mode data for the sulfate and nitrate mass fractions of the total? If not, perhaps the authors could speak to the differences, and the implications for internal vs external mixing.

We have compared the average size distribution derived from LSSP mode and PToF mode (Fig. 3 below). The size distributions of LS-measured mass and PToF-measured mass match for particles with flight time larger than 0.0035 s, which corresponds to particles larger than 600 nm d_{va} (using the calibration curve shown in responses to Reviewer 1, Comment #3). This result is comparable to Fig. 2 (submitted manuscript) that shows the number concentrations derived from LSSP mode and PToF mode match for particles larger than 550 nm d_{va}.

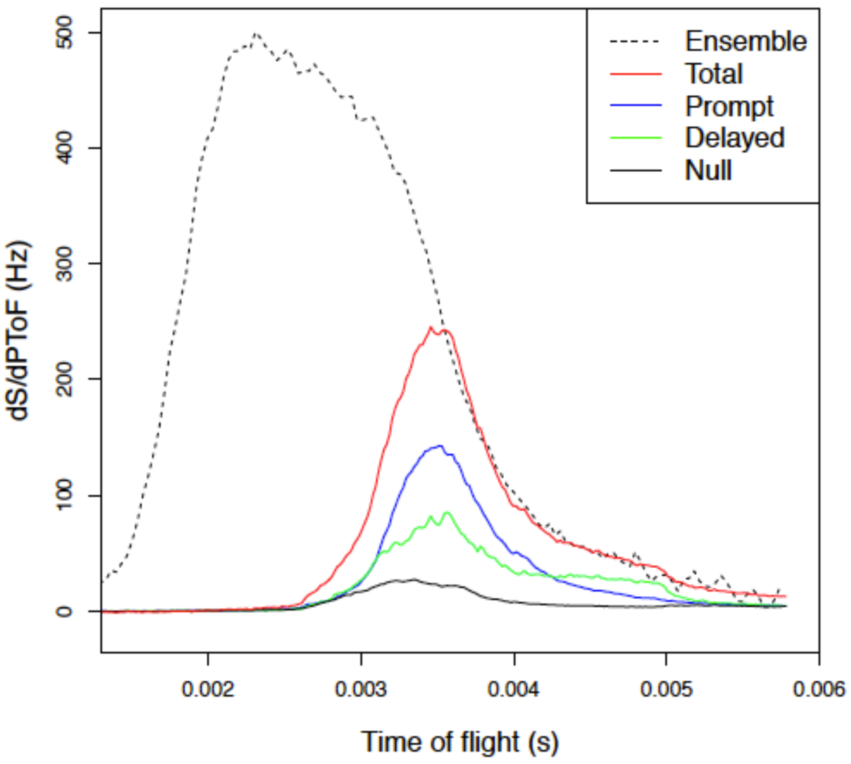

Figure 3. Comparison of campaign-average mass distribution as a function of particle time-of-flight of ensemble (dotted black line; PToF mode) and single-particle measurements (LSSP mode). The total (red) represents the sum of the prompt (blue), delayed (green), and null (black) particle signals measured by the LSSP mode.

The comparison of component mass fraction for single-particle and ensemble measurements is listed in Table 1 below. Mass fractions of organics and sulfate compared well. Single-particle measurements had a higher (5%) mass fraction of ammonium and a lower (6%) mass fraction of nitrate. The ensemble measurements (MS and PToF modes) show that ammonium and nitrate had nearly identical mass size distributions and ammonium correlated to nitrate with r = 0.8 in both single-particle measurements and the ensemble measurements, suggesting that these two components are internally mixed and the difference was not caused by missing of the particles smaller than 600 nm d_{va} during the LSSP mode measurements. Therefore the ~5% difference is likely due to the measurement uncertainty of the LS-ToF-AMS, which is within the expected uncertainty of ~25%. However, the mass fraction of organics, which is the focus for this paper, compared well between the LSSP and PToF mode measurements.

Table 1. Mass fractions calculated from the LSSP and MS mode measurements.

	Single Particle (LSSP mode)	Ensemble (MS mode)
Organics	66%	65%
Sulfate	13%	15%
Nitrate	4%	10%
Ammonium	15%	10%
Chloride	2%	0%

We have added Fig. 3 (above) and the corresponding texts to the revised manuscript:

The original Fig. 2 becomes Fig. 2a and the newly added figure (Fig. 3 shown above) becomes Fig. 2b in the revised manuscript. On P3054, add to the end of the second paragraph: "Figure 2b shows the comparison of campaign-average ion signals measured by the LSSP and PToF modes of the LS-ToF-AMS operation. Particles with time-of-flight greater than 0.0035 s, corresponding to 600 nm d_{va}, showed good agreement between the LSSP mode and PToF mode measurements, consistent with the agreement of number concentrations for particles larger than 550 nm d_{va} (Fig. 2a). Cross et al. (2009) demonstrated that the LSSP mode and PToF mode measured ion signals agreed for particles larger than ~350 nm d_{va}, indicating that the LS system in that work was more optimized."