Anonymous Referee #2

Lee et al., describe results obtained with the Aerodyne Soot-Particle Aerosol Mass Spectrometer equipped with a light scattering module to enable single particle characterization of both refractory and non-refractory particle constituents (for particles larger than the optical detection limit of the instrument). The manuscript focuses on four days of continuous sampling in downtown Toronto, from which the authors demonstrate the capability of the LS-SP-AMS through single particle k-means cluster analysis and bulk ensemble positive matrix factorization (PMF) approaches. The work is an important contribution to the field especially in the context of improving our understanding of the mixing state of ambient particulate matter (including combustion-derived rBC) within urban environments. The manuscript is well written and the insights drawn from the work warrant publication in ACP. The following comments should be addressed by the authors prior to final publication.

Thanks for the reviewer's encouraging comments.

General Comments

Grey area terminology:

- Throughout the manuscript the authors refer to 'low to mid-range aerodynamic diameter' this range should be explicitly defined. The first mention of an actual mid-range diameter is not found until P15337 L12.

  Response:
  Thanks for the comments. The low to mid range dva has been defined as particle size ranging from ~200-400 nm.

- 'HOA-rich': how is this classified?

  Response:
  As mentioned in Section 3.5.2 of the revised manuscript, particles with mass spectral fragmentation patterns of hydrocarbons are identified as HOA particles. In the current study, the HOA-rich particles are primarily composed of HOA-like organics (e.g. > 90 wt%).

- 'Nearly external mixing': I believe the authors wish to convey the fact that they measure nearly chemically pure, distinct, particle populations within the ensemble. For example, a chemically pure rBC-only particle type or HOA+rBC particle type or pure HOA particle type. The authors should carefully consider what they mean by 'nearly external mixing' and discuss external and internal mixing from the ensemble and single particle perspectives. Within any given urban environment there will be a gradient of mixing and the exact nature of this gradient is dependent on many factors.

The authors should make a concerted effort to more clearly define what they interpret as externally vs. internally mixed particle populations in the context of the real-world gradients of particle chemistry encountered in an urban environment like downtown Toronto.

Response:
Thanks for the reviewer's suggestion. We agree that HOA and rBC are likely gradually mixed in ambient aerosol particles as suggested by other reviewers. We have done an extensive re-examination of the single particle data with the specific focus of understanding the potential for gradual mixing between different particle types. Figures 10, S16, and S17 and Section 3.7 have been added to the revised manuscript to explicitly show the gradual mixing of HOA and rBC in both HOA-rich and rBC-rich particle classes. Furthermore, the degree of mixing of secondary species including nitrate, sulfate, and OOA in the accumulation mode (d_{va} peak at ~ 400 nm) is discussed in Section 3.6 and Figures 9 and S15 of the revised manuscript.

- In paragraph 2 of P15325 the authors introduce the term refractory BC (rBC) in connection with the SP2-defined measurement technique. Prior to (and following) this the authors use 'BC'. I think it would be helpful to the general reader to include a sentence describing the difference between rBC and BC. The authors should make a point not to switch back and forth between using these two terms throughout the manuscript, if possible.

  Response:
  Thanks for the comment. rBC has been used more frequently than BC throughout the manuscript unless a more general description of ambient BC issues is needed.

- The authors make an effort to differentiate the SP-AMS from the LS-SP-AMS and this ends up causing more confusion than clarity. I recommend that they use LS-SP-AMS throughout the manuscript and describe the menu-switching modes of operation to differentiate single particle from ensemble modes of operation. The introduction of the LSSP mode (which is not defined, when introduced on P15328, L6) further confuses the acronym-overloaded of the text. Consider removing this, while still clearly defining the single particle mode of operation.

  Response:
  LS-SP-AMS has been used throughout the manuscript unless more general SP-AMS issues are discussed. To avoid confusion, "LSSP mode" has been changed to "LS mode".

- P15331, L23: Authors should specify the # of clusters that can be combined with the CAP program – not just 'a few'.

Response:
We didn't perform any testing on the maximum number of clusters which can be handled by the CAP program. In the current study, we successfully combined 4 nitrate related clusters to a single nitrate-rich cluster. Therefore, we decided to keep the current sentence in the revised version.

Specific comments:

P15324, L20-21: The general reader may not be familiar with 'the conventional interpretation' of PMF results and as such, this language should be avoided or more concretely defined.

Response:
As suggested by the reviewer, "conventional" has been removed from the last sentence of the abstract.

"The similar temporal profiles and mass spectral features of the organic classes identified by cluster analysis and the factors from a positive matrix factorization (PMF) analysis of the ensemble aerosol dataset validate the interpretation of the PMF results."

P15325, L1: Do the authors mean to highlight the varying morphology of the 'coating' on the BC or the particle as a whole.

Response:
We would like to highlight the varying morphology and thickness of the coating on the BC. To make it clear, additional description about coating morphology (e.g. partly coated and embedded) has been added to the sentence.

"Coatings on BC aerosol surfaces with varying morphology (e.g. partly coated and embedded) and thickness have been observed using electron microscopy (China et al. 2013, 2014)."

P15326, L18: Should read 'flash vaporize at 600 C'

Response:
Done

P15327, Section 2: Should include a more comprehensive description of the sampling location and sampling inlet configuration relative to near-by source of pollution. Specifically, proximity to major roadways and COA sources (such as food trucks, carts, etc.) would help place the results in a more relevant context. If possible, inclusion of a map of the area surround the sampling site may be particularly useful for the reader.

This inclusion would also allow the authors to draw finer lines of connectivity between their results and important sources of particulate matter within busy, active, urban environments.

They should also make a point of identify the days of week across which sampling occurred (weekday vs. weekend) – and the difference that makes to likely emission sources in the area.

Response:
Thanks for the reviewer's suggestions. A new paragraph has been added to Section 2.1 (Sampling location and instruments) to describe the sampling location and inlet configuration. A map showing the sampling location and surrounding environment has been added to the supplementary information (Figure S1). The sampling period was from Tuesday evening to Saturday afternoon, which has been added to Section 2.1.

P15327, L22: V-mode should be described. This is a meaningless term to readers not familiar with the AMS. Define mass resolving power for your instrument, during this campaign.

Response:
The sentence has been modified.

"The ions are then detected by a high-resolution time-of-flight mass spectrometer operated in V-mode, which provides a lower mass resolving power (~2000) but a higher sensitivity compared to W-mode (mass resolving power ~ 4000) (DeCarlo et al. 2006)."

P15327, L23: It would be helpful to add a sentence describing the motivation behind running the instrument in laser-on vs. laser-off mode throughout your sampling campaign. To the unfamiliar reader, this just looks like you are cutting your duty cycle on sampling rBC down by 50%.

Response:
Thanks for the suggestion. A sentence has been added to Section 2.2 of the revised manuscript.

"The SP-AMS was operated with two vaporizer configurations during sampling, laser-on and laser-off, to maximize the information obtained and to enable comparisons and correlations between the two different vaporizers.. In particular, previous work has shown vaporizer-dependent differences in collection efficiencies and fragmentation patterns (Onasch et al. 2012; Willis et al., 2014)."

P15328, L10: Consider adding a header here: Calibration

Response:
A new heading "Calibration and ensemble data analysis" has been added to Section 2.3.

P15328, L22-28: I would strongly recommend removing the equation for effective density from within the text and writing the formula out with label: Eqn. 1. In fact the authors should define effective density in this section. Once organized as Eqn 1, the authors can more easily refer back to this equation later in the manuscript (P15337 L4-5).
- In connection with the discussion of effective density – as the authors point out – highly non-spherical particles (i.e. soot agglomerates, dominated by rBC) will appear at lower dva values than typical accumulation mode particles. Given the importance of this type of particle to results discussed in this manuscript, the authors should briefly discuss the influence that highly non-spherical shape has on the particle beam width as it transits the time-of-flight chamber of the LS-SP-AMS / intersecting different regions (intensities) of the 405 nm scattering laser and 1064 SP laser.

Response:
Thanks for the suggestion. The equation has been defined as Eq. 1 in the revised version. The highly non-spherical particles result in a wider particle beam than the spherical particles. The SP laser (1064 nm) and particle beam overlapping remains uncertain and has to be further investigated by SP-AMS community. Our group recently studied the particle-beam width of ambient BC particles in urban environments and laboratory-generated BC standard (i.e. Regal Black). We observed that the particle beam width of BC particles decreases with coating thickness. In particular, the collection efficiency of bare Regal Black particle is ~0.6 due to incomplete overlap between SP laser and particle beam (Willis et al. 2014). Such information has been provided in Section 2.3 and 3.1.

The overlapping of LS laser (405 nm) and particle beam is unlikely an issue because the LS laser beam is not focused and diverges in order to ensure a complete overlapping. This information is provided in the original manuscript.

Reference: Willis, M. D., Lee, A. K. Y., Onasch, T. B., Fortner, E. C., Williams, L. R., Lambe, A. T., Worsnop, D. R., and Abbatt, J. P. D., Collection efficiency of the soot-particle aerosol mass spectrometer (SP-AMS) for internally mixed particulate black carbon, Atmos. Meas. Tech. Discussion, 7, 5223-5249, 2014.

P15329, L10: Consider revising sentence: 'overlaps perpendicularly with the particle beam _ 0.265 m downstream of the chopper and _ 0.130 m upstream of the tungsten vaporizer as shown in Fig. 1.

Response:
Done

P15329, L15: The authors should define what they mean by 50% cut-off diameter.

Response:
The 50% cut-off mobility diameter has been defined.

"The 50% cut-off mobility diameter (d_m) (i.e., a diameter that represents 50% counting efficiency of particle number when compared to a CPC) of our light scattering module determined using dry NH_4NO_3 particles is ~250 nm,..."

P15329, L19: should read: 'may have a lower cut-off dva than: : :.'

Response:
Done

P15330, L2: Consider adding a sentence describing the width of the chopper slit used in the LS-SP-AMS (0.5, 1, 2%) and how this width would impact the ability to accurately size (LS_dva) and predict arrival times at the vaporizer.

Response:
Thanks for the suggestion. A sentence has been added to describe the chopper slit throughput in Section 2.2.

"A single slit chopper with ~2% throughput was used in our LS-SP-AMS."

Furthermore, two major uncertainties for particle sizing measurement have been added to Section 2.5 of the revised version:

"There are two major timing uncertainties for particle sizing measurement: 1) the initial time of the chopper cycle due to the slit width of the spinning chopper (~2%), and 2) the extra time required for vaporization, ionization and detection."

P15330, L7: Avoid use of term 'rotten'

Response:
The term "rotten" has been changed to "noise" throughout the revised manuscript as suggested by another reviewer.

P15330, L9: Is it possible to relate the >/= 6 ions/spectra threshold to an estimate of mass-based (fg/particle) detection limit?

Response:
It is not straightforward to provide an estimate of mass-based detection limit based on the ion-based threshold as all chemical species (nitrate, sulfate, ammonium, organics, black

carbon) have different relative ionization efficiency (RIE) in AMS. That is why we use ion-based mass spectra in our manuscript most of the time. However, using 6 ions and mass-based ionization efficiency of rBC determined in the current study, it can be estimated that the detection limit of a pure rBC single particle is 25 fg of rBC per particle. This information has been added to the last paragraph of Section 3.8.

"Using 6 ions as a detection limit of a single particle (i.e. a criteria for “prompt” particle type) and a mass-based ionization efficiency of Regal Black determined by calibration, it can be estimated that the detection limit of a pure rBC single particle is ~25 fg of rBC per particle."

P15330, L13: It would be informative to include the Gaussian distribution figure in the supplemental. Why did the authors choose the 3 sigma boundary as their classification of prompt vaporization-ionization? What is the physical explanation for an ‘early’ ion pulse arrival time?

Response:
A distribution figure has been added to the supplementary information (Figure S2). We choose the 3 sigma boundary because we would like to include most of the particles within the Gaussian boundary. The physical meaning of "early" particle type is not clear. However, they contribute less than 0.2% of particle LS trigger events (Table 1). The information has been added to the second paragraph of Section 2.5.

"The delayed particle type can be due to the phenomenon of particle bounce upon impact with the thermal vaporizer surface (Cross et al. 2009) but the physical meaning of early particle type remains unclear."

P15330, L25-27: The authors reference Fig S1 as evidence of clear separation of the prompt single particles from all other particle types. Although it is clear that their 3 sigma classification for prompt particles has identified the vast majority of real- LS events from noise events – it is not clear that from the graph that early or delayed particle vaporization types are effectively identified. Rather than plotting the MS ion scatter plot vs. LS_dva – the authors could consider plotting and differentiating the early, prompt, and delayed particle types vs MS_dva, whilst leaving out the 25% of LS events that were noise. This, combined with the Gaussian distribution of arrival times may provide a more comprehensive separation of the prompt-vaporization particle types from all other non-noise particle events.

Response:
Thanks for the reviewer's suggestions. Two new plots have been added to Figure S3e and S3f in the supplementary information. These scatter plots (i.e. MS total ion counts vs. MS d_{va}) show how prompt, early and delayed particle types are separated by our particle type classification procedure. It can be found that early and delayed particle types are concentrated at smaller and larger particle size respectively, which is quite reasonable.

- It is very interesting to see the prominence of single particle events that appear in S1b that result from having the SP laser ON – particles comprised of rBC, rBC+HOA. This begins to show the potential for determining a size and chemistry-dependent collection efficiency for the LS-SP-AMS sampling across a matrix of particle types encountered in an urban environment. Did the authors complete any size-dependent CE assessments (whether from the perspective of non-spherical rBC-dominant particle types or larger, accumulation mode particles with higher SO4 content)?

Response:
It would be useful to study a size and chemistry-dependent collection efficiency of SP-AMS with light scattering module. However, the focus of this paper is to investigate the mixing state of carbonaceous aerosols in an urban environment using LS-SP-AMS. Our group has published a paper in Atmospheric Measurement Techniques Discussion that investigated the collection efficiency of rBC-containing particles using the beam width probe approach (Willis et al. 2014). This is an important issue to be future investigation.

Reference: Willis, M. D., Lee, A. K. Y., Onasch, T. B., Fortner, E. C., Williams, L. R., Lambe, A. T., Worsnop, D. R., and Abbatt, J. P. D., Collection efficiency of the soot-particle aerosol mass spectrometer (SP-AMS) for internally mixed particulate black carbon, Atmos. Meas. Tech. Discussion, 7, 5223-5249, 2014.

P15331, L1: The authors should explain their justification for using only the prompt particles in their cluster analysis. Did the early and delayed particle types show consistently lower total ion counts for the same LS_dva when compared to prompt?

Response:
According to our single particle classification approach, early and delayed particle types should have ion counts ≥ 6 ions. Otherwise, they should be classified as "Null" particle type. We haven't tried to include these two particle types in our cluster analysis. The major reason is that we would like to have a more meaningful particle size information. Also, as shown in Table 1, the two particle types only contribute ~1% of the particle LS trigger events. Therefore, we believe the final results and conclusions would not be affected. This information has been added to revised version.

"Including other particle types with a lower confidence on their PToF d_{va} (i.e. early and delayed) to the cluster analysis would not affect the major observations, as they contributed only ~1% of the particle LS trigger events (Table 1)."

P15332, L12-16: Graph or correlation coefficient should explicitly stated comparing LSSP-AMS mass vs SMPS. SMPS assumptions about particle shape and density should be given.

Response:
Figure S5 and some calculation details have been added to the supplementary information to discuss the CE correction for different particle types based on single particle observation. All the calculations and comparisons between LS-SP-AMS and SMPS particle mass are shown there. A sentence has been added to the manuscript as shown below:

"The total particle mass loading measured by the LS-SP-AMS is similar to that inferred from a simultaneous measurement using a Scanning Mobility Particle Sizer (SMPS, TSI Inc.,) (slope ~ 1.02, R^2 = 0.76), suggesting that the estimated CEs for NR-PM, vaporized from the heated tungsten vaporizer, and rBC, vaporized from the laser vaporizer, are within reasonable ranges (see Figure S5 in supplementary information)"

P15332, L25: Should read 'average ensemble size distributions..'

Response:
Done

Section 3.1: Opportunities to link the observations of particle chemistry back to details about the sampling site and potential sources – this would follow from a more thorough description of the sampling site back in section 2.1.

Response:
Thanks for the suggestions. Two sentences in Section 3.1 have been modified to link the observations to the sampling site characteristics described in Section 2.1.

"Since ambient rBC is only emitted from primary sources, this suggests that a significant portion of sampled rBC was freshly emitted or only slightly aged particles. This is consistent with the fact that vehicle emission are a major local source of rBC in the downtown area of Toronto."

"The relatively low fraction of oxygenated organic aerosol indicates that the sampling site was strongly influenced by local anthropogenic sources, such as vehicle and cooking related emissions, matching well with the site characteristics (see Section 2.1)."

P15334: The authors introduce Figure 4 at this point in the paper, but only describe the PMF portions of the analysis. The next mention of Figure 4 comes in the very last section of the paper (3.7) – connecting the cluster analysis results (also displayed in Figure 4). Splitting the descriptions of Figure 4's overlapping content is confusing and the authors should re-consider reorganizing this content so that the resultant figure is more coherent with the text or vice versa. One thing that draws the reader's eye is the presence of the three red rectangles in the figure – which are highlighting areas of agreement and disagreement within the data. These are not mentioned until P15342, L23.

Response:
Thanks for the reviewer's comment. This manuscript involves many observations obtained from different data analysis. After considering many factors, we would like to keep the current paper structure. To improve the connections between Figure 4 and discussions, the Figure 4 captions has been modified and an additional sentence has been added to the end of Section 3.2.

Section 3.2: "The comparison between PMF and single particle cluster analysis (Figure 4, line vs. filled area) will be discussed in Section 3.9."

Figure 4 Caption: "Time series (local time) profiles of rBC, PMF factors of organic components (from laser off mode MS measurements) and different organic clusters (from laser on mode LS measurements). The red rectangles indicate three major rBC and HOA peaks throughout the sampling period."

P15339, L16: How does the rBC-rich cluster's C1/C3 ratio of 0.53 impact the quantification of total BC mass concentration, given that the frag table assumes a C1/C3 ratio of 0.61? Related to this, it is not clear why the authors choose to use the C1/C3 ratio obtained from regal black instead of that acquired from the HR analysis of the ambient rBC (which is used in the case of the C4/C3 and C5/C3 ions as described in Table S2).

Response:
This is a very good question. A significant signal of C1 fragment can be contributed by organic aerosol based on the laser off measurements (or standard AMS measurement). The AMS community is still trying to improve the estimation of the C1 signal from rBC using the C1/C3 ratio. Therefore, we decide to use C1/C3 ratio of 0.61 obtained from Regal Black in the current study, which is also a common practice within the community at this stage, and provide the single particle C1/C3 ratio as a reference for future development.

P15341, L14: The authors should take care in explicitly stating that the rBC-rich particles they measure have a 'thin HOA coating'. As the radiative impacts of this particle type vary dramatically based on the nature of the associated HOA on the surface of the BC, it may not be appropriate to classify this as a thinly HOA-coated rBC particle–based on the LS-SP-AMS measurements alone. It is certainly clear that the authors have a particle population that is comprised of rBC+HOA components, but how they are distributed within the particle itself, remains ambiguous with the current instrumentation. Similarly, classifying HOA coatings as 'thick' may also be inappropriate.

Response:
The authors agree that it may be inappropriate to describe internally mixed rBC and HOA that observed by LS-SP-AMS as a thinly or thickly coated particles as we don't have direct evidence of particle morphology. To avoid misunderstanding, the descriptions of

"thin" and "thick" coatings have been minimized unless we have clearly stated the assumption. In particular, the sentences in Section 3.8 have been changed in the revised reversion.

"Quantitatively, the single particle data analysis demonstrates that: (1) a significant portion of HOA- and COA-rich particles (> 90%) with particle d_{va} larger than ~200 nm did not contain a detectable amount of rBC, e.g., organic-rich particles containing a small rBC core or no rBC (with a mass contribution of rBC to the HOA- and COA-rich classes about 3% on average), and (2) the rBC-rich particles were mixed with ~28 wt% HOA-like material on average, e.g., a thinly HOA coated rBC particle, assuming uniform coating thickness. For example, applying a simple core-shell spherical structure (i.e. rBC core plus uniform HOA coating), a 200 nm d_{va} rBC-rich particle has a coating thickness of ~10 nm with HOA and rBC densities equal to 0.9 and 0.8 g/cm^3, respectively."

Comments on Figures

Obviously, the authors put a tremendous amount of effort into this analysis and as a result of the complexity of the dataset and diversity of analysis approaches applied, have generated many figures. I worry that the sheer number of figures obscure the main take home points of the manuscript. Of the 8 figures within the manuscript body itself, Figures 7 and 8 stand out as important demonstration of the power of the technique for single particle characterization. Given the information in Figure 7, Figure 5 becomes somewhat redundant and the color scheme used in Figure 5 leads to some confusion (red, blue, green – signifying metrics that are not sulfate, nitrate, organic). The same comments applies to the colors used in Figure S9. The data displayed in Figures 2a and 4 could also be re-combined into a single figure, along with appropriate reorganization of text within the manuscript itself. Figures S2 and S10 seem unnecessary. Their content could be effectively conveyed with text alone.

If Figure 5 is kept in the manuscript, the authors should plot their empirical data that comprises the NH4NO3 d50 line. Likewise, this data could be included in Figure S9, if it remains in the final manuscript.

Response:

Thanks for the reviewer's suggestions on our figures. The empirical data that comprise the NH_4NO_3 d_{50} line have been added to Figure 5 and S12. The color scheme used in Figure 5 and S12 has been changed. We decide to not combine Figures 2a and 4 as it would it more difficult to follow the discussions. Figure S4 and S13 are not removed because they give the reader a general idea how we interpret the single particle cluster analysis results.