

Interactive comment on “Single particle characterization using the soot particle aerosol mass spectrometer (SP-AMS)” by A. K. Y. Lee et al.

Anonymous Referee #4

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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

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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.

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 $> \sim 200\text{--}250\text{ nm}$ (D_a). 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 D_a, 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.

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.

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

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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).

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.

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

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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?

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.

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 SP-AMS'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.

This sentence is a real mouthful (page 15328): "The product of density and shape

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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?

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

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.

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.

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 SP-AMS 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.

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

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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.

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?

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.

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.

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?

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,

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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.

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.

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.

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.

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

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?

Sect. 3.6: Nothing is said here about what the LS-SP-AMS actually determined re-

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garding 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.

"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.

"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?

A lot of discussion of thinly coated rBC particles is given here in Sect. 3.6. Can you put any constraints 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?

"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?

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.

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 mea-

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sure than “thinly” and “thickly” coated particles would really increase the scientific value of these results.

“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.

Table 2 is a nice way to present this data.

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.

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.

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.

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.

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

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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).

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