**Anonymous Referee #1**
**General comments:**

In their paper "Single particle characterization using the soot particle aerosol mass spectrometer (SP-AMS)", Lee et al. describe the first deployment of a soot particle aerosol mass spectrometer coupled with a light scattering probe, enabling single particle and ensemble analysis of both refractory black carbon and non-refractory species. They apply k-means clustering to the single particle mass spectra, and compare to the results of positive matrix factorization analysis of the ensemble data. The paper is well and clearly written and provides relevant information on the methods of single particle and ensemble analysis with the SP-AMS, as well as some interesting insights into particle mixing state. However, since the main focus of the paper is rather on a technical (method) development, it could be argued that this paper would be more suitable for AMT than for ACP. I therefore recommend publication either in AMT or as a "Technical Note" in ACP, subject to the following comments.

Response:
Thanks for the reviewer's encouraging comments.

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. Since this is the first time that a light scattering module was deployed with the SP-AMS to measure ambient particles, some technical details have to be included in our manuscript. However, we do not believe that this paper should be limited to a technical note, as we are applying a recently developed technique to a new problem, not developing a brand new technique.

To make our focus clear, the title of the paper has been modified to "Mixing state of carbonaceous aerosol in an urban environment: Single particle characterization using the soot particle aerosol mass spectrometer (SP-AMS)". We have also modified three key sentences, one in the abstract, one in the introduction, and one in the conclusions to help ensure clarity on the science focus. Finally, in responding to the helpful and constructive comments from the reviewers (here and below), we have further enhanced the scientific content of the paper by adding two new sections (Section 3.6 and 3.7) and a several new figures (Figure 9, 10, S15, S16 and S17) to the revised version. With this additional information, the mixing state of rBC and other NR-PM components measured in an urban environment is better described in the paper. We feel that the insights into the mixing states of rBC-containing particles obtained as part of this work are important and are of interest in the aerosol community served by ACP.

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:**

1. It is not made clear from the experimental section what data is acquired in LSSP mode and how this data is processed. Specifically, the statement on p. 15329, lines 24-25, is not correct: the computer is not triggered to save "the corresponding mass spectrum from the single particle", it saves the whole PToF trace, from which afterwards the single particle mass spectrum is obtained. This is especially important as both PToF traces and integrated mass spectra are used later on (in Figs. 5 and 7, I think; this should be stated more clearly). Is the dva from LS or MS signal used in Fig. 7?

   Response:
   The reviewer is correct; the whole PTOF trace is saved for each light scattering event and the single particle mass spectrum is obtained from the saved PTOF trace. The sentence under question has been corrected in Section 2.5 as the reviewer suggested. It now reads:

   "Once a light scattering signal is detected, the computer is triggered to save the whole PToF trace, from which the single particle mass spectrum is subsequently obtained."

   Figure 7 shows the integrated single particle PTOF ion signals for different chemical species for the IR laser off (a) and on (b) conditions. The $D_{va}$ used in Figure 7 is from the PTOF ion signals, and not from the LS light scattering signal.

2. The categorization of single particle mass spectra. First of all, "rotten" sounds rather colloquial to me to describe a category of mass spectra. The single particle data the authors describe rather seem to be "low in LS signal" or something similar. By looking at Fig. S1, it seems that the threshold during the data acquisition was set rather low, i.e. many saves were triggered by noise in the LS signal. So, instead of

using rather arbitrary values ("signal < 0.2"), why not simply calculate a new threshold from the data in Fig. S1 using some kind of "baseline" region (e.g., dva < 40nm)? A similar approach could be used to determine a threshold for "null" mass spectra.

Response:
The term "rotten" has be replaced by "noise" to describe the light scattering threshold crossing events that were likely caused by noise, rather than real particles. We used "rotten" in the original version because it is a default terminology used in the software package - Sparrow.

The reviewer points out an important issue that we actually set the threshold very close to the limit of our light scattering module during data acquisition. The primary reason is that we wished to maximize our particle counts from LS, especially for nearly pure BC particles that may have a weaker LS signal. The major drawback is that we detected significant numbers of LS noise events (i.e., false positive particle signals). As we have two direct measurements per single particle event, light scattering and mass spectrum, we use two different thresholding criteria, one based on light scattering signal and one based on ion signals. The mass spectrum ion threshold criteria is actually the more stringent threshold. The threshold of > 6 ions was established, in part, using the "effective noise level" shown in the new Figure S3e and f, following the concept described by the reviewer. The > 6 ions threshold was also chosen, in part, based on having sufficient ion signal per mass spectrum to enable useful chemical detection from the mass spectrum. With the chemical ion signal as the primary (i.e., most effective) threshold, the light scattering threshold (0.2 volts) helps to further refine the discrimination between real particle events and noise.

In relation to this, I am not quite sure about the comparison to the fraction of "null" particles found by Cross et al. and Liu et al. (p. 15336). While most of the reasoning seems valid, I am not sure on which evidence the authors base their assumption they had "a more sensitive light scattering detection system" than Liu et al. (lines 13-14). Furthermore, as said above, the threshold settings for data acquisition may have a large influence here; there may also be influences like different size distributions / chemical composition.

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.

3. As written, there seem to be some contradictions regarding the collection efficiencies: on p. 15332, the authors claim CE = 1 for NR-PM after comparison to an SMPS system. They do not base this CE on any theoretical reasoning (average chemical composition to justify this?). Later on (Section 3.3), it is observed that NR-PM components are biased low by 10-20% in laser off compared to laser on mode, which

implies CE >1 for laser on mode. Then in several places (e.g., p. 15337), particle bounce is discussed, implying CE <1. Furthermore, when single particle data are analyzed, it becomes obvious that about half of the particles giving an LS signal do not give significant ion signal, i.e. CE <1. This needs some clarification.

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.

4. Concerning the statement on p. 15339, lines 22-25 (and related statements elsewhere): "In contrast, the clustering analysis clearly suggests that two major types of particles contributed to the PMF-HOA factor. The different size distributions of the two clusters also indicate two distinct particle types." This claims there are two particle types, wholly unconnected, separated into two clusters. Is it not more likely that there is a gradual degree of mixing between HOA and rBC? This could be easily tested by plotting e.g. HOA vs rBC mass for particles from these two clusters. Moreover, in other places of the manuscript the authors seem to contradict themselves on this topic (e.g., on p. 15341, lines 17 and 21, they suggest that also the "pure" HOA particles contain a small rBC core, which rather seems an indication of gradual degree of mixing). This needs clarification. Furthermore, can the detection limit of

rBC be somehow approximated? It is discussed on p. 15342, line 12, that rBC may be underestimated due to low ion counts. Could this be tested by comparing the average chemical composition derived from ensemble and single particle measurements?

Response:
Thanks for the reviewer's suggestion. We agree that HOA and rBC are likely gradually mixed in ambient aerosol particles. Based on the reviewer's comments, 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. Figure 10 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, as suggested by the reviewer.

Onasch et al. (2012) reported that the 3σ detection limit for rBC mass concentration measurements is 0.03 μgm−3 for 1 min collection. This information has been added to the experimental section (Section 2.3). However, it is not straightforward to compare the average composition derived from ensemble and single particle measurements for rBC-containing particles because the light scattering detection bias to the large particles (e.g. > 200 nm). Most of the rBC particles are smaller than the light scattering cut size (please see Figure 2c and 5).

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.

5. Similar to the discussion of distinct particle types vs gradual degree of mixing of rBC and HOA, it should be noted that the four particle cluster types of nitrate, sulfate, OOA cluster 1 and 2 likely represent four "extremes" of a large group of particles, all of the same type (internal mixture of sulfate, nitrate, OOA). This again should be easy to see in an according diagram (e.g. ternary plot).

Response:
We agree that all the secondary species (i.e., nitrate, sulfate and OOA1 and OOA2) are gradually mixed to some degree. As described above, 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. In order to better describe the mixing state of the secondary aerosol species in the accumulation mode ($d_{va}$ peak at ~ 400 nm), ternary diagrams of mass fractions of nitrate, sulfate and total organics are shown in Figure 9 and S15 of the revised version as suggested by the reviewer. A new section (Section 3.6) has been added to the revised manuscript to describe the relative contributions of each secondary species in the particle classes identified by cluster analysis.

6. p. 15327, line 15: Can the measurement location be described a bit more in detail? Is it adjacent to a road, or rather in a backyard? What's the traffic density, inlet height?

   Response:
   A paragraph has been added to Section 2.1 (Sampling location and instruments) to describe the sampling locations. A map has been also added to the supplementary information (Figure S1).

7. p. 15332, line 15: provide model of SMPS instrument. What assumptions were used to infer mass from the SMPS measurements, and how well did it correlate exactly (slope?)

   Response:
   The model of the SMPS instrument has been added to Section 2.1. Please refer to comments 3 above about the assumptions used for SMPS mass calculation.

8. p. 15332, lines 20-24: Which m/z range was investigated in this study? I think the information on fullerenes could be easily improved by a simple back-of-the-envelope calculation: assuming the ratio found by Onasch et al. from the fullerenes to the smaller Cx ions, would a significant signal of fullerenes be expected at the observed signal of lower Cx fragments?

   Response:
   Thanks for the reviewer's suggestion. Based on a previous laboratory study, small Cx fragments only have small contributions (~10%) to the total rBC mass of fullerenes (information from AMS users meeting wiki site - http://cires.colorado.edu/jimenez-group/UsrMtgs/UsersMtg11/SPAMSpresentationOnasch.pdf). Since fullerene is likely a minor contributor to the total rBC mass in ambient rBC-containing particles (Onasch et al., 2012) and there is only limited information available in the literature, we have modified the original sentences as follow instead of doing the estimation.

   "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 ~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."

9. p. 15335, line 21: KNO3 is not a good example of refractory species, since it is very easily thermally decomposed and detected very well with the AMS. Why should more acidic material be present in internally mixed rBC particles than in others? For very aged material, this does not seem very likely.

   Response:

> To avoid any confusion, the discussion about the KNO3 and acidic particles has been removed from Section 3.3. The revised sentences are shown as below:
>
> "For inorganic species, the enhancement of $NH_4^+$ mass between the two operational modes is smaller than those observed in the case of $NO_3^-$ and $SO_4^{2-}$ (Figure S10). The reason of this observation is unclear but one of the possibilities is that some refractory nitrate and sulfate (e.g., $Na_2SO_4$) coexisted with rBC."

**Technical corrections:**

The authors use the different terms "LS-SP-AMS" and "SP-AMS" sometimes on purpose to distinguish between SP-AMS with and without light scattering module; but sometimes, both terms seem to be used interchangeably (e.g., p. 15342: In line 3, it is "SP-AMS" on purpose, because here we talk about an "usual" SP-AMS. But in line 7, again "SP-AMS" is used, where it is talked about the single particle data from this work. So, it should be more precisely "LS-SP-AMS" here.) More care should be taken in the whole manuscript to use the more appropriate of both terms in each situation.

Response:
Done

Also, it might be confusing to the reader that on the one hand, there is the "LS-SPAMS", on the other hand, there is the "LSSP mode". Maybe it could be shortened to "LS mode" to make the difference more clear? Especially since in one case SP means "soot particle", in the other "single particle".

Response:
Done

p. 15324, line 18; Section 3.6; and p.15344, line 4: "low to mid-range aerodynamic diameter" could mean anything from a few nanometers to several _m. Please specify at least once the size range.

Response:
We define low-to-mid range aerodynamic diameter as ~200-400 nm.

p. 15325, line 13: "quantitative single particle detection": do you really mean that the (optical) detection of the particles should be quantitative (i.e., the number concentration should be correct), or do you mean quantitative chemical composition analysis of the single particles which were detected (i.e., getting quantitative mass per particle information, i.e. do you want to stress the difference between AMS and ATOFMS single particle data)? Maybe reword to make more clear.

Response:

This is a sentence to generally describe the features of ideal techniques for single particle detection. The sentence has been revised to specify the meaning of "quantitative single particle detection" in the introduction.

"Real-time quantitative single particle detection (i.e. number concentrations and chemical composition by mass in a single particles basis) is necessary to determine the mixing state of ambient particles."

p. 15326, line 20: “which is able to quantify and characterize rBC and NR-PM”: sounds strange. How do you “characterize rBC”?

Response:
It has been reported within the AMS community that ambient particles can consist of different types of rBC (e.g. flame soot, fullerene, etc. - http://cires.colorado.edu/jimenez-group/UsrMtgs/UsersMtg11/SPAMSpresentationOnasch.pdf). Furthermore, recent study has reported that soot particles can have different fragmentation patterns and surface properties (functional groups) (Corbin et al. 2014). To make it clear, the related information has been added to the manuscript.

"The utility of the AMS was recently extended by development of the Soot-Particle Aerosol Mass Spectrometer (SP-AMS), which is able to quantify and characterize rBC (i.e. $C_x$ fragmentation pattern and surface functionality) and NR-PM simultaneously (Cross et al. 2010, Onasch et al. 2012, Corbin et al. 2014)."

Reference: "Corbin, J. C., Sierau, B., Gysel, M., Laborde, M., Keller, A., Kim, J., Petzold, A., Onasch, T.B., Lohmann, U. and Mensah, A. A.: Mass spectrometry of refractory black carbon particles from six sources: carbon cluster and oxygenated ions, Atmos. Chem. Phys., 14, 2591-2603, 2014."

p. 15327, line 6: “SP-AMS ensemble measurement data”

Response:
Done

p. 15327, lines 13 and 22: give a reference for “standard HR-ToF-AMS” and “V-mode”.

Response:
A reference has been added.

"DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimene, J. L.: Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer, Anal. Chem., 78, 8281–8289, 2006."

p. 15328, line 2: “the NR-PM that is internally mixed with rBC core”: strange wording. Maybe just delete “core”?

Response:
The word "core" has been deleted.

p. 15328, lines 18-19; and p. 15330, line 4: As reference, the URL should be provided where Squirrel / PIKA / Sparrow can be obtained.

Response:
Two URL have been provided in the revised version.

AMS data analysis software (Squirrel, version 1.51H for unit mass resolution (UMR) data and Pika, version 1.10H for high resolution peak fitting) -
http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html

Single particle data processing software, Sparrow (1.04E) -
http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html

p. 15330, line 18: “number of ions is the sum” should read “number of ions was calculated as the sum”

Response:
Done

p. 15331, line 8: this should read “total ion signals in a single particle mass spectrum” more precisely

Response:
Done

p. 15333, line 4: specify “SOA”

Response:
Secondary organic aerosol (SOA) has been changed to oxygenated organic aerosol (OOA) in the revised version as suggested by another reviewer.

p. 15337, line 4: “Chi” should read “S”. Also, the same equation is given before (p. 15328). Maybe break up into a separate line there and simply refer to “Eq. (1)” later.

Response:
The symbol has been changed in the Eq. 1 of the revised manuscript. Also, the latter part of the manuscript refers to Eq. 1 if needed.

p. 15337, line 26-28: It is unclear what this sentence is supposed to say in the present form. If I understand correctly, what is meant is that clusterings of both laser on and laser off datasets were performed, and here only laser on clustering results are shown as an example. This should be made clearer here, especially since the results from both clusterings are compared later on.

Response:
Thanks for the suggestions. Below is the revised sentence in Section 3.5:

"The k-means clustering algorithm was used to separately classify all the prompt particle mass spectra into chemically distinct groups for both laser-on and laser-off datasets. 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)."

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...."

p. 15338, line 3: should read “reduces” to not mix different tenses within one sentence.

Response:
Done

p. 15338, line 11: “procedure” – do the authors mean “produce”?

Response:
Done

p. 15339, line 9: rather “do not contain any inorganic species”

Response:
Done

p. 15339, line 10: considering the associated uncertainty, “about 6%” seems more appropriate than “6.4%”

Response:
It has been changed to "about 6%".

p. 15343, line 18: comma missing: “other, non-refractory”

Response:
Done

Table 2: define “NA”. What does “measurable m/z 36 signal” mean? Any signal larger than zero? Signal above a certain threshold?

Response:
NA has been defined as "Not applicable" in Table 2. "Measurable m/z 36 signal" means any signal larger than zero and has been defined in Table 2.

Figure 2: define “Org44”; it should be noted that these data are from ensemble measurements.

Response:
The caption of Figure 2 has been revised as below:

"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., $CO_2^+$)."

Figures 2 and 4: Is this local time? Please specify.

Response:
They are local time. The information has been added to the captions.

Figures 5, 7 and S9: The purple and grey lines are hard to distinguish.

Response:
The purple lines have been changed to pink lines in Figure 5, 7 and S12 of the revised version.

Figure 6: b) how thin is a “thin” coating? Maybe would be better described as an “internal mixture of rBC and HOA”. c) should be “is classified” instead of “are”.

Response:
The caption of Figure 6 has been modified as follow:

"Figure 6: Examples of single particle mass spectra of rBC-containing particles: (a) Black carbon, (b) black carbon internally mixed with HOA, and (c) black carbon internally mixed with OOA and sulfate. Particles (a) and (b) are sorted into the rBC cluster, and particle (c) is classified into the OOA cluster 2 identified in this study (See Section 3.5)."

Figure 8: For clarity, it could be stated in the figure caption that these are results for the clustering of the "laser on" dataset. Also, what is the inset in panel (d)? Please clarify.

Response:
The caption of Figure 8 has been modified as follow:

"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): (a, h and p) $NO_3$ class, (b, i and q) $SO_4$ class, (c, j and r) HOA class, (d, k and s) rBC class, (e, m and t) COA class, (f, n and u) OOA class 1 – less oxygenated, (g, o and v) OOA class 2 – more oxygenated. The insert in 8d shows the organic mass spectrum associated with the rBC-rich particle class."

Figure S7: in which units are the signal intensities given?

Response:
They are ion signals. The information has been added to the figure caption (Figure S10 in the revised version).

" Figure S10: Comparison between the IR laser on and off measurements (ion signals): (a) $NH_4^+$ (b) $SO_4^{2-}$ (c) $NO_3^-$ and (d) Organic. Dashed line = 1:1 line, red line = data fitting."

Figure S9b: Label on the right y-axis is unclear. Should this read ": : :ratio or Total: : :"?

Response:
The correction has been made. It should be "ratio or total".