Anonymous Referee #4

Lee et al. describe a unique set of ambient particle measurements obtained with a soot particle aerosol mass spectrometer (SP-AMS) that was combined with a light scattering module to obtain the first light scattering single-particle (LSSP) SP-AMS measurements of the size and chemical composition of black carbon and non-black carbon containing particles. A few days of measurements of ambient aerosol in downtown Toronto are analyzed. These exemplary results and the associated data analysis method used provide a good illustration of this instrumental method's ability to assess the mixing state of black carbon containing particles, and also reveals some of the method's limitations. The single-particle data analysis is inherently complex, and the manuscript would benefit from some major revisions to clarify certain key aspects of the data analysis and interpretation of the results. Issues related to particle sizes measured were particularly unclear to me, as were changes in the ionization/collection efficiencies in the different analysis modes. This manuscript should be suitable for publication in ACP after the issues below are addressed. I am ambivalent as to whether this manuscript is more suitable for AMT or ACP; depending on the revisions it could be suitable for either journal.

Response:
Thanks for the overall comments on our manuscript. We have made major changes in the revised manuscript to make it more suitable for ACP. To improve the quality of this paper in terms of science and atmospheric relevance, two new sections (Section 3.7 and 3.8) and a few figures (Figure 9, 10, S15, S16 and S17) have been added to the revised version to have a more comprehensive discussion about the degree of mixing state of secondary species in the accumulation mode particles, and HOA and rBC in the two vehicle related particle types (i.e. HOA- and rBC rich particle classes). Given that the light scattering AMS and the SP-AMS have already been described in previous publications, this paper does not seem appropriate for AMT, with the focus more on the new science from the new measurements.

The measurable particle size ranges should be stated and discussed more upfront, and even mentioned in the abstract. The LS-AMS can typically only measure individual particles > _200-250 nm (Dva). Due to the fractal nature of soot and effective density effects, smaller vacuum aerodynamic diameter black carbon particles were measured here with the LS-SP-AMS. Can you impose any constraints on what the physical or other equivalent diameter of these BC particles detected may have been, perhaps by comparison to the SMPS data? It is important to clarify these particle size issues as fresh combustion-derived BC-containing particles are initially emitted at sizes well below 100 nm, especially for gasoline vehicles. If the LS-SP-AMS can only measure significantly larger BC particle sizes, it will have an inherent bias towards the more aged/coated BC particles, and against the fresh less coated BC. I realize this issue is difficult to constrain due to the complexities of particle effective density on the measure Dva, but some additional and earlier discussion of this important issue is warranted. The first paragraph on Page 15326 where the different types of AMS instruments are discussed would be a good place to bring in the particle size limitations. The AMS also typically measures only a few ions in single-particle mode, which also hampers the analysis.

Response:
The cut-size limitation of light scattering has been mentioned in the introduction.

"LS-ToF-AMS typically measure individual particles in ambient air with vacuum aerodynamic diameters (d_{va}) > 350 nm due to the lower sizing limit of the light scattering module (Cross et al. 2009, Freutel et al. 2013, Liu et al. 2013). It is crucial to investigate whether the LS-SP-AMS can detect fresh, less-coated rBC-containing particles derived from vehicle combustion, which are generally emitted at d_{va} well below the typical light scattering cut-off diameter (Massoli et al. 2012)."

Ellis et al. (2013) recently reported the unique application of the LS-AMS to study mixing of organic aerosol populations in a smog chamber. As this is one of the few other papers to use the LSSP mode of the AMS the authors should consult this paper and include any relevant discussion that relates to their analysis here.

Response:
The information about the single particle study by Ellis et al (2013) has been added to the introduction.

“Ellis et al. (2013) recently deployed LS-ToF-AMS to determine the mixing state of laboratory-generated organic aerosol in a smog chamber.”

The references to other single-particle mass spectrometry based paper come largely from one group (Greg Evans) at U. Toronto associated with these authors. A more complete discussion and references to other related SP-MS measurements should be provided. For example, there is a series of ATOFMS papers from Kim Prather’s group focused on vehicular and carbonaceous particle measurements (Cahill et al., 2012; Moffet and Prather, 2009; Shields et al., 2007, 2008; Sodeman et al., 2005; Toner et al., 2006, 2008).

Response:
Thanks for the important suggestion. The suggested references have been added to the introduction of revised version.

I do not agree with this statement: “Specifically, the application of positive matrix factorization (PMF) analysis to AMS measurements is well developed for source apportionment of organic aerosol and evaluation of aerosol aging.” (Page. 15326) The AMS induces extensive fragmentation precluding the true identification of the aerosol sources. This combined with the fact that the AMS only measures the non-refractory aerosol (except when the soot particle mode is used, of course) such that it cannot measure the primary particles makes it quite unable to truly do source apportionment on the complete aerosol. Also the PMF factorization typically only segregates the organic aerosol mass fraction, ignoring the inorganic components. Thus the PMF factors have more to do with the average chemical composition of different slices of the organic aerosol segregated based on their ion fragments. The factors obtained are typically associated with hydrocarbon-like (HOA) or oxygenated (OOA) organic aerosol, and thus do provide insight into "aerosol aging" as stated. While factors these have some connection to "sources" they are not really aerosol source profiles in the typical sense. COA, BBOA, and a marine OA factor, which are more closely related to the actual aerosol source, have also been retrieved in some cases. Considering these issues it is not accurate to say that PMF applied to AMS data can produce source apportionment. It is really a statistical analysis of the OA's chemical composition, which /may/ indicate something about its sources.

Response:
Thanks for the reviewer's comments. The sentence has been changed as follow:

"Specifically, the application of positive matrix factorization (PMF) analysis to AMS measurements has been developed to provide information on possible sources of organic aerosol and the extent of aerosol aging"

Some discussion and justification of why k-means was used as the clustering algorithm is warranted. One issue with k-means is that the number of clusters must be prescribed. And it tends to more evenly distribute members throughout the clusters, and can thus miss small numbers of unique particle types. Reviewer #3 brought up c-means (fuzzy or non-exclusive clustering). While this can better reflect the mixed/evolving nature of atmospheric aerosol mixing state, a non-exclusive clustering can also complicate the analysis. How do you decide which particle belong to which clusters/classes, or do you never assign the particles to one class? An advantage of ART-2a is it finds the number of clusters required to sort the dataset at the prescribed vigilance factor, and thus provides a quantitative measure of the heterogeneity of the aerosol population. Rebotier and Prather (2007) have I believe the most extensive discussion and comparison of clustering methods for SP-MS data – please consult and cite this paper. While using k-means is fine, the authors should better justify their choice of 12 clusters to solve their dataset. Something was said about gaining little additional separation with higher cluster number, but what was lost when fewer than 12 clusters were used?

Similarly, in Sect. 3.5: While the use of more than 12 clusters is explained, why fewer than 12 clusters was not used to "solve" this dataset is not explained. Since the 12 cluster solution produces several quite similar clusters than are they manually regrouped, the authors should explain what happens when fewer than 12 clusters are used. Why is the 12 cluster solution considered optimal?

Response:
A sentence with the support of references (Rebotier and Prather, 2007, Giorio et al. 2012) has been added to the introduction and Section 2.8 to highlight the comparison between

k-means and other clustering algorithm from previous studies.

Introduction: “Previous studies have shown that k-means clustering can classify ambient particle types measured by ATOFMS in good agreement with other clustering algorithms such as ART-2a and hierarchical clustering (Rebotier and Prather, 2007, Giorio et al. 2012).”

Section 2.6: "It is worth noting that k-means clustering can classify ambient particles measured by ATOFMS into particle types that are highly consistent with other clustering algorithms such as ART-2a and hierarchical clustering (Rebotier and Prather, 2007, Giorio et al. 2012)."

More information has been provided in Section 3.5 to better explain the use of 12 clusters results. Also, a few sentences were used to briefly describe the selection criteria (see Section 2.6 in the revised version).

Section 3.5: "To demonstrate the capability of the LS-SP-AMS to investigate the mixing state of ambient aerosol particles, the twelve-cluster solution from the laser-on mode measurements is presented here. The number of particles and the ion fractions of nitrate, sulfate, organics and rBC in each cluster are shown in Figure S13. Increasing the number of clusters from 12 to 25 only gradually reduces the total Euclidian distance between the cluster centers and each single particle mass spectrum (Figure S4), and does not generate any new particles classes with significant physical meaning (i.e. determined by clusters re-combination as discussed in the next paragraph). Note that an rBC-rich particle class (see Section 3.5.2) can be clearly identified starting from the nine-cluster solution (up to twenty five-cluster solution). However, for the eleven-cluster solution, the rBC-rich particle class cannot be separated from OOA in the accumulation mode (i.e. dva peak at ~ 400 nm). Therefore, the twelve-cluster solution is considered as the optimal clustering solution."

Section 2.6: "All single particle mass spectra were normalized by their total ion signal, and solutions with up to 25 clusters were tested. Euclidian distance (the square root of the sum of the squares of the differences between corresponding values) was used to evaluate the total distance between the cluster centers and each single particle. In general, increasing the number of clusters can better represent the dataset mathematically (i.e., reduce the total distance) as shown in Figure S4. However, a very large number of clusters compromises the physical meaning of each cluster."

A note on terminology. For SP-MS data, when similar clusters are manually combined or “regrouped” into one group this is often referred to as a particle “class”. For this dataset there would be a nitrate class, rBC class, etc. The authors might adopt this terminology for consistency, and to distinguish between classes and clusters.

Response:

Thanks for the reviewer's comment. The terminology has been changed to describe the clustering results after combining clusters.

Appropriate black carbon calibrant standards remain an issue, for both the SP-AMS and SP2. More justification to support the use of Regal Black to calibrate the SPAMS's response to ambient combustion-derived particles should be provided. While the spectra do appear similar, it is a bit hard to believe that printer toner ink really simulates combustion soot.

Response:
We agree with the reviewer that calibration standards of BC can be an issue and it should be further investigated in the future. Regal Black is a recommended rBC standard based on a study of SP-AMS development (Onasch et al. 2012) and has been widely used within the SP-AMS community. Since the focus of this paper is not to describe the details of the SP-AMS development, we decide to modify a related sentence as below:

"Similarly, a water suspension of Regal Black (Regal 400R Pigment Black, Cabot Corp., a calibration standard recommended by Onasch et al. 2012) was atomized to generate standard BC particles."

Reference: Onasch, T. B., Trimborn, A., Fortner, E. C., Jayne, J. T., Kok, G. L., Williams, L. R., Davidovits, P. and Worsnop, D. R.: Soot Particle Aerosol Mass Spectrometer: Development, Validation, and Initial Application, Aerosol Sci. Technol., 46, 804-817, 2012.

This sentence is a real mouthful (page 15328): "The product of density and shape factor, derived from the ratio of the vacuum aerodynamic diameter (dva) measured by the PToF mode of the SP-AMS to the mobility diameter (dm) determined by the DMA (DeCarlo et al., 2004): : :". Can you reword so the meaning is clearer?

Response:
The sentence has been revised as follow:

"The product of density and shape factor of the dried 300 nm Regal Black particles is ~0.8 g/cm^3, which is derived from the ratio of the vacuum aerodynamic diameter (d_{va}) measured by the PToF mode of the LS-SP-AMS to the mobility diameter (d_m) determined by the DMA (DeCarlo et al. 2004) as follows:"

Do the RIEs of the various components measured not change with the IR laser is used? Was this tested?

Response:
This is a good question. The RIEs of NR-PM do change if they are evaporated from the

rBC surface. We mention a few possibilities in Section 3.3 and it is an issue that should be investigated in the future. To make this message clear, a sentence in Section 3.3 has been modified.

"(2) Particle vaporization by the IR laser and the tungsten vaporizer do not occur at exactly the same location inside the ion chamber, possibly resulting in different ionization rates and ion transmission efficiencies (i.e., from the ion chamber to the ion focusing optics) between the two operational modes. This difference may also be a reason for the observed enhancements in the RIE of NR-PM evaporated from rBC particles."

Section. 2.2. The light scattering module's cut-off size should really be characterized with particles more appropriate to these ambient BC measurements than ammonium nitrate aerosol. Some speculation about the cut off size for hydrocarbon oil droplets is given but these were not actually measured. Why not? Some attempt to also determine the cut-off LS detection size for size-selected black carbon particles should have also been made, though I realize the fractal particle shape would complicate this.

Response:
We agree with the reviewer that it would be ideal to have other particle types for determining the LS cut-off diameter of our instrument. Unfortunately, our instrument is in a new configuration and the data acquisition algorithm does not allow us to perform such testing. Nevertheless, it is worth noting that our estimation of cut-off size for oil-like particles (i.e. HOA and COA) matches well with the shape of ambient single particle size distribution.

Why was the K+ signal at m/z 39 excluded from the clustering analysis? This is a useful marker for biomass-combustion derived particles. While it seems likely that most of the combustion particles detected here were vehicular, it can be quite useful to include markers such as K+ in the analysis.

Response:
Surface ionization of heated thermal vaporizer can be a significant source of potassium in AMS. Therefore, K^+ is removed in our analysis in this study. However, we agree with the reviewer that K^+ is an important tracer for biomass burning. In another urban study, we observed a much higher K^+ signal during biomass burning influence period compared to the instrumental background. This will be discussed in our future publication. To provide this information, a sentence has been modified in the revised manuscript.

"... the total number of ions was calculated as the sum of all ion signals except m/z 14 (N^+), 15 (NH^+), 16 (NH_2^+), 17 (NH_3^+), 18 (H_2O^+), 28 (N_2^+), 32 (O_2^+) and 39 (K^+) either due to the strong interferences from air and instrument background (i.e. surface ionization on the tungsten vaporizer for K^+) or the noisy baseline of ammonium fragment ions."

Similarly, no mention of metals detected from the laser on mode of the SP-AMS analysis is given. Metals may be present in traffic-dominated aerosol from brake dust, or calcium from lubricating oil, for example. There has been some discussion of the SPAMS being able to detect metals that the normal mode of the AMS would not detect as they do not evaporate at 600 C. Were metals detected in these measurements? It seems like metals were not detected looking at the spectra. Any discussion the authors can add to the paper about what they have determined for the SP-AMS's ability to measure metals in PM would be valuable. Dallmann et al. (2014) recently reported SP-AMS measurements of vehicular combustion aerosol, and did detect trace metals such as zinc and phosphorous.

Response:
We agree that the SP-AMS has great potential to detect trace metals in the particle phase and we believe that this is an important area to explore in the future. To highlight this information, the following sentences have been added to Section 3.1.

"Furthermore, Dallmann et al. (2014) have demonstrated the capability of the SP-AMS to detect trace metals such as zinc in on-road gasoline and diesel vehicles emissions. However, no trace metals were clearly observed in this study."

Section 3.1. The authors should make it clear that this and the following sections discuss results only from the ensemble (not single-particle mode) measurements. While the section title does say "ensemble measurements", it took me awhile to realize that this was not discussing single-particle data, since the rest of the paper had thus far focused on single-particle measurements. A disclaimer at the beginning of the section's text would help clarify this.

Response:
Thanks for the suggestion. A short paragraph has been added at the beginning of Section 3.

"The results and discussion section is divided into two main parts. The first part (Section 3.1-3.3) presents the observations from SP-AMS ensemble aerosol mesurements and PMF analysis of the organic components. The second part (Section 3.4-3.9) focuses on identification of particle types and characterizing the mixing state of carbonaceous aerosols based on cluster analysis of LS-SP-AMS single particle measurements."

Much of the discussion of the results would be greatly improved if the size range of the reported measurements was stated. For example, "In general, organics dominated the particulate mass, whereas rBC contributed 5–8 % of the average particle mass: : :" (page 15332, line 5). For what size range do these mass measurements refer to? Starting on line 25 some discussion of the sizes measured for NR-PM and rBC is given. It would be very useful if the typical measurable size ranges for these two aerosol types was provided in a clear summary statement early in the results. Also make it clear if the measurable size range from LSSP mode differs from the ensemble measurements. The authors need to make the instrument's measurement capabilities much more clear. What was it capable of measuring reliably, and what did it likely not measure?

Response:

The measurable size range of single particle data has been discussed in Section 3.4. In particular, a few particle types which show different light scattering cut-off diameters have been discussed in the original manuscript. To make it clear, a sentence has been added at the beginning of results and discussion section.

"Note that the ensemble measurements detect particles with d_{va} starting from ~50 nm and up to ~1 µm, whereas the single particle measurements only detect particles greater than 200 nm d_{va} (the LS cut-off diameter for different particle types will the discussed in Section 3.4)."

How is assuming that the collection efficiency for all NR-PM evaporated from the tungsten vaporizer is equal to 1 justified? (Page 15332, line 9) CE is typically _0.5 for ambient aerosol, but can experience significant variations with changing PM composition. This statement really confuses me.

Response:

Thank you for pointing out the confusion concerning the CE issue. It is important that we present a clear discussion of CE. Figure S5 and corresponding calculation details have been added to the supplementary information to discuss the CE correction factors applied for different particle types based on our single particle observations. In brief, we assume inorganic species (internal mixtures of ammonium nitrate and ammonium sulfate) vaporized by the heated tungsten vaporizer have CE equal to 0.5, which is commonly applied for ambient aerosols. On the other hand, oil-like organic droplets (HOA and COA) dominated the total organic aerosol mass, and they are unlikely to have a significant particle bounce on the tungsten vaporizer surface. Therefore, we assume that the CE of the total organic aerosol equal to one and, furthermore, the total organic signal is likely dominated by vaporization from the tungsten vaporizer. However, OOA that is likely internally mixed with inorganics may have CE lower than unity from the heated tungsten vaporizer, and this adds a potential uncertainty. The CE for rBC vaporized by the laser is assumed to be 1, but it is actually highly uncertain as discussed in Willis et al (2014). However, due to the low mass loading of rBC, the calculation is not sensitive to the CE of rBC. The overall correlation between LS-SP-AMS, using the various CE's stated above, and SMPS-derived particle mass, assuming spherical particles, is close to 1, suggesting our assumptions on CE's are reasonable.

Sections 3.1, 3.3 and 3.4 have been modified accordingly to ensure all the discussion related to CE is consistent throughout the 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.

Page 15333, line 4: To be accurate and consistent, better to say that m/z 44 is a tracer for oxidized OA (OOA), rather than of SOA.

Response:
The suggested change has been made.

Page 15334, line 19: “Based on the PMF analysis, the rBC associated with HOA, COA and OOA accounted for: : :”. What does “associated” mean here? Correlated with, or the mass of rBC in each of those PMF factors?

Response:
The sentence has been changed.

"Based on the PMF analysis, the rBC mass in HOA, COA and OOA factors accounted for about 51% (±20%), 9% (±11%) and 40% (±18%), respectively, of the total rBC mass loading on average (± standard deviation)."

Sect. 3.3. “The IR laser on mode exhibited a higher sensitivity to all NR-PM components than 25 the IR laser off mode by _ 10–20 %”. This goes back to my earlier question regarding how the IE changes with the laser on versus off. It seems that this “higher sensitivity” might be explained by changes in IE in addition to changes in CE, but this is difficult to tease out from the text here as the term ionization efficiency is not actually stated. Please clarify this section. Page 15336, line 8: “a higher mass spectral sensitivity in the laser on mode as described in Sect. 3.3.”. As discussed above, this important effect was not actually described very well in Sect. 3.3.

Response:
Similar to our previous response. We think that the RIE of NR-PM would be enhanced if it is evaporated from rBC surface. We mention this possibility in Section 3.3 and this is something to be investigated in the future. To make this message clear, a sentence in Section 3.3 has been modified.

"(2) Particle vaporization by the IR laser and the tungsten vaporizer do not occur at exactly the same location inside the ion chamber, possibly resulting in different ionization rates and ion transmission efficiencies (i.e., from the ion chamber to the ion focusing optics) between the two operational modes. This difference may also be a reason for the observed enhancements in the RIE of NR-PM evaporated from rBC particles."

Page 15334, line 30: “particle bounce issues for tungsten vaporizers” is mentioned, which goes back to my earlier question about the CE for NR-PM being assumed to be 1, when it is known that the CE is variable and less than 1 for ambient PM. Please explain the earlier assumption of CE = 1.

Response:
Please refer to the above response regarding CE issue. Sections 3.1, 3.3 and 3.4 have been modified accordingly to ensure all the discussion related to CE is consistent throughout the manuscript.

Page 15335, line 18: “This is indirect evidence that a larger fraction of HOA material was internally mixed with rBC compared to the COA and OOA components.” This sentence was part of my original confusion in reading this section, as it wasn’t immediately clear that the ensemble measurements were being discussed. The authors might add a sentence here stating that the direct measurements of mixing state from the single particle data will be discussed in the following section, so the connection is clear.

Response:
Thanks for the comments. A sentence has been added to the end of Section 3.3.

"The direct measurements of mixing state from the single particle data will be discussed in the following sections."

Page 15338, line 17: “Note that the overall clustering analysis results for NR-PM are quite similar for both the IR laser on and off data sets.” Could the authors add some brief discussion of the implications of this finding? As this is a very new type of analysis I don’t think it will be clear to most readers. It could also suggest that little additional data is collected using the SP laser, but I do not think that is true. Would be good to clarify what additional data the IR laser on mode provides even if the clusters are similar.

Response:
Thanks for the suggestions. The sentence has been extended and moved to the beginning of this section to better highlight the difference between laser on and laser off mode clustering results.

"The overall cluster analysis results for NR-PM are similar for both the IR laser-on and off datasets, with the primary exception being an additional particle class, rBC, obtained from the laser-on mode single particle data. The major NR-PM particle classes obtained via independent cluster analysis for both datasets included nitrate, sulfate, HOA, COA, and 2 types of OOA (Figure 8). These particle classes represented similar particle number fractions and time series, and differed only slightly in average mass spectra (not shown)."

Page 15339, line 9: Should be “HOA-rich particles are largely externally mixed /from/ inorganic species: : :”

Response:
Based on the suggestion by another reviewer, the sentence has been revised as below.

"Most of the HOA-rich particles do not contain any inorganic species (Figure 8c and 8j)."

Sect. 3.6. I find the term “low to mid-range dva particles” really confusing and meaningless. Can you please just state the actual size range being discussed?

Response:
As commented by other reviewers, we define low-to-mid range aerodynamic diameter ranging from ~200-400 nm.

Sect. 3.6: Nothing is said here about what the LS-SP-AMS actually determined regarding the mixing state of rBC with HOA and other components, which I thought was a major point of this paper. Please summarize these findings here.

Response:
We agree with the reviewers that we need to extend the discussion about the mixing state of rBC and HOA in more detail. Section 3.7 and Figures 10, S16 and S17 have been added to the revised version. Furthermore, as suggested by reviewer 1, Section 3.6 and Figure 9 and S15 have been added to discuss the mixing state of secondary aerosol species in accumulation mode particles.

“This suggests that the HOA-rich particles were likely associated with small rBC cores.” This seems like an important, though not concrete finding that warrants more than one sentence of discussion.

Response:
Similar to the above response, Section 3.7 and a few figures have been added to the revised version to discuss the mixing state of rBC and HOA. Moreover, a simple core-shell structure model has been applied to estimate organic coating thickness on rBC particles in Section 3.8 (see details in later response)

“a significant portion of HOA- and COA-rich particles (> 90 %) with particle dva larger than _ 200 nm did not contain a detectable amount of rBC, i.e., the particles can be thought of containing a small rBC core with a thick HOA coating: : :” Couldn’t these particles also just have had no rBC?

Response:
The sentence has been modified in Section 3.8.

"(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),..."

A lot of discussion of thinly coated rBC particles is given here in Sect. 3.6. Can you put any constrains on just how thin these coatings were that would explain your results for the average _28 wt% of HOA on the typical range of rBc core sizes?

Response:
Thanks for the comments. The estimation of coating thickness based on a simple core-shell spherical structure and uniform coating thickness has been done in Section 3.8.

"(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."

“We cannot rule out that the SP-AMS is missing ion signals from small rBC cores”. Any constraints on how small an rBc core has to be to go undetected?

Response:
The single particle detection limit of a pure rBC particle is estimated and the information has been added in 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."

Sect. 3.7. It is important to make it clear that the LS-SP-AMS provides a rather selective lens for determining aerosol mixing state. As it cannot detect many potentially important primary aerosol components, the mixing state measurements obtained are rather skewed from the real total mixing state. This is not to say that the LS-SP-AMS measurements are not valuable, but the limitations should be made clear, especially to a non-expert reader.

Response:
Thanks for the comments. A sentence has been added to the first paragraph of Section 4 to highlight the limitation of single particle measurements by LS-SP-AMS.

"That being said, it is important to note that because the LS-SP-AMS may not be able to detect certain primary aerosol components, such as mineral dust, and non-IR absorbing refractory PM, and therefore the mixing state measurements obtained may not reflect the mixing state of the entire aerosol population."

Sect. 4. The summary has a lot of valuable and interesting discussion. While it is a summary, it would benefit from some expansion. For example, this deserves elaboration, as I don't think it was clearly explained earlier in the paper: "While it is recognized that HOA factors, identified by PMF analysis of standard HR-ToF-AMS data, and rBC originate from combustion sources, the mixing states of these primary aerosol species cannot be easily characterized in this manner." And again, a more quantitative measure than "thinly" and "thickly" coated particles would really increase the scientific value of these results.

Response:
The following information has been added to further elaborate that PMF analysis of ensemble measurements can only provide information to evaluate the potential sources and aging of organic aerosol but not mixing state without the support of measurements in single particle basis.

"PMF analysis of ensemble measurements can provide information to evaluate the potential sources and aging of organic aerosol. While it is recognized that HOA factors, identified by PMF analysis of standard HR-ToF-AMS data, and rBC originate from combustion sources, the mixing states of these primary aerosol species cannot be easily characterized in this manner without the support of single particle measurement."

We agree that a more quantitative measure of coating thickness would be valuable. Please refer to the previous response to the comments about the estimation of organic coating thickness. The information has been added to Section 3.8.

"The single particle data also provide insight to the sources of low to mid-range dva organics in a typical urban environment. According to our clustering analysis, those organics are mainly composed of HOA- and COA-rich particles emitted from primary sources such as vehicle exhaust and kitchen emissions instead of processed particles associated with condensed secondary materials." Please clarify if these "low-to-mid range dva organics" (and use a more specific description of their size) were or were not mixed with rBC, or if you could not reliably determine this.

Response:
The additional information has been added to the revised sentence.

"The single particle data also provide insight to the sources of low to mid-range d_{va} organics (~200-400 nm) in a typical urban environment. According to our cluster analysis, those organics are mainly composed of HOA- and COA-rich particles (with rBC content about 3% on average) emitted from primary sources such as vehicle exhaust and kitchen emissions instead of processed particles associated with condensed secondary materials."

Table 2 is a nice way to present this data.

Response:
Thanks for the reviewer's encouraging comments.

Fig. 2: The figure legend could be clarified. I believe the data from the laser on and off modes is combined here, but this is not clearly stated.

Response:
This information has been clearly stated in the caption of Figure 2.

"Figure 2: Summary of ensemble measurements (a) Time series (local time) of laser-off (Org, NO_3, SO_4, NH_4) and laser-on (rBC) aerosol compositions. (b) The average mass spectrum of laser-on ambient rBC and Regal Black (insert). (c) Average size distributions of laser-off (Org, NO_3, SO_4, Org44) and laser-on (rBC) aerosol compositions. Org 44 represents organic signal at m/z 44 (e.g., CO_2^+).

Fig. 3: I think this figure would be easier to interpret if C from OA was in green while C from rBC was in black. That will make the difference from laser on vs off more obvious.

Response:
Thanks for the suggestions. We prefer to keep the original color scheme because it is not straightforward to differentiate whether the C atom from OA or rBC for the laser on data set.

Fig. 5: Again, the LS cut-off detection size should really be measured using aerosol more appropriate to the combustion and OA focus of these measurements.

Response:
We agree with the reviewer that it would be ideal to have other particle types for determining the LS cut-off diameter of our instrument. Unfortunately, our instrument is in a new configuration and the data acquisition algorithm does not allow us to perform such testing. Nevertheless, it is worth noting that our estimation of cut-off size for oil-like particles (i.e. HOA and COA) matches well with the shape of ambient single particle size distribution.

Fig. 6: Are all these spectra from ambient data? The caption does not specify. Is a presumably “fresh” BC particle with almost no coating and dva = 549 nm realistic for ambient combustion aerosol? That seems huge for fresh vehicular soot, unless the effective density can explain such a large dva for a fresh combustion particle.

Response:
The three examples are ambient data. The caption of Figure 6 has been changed as below. The black carbon with almost no coating (in panel a) is only an example of this particle types. In Figure 8, it can be found that most of the particles classified to the rBC classes have a relatively small dva (peak at ~200 nm).

"Figure 6: Examples of single particle mass spectra of rBC-containing particles in ambient air:..."

Fig. 8: As suggested earlier, I would call these “classes” rather than “clusters”, since they are produced by manually regrouping some k-means clusters into particle type classes.

The figure caption should specify that these classes come from k-means clustering applied to LS-SP-AMS single-particle data. A better way to display the richness of single-particle mass spectra is using a “digital color stack”. This is basically a combination of the spectra in the left and middle panels, where the height of the bar represents the fraction of particles in that cluster/class that had that ion, while the color stack at each m/z displays the ion peak area measured for that fraction of particles. For example, see Figure 1 in Sullivan et al. (2007).

Response:
The "clusters" have been changed to "classes" in Figure 8. The caption of Figure 8 has been revised as below:

"Figure 8: Normalized mass spectra (left column), normalized histograms displaying the relative frequency of each m/z (middle column), and size distributions (right column) of different particle classes identified from k-means clustering of LS-SP-AMS single particle dataset (laser on)..."

Thanks for the suggestions about modifying Figure 8. However, we decide to keep the current format as the color scheme (blue: nitrate, red: sulfate, green: organics and black: rBC) used in the right column helps the reader to identify the aerosol chemical composition in each particle classes.

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