

### **Anonymous Referee #3**

The manuscript “Single particle characterization using the soot particle aerosol mass spectrometer (SP-AMS)” by Lee and coworkers reports the first deployment of an Aerodyne aerosol mass spectrometer equipped with both an infrared intracavity laser for black carbon measurement and a single particle light-scattering probe. This combination was used during a four days period in downtown Toronto. The collected data was then analyzed using standard AMS methods, positive matrix factorization as well as cluster analysis using the k-means algorithm.

#### **General comments:**

The manuscript is well structured and written, although in a few places the language could use a revision regarding sentence structure, grammar (tenses) and punctuation.

In some parts the use of abbreviations and “AMS” specific terms could be reduced to improve readability for readers less familiar with the Aerodyne AMS. The manuscript has some major shortcomings that should be addressed prior to publication.

Thanks for the reviewer's encouraging comments.

- In large parts it deals with the techniques and methods applied to obtain and analyze the data. The results of the mathematical methods are compared regarding the methods used; the atmospheric relevant results and their implications, however, are only shortly mentioned and not really discussed.

#### **Response:**

In order 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 discuss 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).

- It is not comprehensible nor explained, why the authors use the k-means algorithm instead of its successor. K-means cluster analysis has some major shortcomings that have been addressed long ago by the c-means (Fuzzy) algorithm. K-means requires each data point to belong to one (and only one) cluster, a condition which is difficult to justify for atmospheric aerosols with a history of constant mixing and exchange.
- In general both algorithms (k-means as well as c-means) do require equal distribution of data points into all clusters and thus are prone to oversee small clusters. This issue could be addressed by in addition using a different cluster method for comparison, for example hierarchical clustering or a neuronal network like ART-2A.

#### **Response:**

Cluster analysis of single particle data from Aerodyne LS-ToF-AMS is rather limited in the literature. Liu et al. (2013) first applied k-means clustering to analysis LS-ToF-AMS single particle data. On the other hand, a few previous studies have shown that k-means clustering can classify ambient particle types measured by ATOFMS in good agreement with other cluster analysis techniques such as ART-2a and hierarchical clustering. This information has been added to the introduction and Section 2.6 so that the reader can better understand the potential differences between those cluster analysis techniques.

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)."

- I recommend that the authors reconsider the main focus of the manuscript. If they want to keep the current focus, the methodical part should be enhanced, and the manuscript should be moved to AMT. To merit publication in ACP, the authors have to shift the focus towards a more scientific (non-methodical) discussion and atmospheric relevance.

Response:

Thanks for the reviewer's comments. As described above (in comment 1 to reviewer 1), the focus of our paper is on the investigation of carbonaceous particle mixing states in an urban environment. While our single particle measurements do represent the first application of the combined light scattering module with the soot particle aerosol mass spectrometer (LS-SP-AMS), the combined light scattering – aerosol mass spectrometer (LS-AMS) technique has been developed elsewhere (Cross et al. 2009, Freutel et al. 2013, Liu et al. 2013). Here we are applying the technique with a new focus on refractory black carbon (rBC)-containing particles enabled by the laser vaporizer in the SP-AMS. Two new sections have been added to the revised version to have a more comprehensive discussion about the mixing state of secondary aerosol species (Section 3.7), and HOA and BC (Section 3.8). This modification improves the paper quality in terms of science and atmospheric relevance and makes it more suitable to be published in ACP. Given that light scattering AMS and the SP-AMS have been previously described, we do not consider this paper appropriate for AMT.

References

Cross, E. S., Onasch, T. B., Canagaratna, M., Jayne, J. T., Kimmel, J., Yu, X. -, Alexander, M. L., Worsnop, D. R. and Davidovits, P.: Single particle characterization using a light scattering module coupled to a time-of-flight aerosol mass spectrometer,

Atmos. Chem. Phys., 9, 7769-7793, 2009.

Freutel, F., Drewnick, F., Schneider, J., Klimach, T. and Borrmann, S.: Quantitative single-particle analysis with the Aerodyne aerosol mass spectrometer: development of a new classification algorithm and its application to field data, Atmos. Meas. Tech., 6, 3131-3145, 2013.

Liu, S., Russell, L. M., Sueper, D. T. and Onasch, T. B.: Organic particle types by single-particle measurements using a time-of-flight aerosol mass spectrometer coupled with a light scattering module, Atmos. Meas. Tech., 6, 187-197, 2013.

### Specific comments:

P15324, L21: What is “the conventional interpretation of the PMF results”?

Response:

As suggested by the reviewer, "conventional" has been removed from the sentence.

"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."

P15324, L25-26: “Processes such as : : : are the primary sources of ambient BC.” This suggests that there are other sources for atmospheric black carbon particles. Which sources would that be?

Response:

Thanks for the comments. The sentence has been changed as below:

"Fossil fuel combustion and biomass burning are the primary sources of ambient BC."

P15325, L13: “Real-time, quantitative single particle: : :”: the comma is unnecessary.

Response:

Done

P15326, L1: “In contrast, the Aerodyne : : : separates the particle vaporization and ionization steps : : :”: “In contrast” should be removed because in this context it is wrong. For example, the SPLAT II (Zelenyuk et al., 2009) also uses a two-step vaporization and ionization process.

Response:

Done

P15326, L3-5: (Jayne et al., 2003) should be cited as a reference for the Q-AMS (when mentioning different versions of the AMS).

Response:

A reference for the Q-AMS has been added to the revised manuscript.

"Jayne, J.T., Leard, D.C., Zhang, X., Davidovits, P., Smith, K.A., Kolb, C.E. and Worsnop, D.R.: Development of an Aerosol Mass Spectrometer for Size and Composition. Analysis of Submicron Particles, Aerosol Science and Technology, 33, 49-70, 2000."

P15327, L1: "Clustering analysis" should be changed to "Cluster analysis" or simply "Clustering".

Response:

Corrections have been made throughout the manuscript.

P15327, L9ff: More details on the measurement location would be favorable, e.g., was it close to a major street, restaurants, etc.

Response:

A paragraph has been added to Section 2.1 (Sampling location and instruments) to describe the sampling locations.

P15327, L23: "The IR laser was switched on and off during data acquisition." This sentence sounds very trivial.

Response:

It is an important description about the LS-SP-AMS operation. To make it clear, the sentence has been modified as below:

"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)."

P15327, L23-26: Please correct the grammar: " : : the SP-AMS was operated : : :., whereas the instrument : : : detects both : : :"

Response:  
Done

P15328, L14: “Regal 400R Pigment” should be “Regal 400R Pigment black”.

Response:  
Done

P15329, L10: “: : : of a particle sizing chamber : : :” should be “: : : of the particle sizing chamber : : :”.

Response:  
As suggested by another reviewer, this sentence has been revised to better describe the instrument.

"Briefly, the light scattering module consists of a 50 mW diode pumped 405 nm continuous wave laser (CrystaLaser, LC BCL-050-405) that 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 Figure 1."

P15329, L15: What was the lower cut-off diameter for the “Regal black” particles?

Response:  
We did not determine the lower cut-off diameter of light scattering laser for the Regal black particles during the field study. Unfortunately, our instrument is in a new configuration and the data acquisition algorithm does not allow us to perform such testing.

P15330, L5-6: “The weak scattering trigger events (i.e., : : :).” Where do these values come from? What is the unit of the scattering signal?

Response:  
The unit of light scattering signal is volts. A total scattering signal of 0.2 volts is roughly the average value of the noise signal as shown in Figure S3. However, it should be noted that a signal-to-noise ratio plays a more critical role in screening out the useless data.

P15330, L7: Please replace “rotten” with another expression, for example “useless”. Or just paraphrase it.

Response:

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

P15330, L8-9: How is a "strong" scattering signal defined? Why six ions? And how are the ions calculated? By integrating over the mass spectrum divided by the (measured) single ion?

Response:

Based on Figure S3, 6 ions is a reasonable cut-off to remove the MS signals close to the noise level. As mentioned by the reviewer, the total ions calculated by integrating over the mass spectrum divided by the measured single ion during the calibration. To avoid confusion, the sentence has been modified as below:

"For particles that gave a sufficiently strong LS trigger event (i.e. those are not classified to as "noise") and a total number of ions  $\geq 6$  in their mass spectra (calculated by integrating the ion signals in the single particle mass spectrum), they were either categorized as "prompt", "early" or "delayed" particle types based on their PToF information (see supplementary information for information on setting the LS signal and total number of ions thresholds)."

P15330 L10-12: " : : : could accurately predict : : : the particle is categorized : : : " Correct the grammar. Why "Specifically: : : " ?

Response:

"Specifically" has been deleted in the revised version.

P15330, L19: Was there a reason for removing potassium? If so, where did the high background come from? For sure, it did not come from the gas phase. Did you use the high resolution data do check if m/z 39 really was potassium, and not for example C<sub>3</sub>H<sub>3</sub><sup>+</sup>?

Response:

Surface ionization on the heated tungsten vaporizer can be a significant source of potassium. The sentence has been modified as below:

"... the total number of ions was calculated as the sum of all ion signals except m/z 14 (N<sup>+</sup>), 15 (NH<sup>+</sup>), 16 (NH<sub>2</sub><sup>+</sup>), 17 (NH<sub>3</sub><sup>+</sup>), 18 (H<sub>2</sub>O<sup>+</sup>), 28 (N<sub>2</sub><sup>+</sup>), 32 (O<sub>2</sub><sup>+</sup>) and 39 (K<sup>+</sup>) either due to the strong interferences from air and instrument background (i.e. surface ionization on the tungsten vaporizer for K<sup>+</sup>) or the noisy baseline of ammonium fragment ions."

P15331, L1-8: Again, c-means should be favored over k-means, especially for an atmospheric data where a distinct separation of different populations is very unlikely.

Response:

Please refer to the previous response.

P15331, L17: “A Clustering Analysis Panel was developed : : :”: This is “IGOR slang”. A reader not familiar with Wavemetrics IGOR Pro will not understand, what a panel is (in this context), or why it is worth mentioning. Please rephrase.

Response:

We agree with the reviewer that IGOR Pro has a built in k-means cluster analysis function. However, it is not designed for ambient single particle mass spectra so that the direct output cannot fit the specific needs of our application. The Cluster analysis panel used in our study is a template that can be used to analyze output from Sparrow and provide some output (for example, size distribution, time series, etc.) for presentation. Also, we wrote a function that can be used to combine a few clusters to a single class. We understand the concern from the reviewer. We rephrased the sentence in Section 2.6 as following.

"A Cluster Analysis Panel (CAP) recently developed by our group was used to perform the built-in k-means clustering algorithm in IGOR Pro. The following information for each cluster can be directly generated by CAP:..."

P15332, L7-8: Why is the “collection efficiency” for uncoated Regal Black particles lower than for coated? Besides, I find the term “collection efficiency” not really suitable when used with the intracavity laser vaporizer. Wouldn’t “incandescence efficiency” be a better term?

Response:

Our group recently published a paper in Atmospheric Measurement Technique Discussions regarding the collection efficiency (CE) of ambient black carbon and laboratory generated Regal Black in SP-AMS (Willis et al. 2014). The heavily coated Regal Black has a more spherical particle morphology than bare Regal black. As a result, the coated Regal Black beam width is narrower than the bare one, resulting in larger overlap of the particle and laser beams. Since it has been discussed in our previous publication and is not the focus of this paper, we decide to refer the details to our previous publication. Also, the CE has been widely used in the AMS community and therefore we would like to keep this term in our paper.

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.

P15332, L21-24: Why are these observations by Onasch et al. mentioned, if the authors did not see anything alike (as mentioned before)?

Response:

The sentence has been changed as below. We did not have the similar observation but it is worth noting some recent literature highly relevant to this work.

"Fullerene type rBC spectral features (i.e.,  $C_x^+$  fragments with carbon number  $> 32$ ) cannot be evaluated because their  $C_x^+$  peaks are out of the m/z range (up to  $\sim 300$ ) investigated in this study. Onasch et al. (2012) observed carbon cluster ions up to  $C_{82}^+$  in laboratory generated ethylene flame soot particles and detected  $C_{32}^+$  to  $C_{70}^+$  that accounted for about 4% of the total rBC signals at an urban roadside environment."

P 15333, L1: Why is that? Are there only local sources for rBC, or are there any sinks? If so, what could these local sources be? Could it be that particles containing aged rBC are simply not vaporized by the laser (e.g., low black carbon content, high organic and inorganic content, low absorption at 1064 nm)?

Response:

Thanks for the comments. The sentence has been modified in the last paragraph of Section 3.1 to describe the possible local sources of rBC in our sampling location. Furthermore, our group recently reported that particles with 5 wt% of rBC can be vaporized and detected accurately by SP-AMS (Willis et al. 2014), supporting our argument regarding local sources as major contributors to the observed rBC.

"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."

P15334, L6, and Figure S4: The residual (of the PMF analysis) is quite high, especially in the first two days and at the end (10% and higher). Any explanation?

Response:

This is mainly because the aerosol loading is quite low during the first two days of our sampling period. This information has been added to the caption of Figure S7.

"Figure S7: Mass fraction contributions of each PMF factor (Blue: HOA, Red: COA, Orange: OOA, Grey: Residual) to the total organics from IR laser-off measurement. The relatively high residual for the first two days of our sampling period is mainly due to a low loading of organic aerosol."

P15334, L28: If there was significant particle bounce, why did the authors assume a



CE=1 for the tungsten vaporizer?

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.

P15335, L28: 75% in “laser on” mode, in “laser off” mode, or total?

Response:

To avoid confusion, the sentence has been revised as below:

"75% of them in both laser-on and laser-off mode were recognized as particle LS trigger events."

P15336, L13-15: How do the authors know that their light scattering system was more sensitive than the one used by Liu et al. (2012)?

Response:

Liu et al. (2012) reported that their LS laser was not well aligned. However, to avoid any confusion, the related sentence has been removed in the revised version.

P15336, L22-24: “: : the single particle size distributions measured : : are generally consistent with the ensemble PToF data (Fig. 2c).” This cannot be seen in this Figure.

Response:

Thanks for the comments. The sentence has been removed in the revised version.

P15337, L20-21: How should the laser vaporizer have bounce effects?

Response:

This sentence has been rewritten as below:

"The former is suggestive of potential bounce effects on the tungsten vaporizer and/or better ion transmission efficiency in the laser-on mode as discussed in Section 3.3; the latter, for particles smaller than 200 nm, is likely due to rBC particles dominating the ion signals (Figure S12b)."

P15337, L26ff: It would be helpful to mention why the twelve-cluster solution was selected.

Response:

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

"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."

P15340, L17: What does low-range Dva, what mid-range Dva stand for?

Response:

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

P15344, L8-9: As stated by the authors before, it could well be that they were not able to detect rBC in larger particles. Thus this statement should be modified.

Response:

Thanks for the reviewer's comment. The sentence has been revised in the last paragraph of Section 4.

"During our study, most of the rBC was likely freshly emitted from nearby vehicle exhaust and therefore we did not observe significant mixing, even though missing ion signals from small rBC cores in the aged particle types is also possible"

As suggested by another reviewer, we estimated the detection limit of a pure rBC single particle using 6 ions as a criterion and the mass-based ionization efficiency of Regal Black. The information has been added to 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."

Table 2: What are the uncertainties and errors of these values? Is a difference of 6.4% between "laser on" and "laser off" HOA significant at all?

Response:

We don't have a good estimation of uncertainties and errors of single particle counting. Even though the percentage difference is only a few percent for HOA type particles, the absolute number of HOA type particles in laser-on mode is 5 times higher than that in laser-off mode. Therefore, the difference between the two modes is significant.

Figure 2: Please hyphenate "laser on" and "laser off", or use it with quotes (throughout the manuscript).

Response:

Both terms have been hyphenated throughout the manuscript.

Figure S1: The sharp cut-off for "laser on" prompt particles should be explained either in

the diagram or in the caption.

Response:

The shape cut-off for laser-on prompt particles in Figure S1b is due to the fact that we set the absolute total ion threshold at 6 ions. The similar cut-off is also observed for the case of laser-off mode as shown in Figure S1d.

Figure S2: Why did the authors select 12 clusters for their analysis? Is there a relation with the cluster distance? What is the purpose of this plot?

Response:

Similar to the above response, a few sentences have been modified or added in the main text (Section 3.5 and 2.6) to briefly explain the selection of 12 clusters in our analysis.