Response to Referee #1 – Joel Corbin

The manuscript "Effect of secondary organic aerosol coating thickness on the real-time detection and characterization of biomass burning soot by two particle mass spectrometers", by A. Ahern et al. presents an environmental-chamber based study of two commercially-available aerosol mass spectrometers, the SP-AMS and the LAAPTOF, using soot produced by a wood burning.

The aerosols sampled were thoroughly characterized, the measurements are presented in detail, and the results are thoroughly discussed and interpreted. The study was exceptionally well designed and used a realistic sample, birch-bark soot from a wood stove, ensuring that soot microstructure and impurity content were representative of an atmospheric aerosol. Moreover, the results for the SP-AMS are not at all what would have been predicted from previous understanding. The measurements therefore represent a very valuable contribution to our understanding of both SP-AMS and include useful data for the LAAPTOF.

Although I think the study and manuscript are excellent, I still have a number of comments. The bulk of these relate to Fig. 9, which I think contains the manuscript's main message, and which I think should be improved to make a direct estimate of the overlap of the particle beam with the laser beam.

In the following I will write p1.5-10 to refer to lines 5 to 10 on page 1.

We would like to thank Dr. Corbin for his thoughtful and thorough comments. His insight and suggestions are a credit to the peer review process, and we endeavor to address them with equal care and detail below. The referee's comments are in italics and our response and corresponding revisions to our manuscript follow each comment.

1 ***General comments***

1.1 LAAPTOF

Clearly, the major focus of the analysis was the SP-AMS rather than the LAAPTOF. While there is, of course, no reason why equal amounts of text should be devoted to each instrument, the paper reads as though it is an SP-AMS paper with a few LAAPTOF comments included. The obvious suggestion is that the LAAPTOF results move into another manuscript. Whether or not the authors accept this suggestion, it would also be nice to see more statistics on the LAAPTOF performance. Examples:

During these experiments we were still refining the light-scattering units, which enable rapid and reliable detection of particles with LDI-SP-MS, and so they were not yet operational on our LAAPTOF. Instead we used a LDI free-fire mode to collect a total of 454 individual particle mass spectra over the four experiments. Further data filtering, described on page 17, reduced the total number of particle spectra available for analysis with respect to OM signal on soot particles to 160 mass spectra. A further analysis of the distribution of ions on all 454 detected particles has been included on p17 as follows:

> "As previously stated, for these experiments the instrument was operated in UV laser free-fire mode, without the aid of light scattering modules to more efficiently detect particles and trigger the excimer. As a result, only 454 individual mass spectra were collected by the LAAPTOF across the four experiments. 31 of 454 particles contained only potassium and inorganic species, with no detectable elemental carbon. 4 of 454 particles contained S^+ or SO^+. 11 of the 454 had a negative ion mass spectrum in addition to a positive ion mass spectrum. 5 of these negative ion spectra contained only HSO_4^-, 2 were only C_1^-, and the remaining were a richer spectrum of elemental carbon with larger signal from even carbon number anions, consistent with previous observations (Bloomfield et al., 1985; Onasch et al., 2015). 104 of 454 particles contained Zn^+. 281 particles contained NO^+. "

1.1.1

Fig. 7 could include LAAPTOF "EC" signals, and possibly more,

As stated above, small particle statistics render a meaningful comparison of EC ion distribution difficult.

1.1.2

To what degree is Fig. 8 representative? Could error bars be added, if all particles looked like these? Or clustering be performed to illustrate whether or not all particles looked like these? Likely, future LAAPTOF studies from the community will perform clustering analyses on both source and ambient data sets using the recently-published software (Reitz et al., 2016).

The abundance of various spectral elements has been described on page 17 as discussed above in response to Comment 1.1. Fuzzy c-means clustering was performed on the full data set of particle spectra. However, fuzzy cluster analysis has an inherent tendency towards evenly weighted cluster centers which occluded important differences between individual particle types. Thus, the clusters were mostly similar to the spectrum shown in Fig. 8, with different cluster assignments being dominated by lower MS resolution rather than different ion abundances. It was apparent that the more informed analysis, described in section 3.4, would best answer our fundamental question of whether it was possible to use LDI-SP-MS to obtain quantitative measurements of organic matter on biomass burning.

1.1.3

The dominance of CO+ was noted in Section 3.4, but what about the NO+ ion visible in Fig. 8, which is of equal intensity to CO+ in that spectrum? Where did the N come from?

We believe that NO^+ could be produced from components present in the particles via two pathways. Either from the formation of HNO_3 or the formation of organontirates via NO_3 radicals. We have adjusted the manuscript to reflect this for the LAAPTOF section as follows on page 16:

> “We believe that this may be the result of NO_x and O_3 combining in the chamber and forming NO_3 radicals. These NO_3 radicals may then react with water or organic vapors to form HNO_3 or organonitrates, respectively. Either species could then condense onto the existing particles and fragment to NO^+ in the mass spectrometers. K^+ was readily identified by its isotopic abundance at m/z +39 and +41 (Bahadur et al., 2010; Healy et al., 2012; Silva et al., 1999).”

1.2 Discussion

There is some discussion within the section titled Experimental Methods that would fit better in Results and Discussion. Specifically: p5.12-17, p7.3-20, p7.38-45, Section 2.4.

We moved the content from p5.12-17 and p7.3-20 to the discussion section. We feel that the detailed design discussions from p7.38 provide valuable context to the subsequent topic. We agree that Section 2.4 should be moved to the discussion section and identified as Section 3.1; we have adjusted the section numbering to reflect this move, and will henceforth refer to sections by their old (new) numbering. E.g. Section 2.4 (3.1) has been moved to the Discussion section.

1.3 Conclusions

Perhaps the conclusions are missing a comment on which aspect of the SP-AMS needs to be revised to address the quantification issues reported here? My impression is that this would be the far-from-homogeneous laser beam that the particle beam sees.

With the understanding of the available equipment, we would suggest that researchers can estimate the effect of particle beam divergence using the Beam Width Probe. This must also be evaluated with respect to the individual species' effective IR laser beam effective cross-section. A homogenous or flat-top beam profile would also be beneficial and simplify the SP-AMS's response as any particle passing through the laser beam would experience the same amount of laser energy.
We have included a brief discussion of this idea in the Conclusions, on page 26:

> “Future measurements using the SP-AMS would do well to quantify the particle-beam and effective IR-laser overlap for the species of interest using beam width probe measurements. The fraction of BC-containing particles that experience sufficient laser fluence to vaporize the non-refractory coating should always be greater than or equal to the fraction of particles whose refractory material is also vaporized. The use of optical components to change the IR laser from a Gaussian to a uniform flat-top energy profile would greatly simplify the analysis of BC-containing soot particles by the SP-AMS by ensuring that all particles passing through the laser experience the same amount of energy. This

would eliminate the difference given above regarding the fraction of BC-containing particles whose non-refractory versus refractory components are detected."

1.4 Terms

At various points the terms "soot", "rBC", and "black carbon" were used, as well as "BBA". For example, in the abstract the SP-AMS sensitivity is first described relative to rBC and then later to black carbon. As another example, in the introduction I wasn't sure if BBA meant only soot from BB, or only efficient combustion (certain stages of biomass burning don't produce soot), etc. On p3.5 it is stated that particles contained "BBA, rBC, and SOA", so I'm confused about what BBA is. Isn't rBC a subset of BBA? Maybe this should read "rBC, SOA, and ash"?

We agree that our terminology was inconsistent and thus confusing. We have corrected page 3 to the following:

"The feasibility of quantitative measurements of organic matter (OM) by the LAAPTOF in complex and realistic particles containing inorganic salts, rBC, and SOA was also investigated."

Similarly, the term SOA was used sometimes while OM was used at other times. I per-sonally prefer OM, which can refer to both the particulate phase SOA and the category of ions observed in the mass spec, as the authors did on p3.5-6.

If the authors retain the pairs of terms rBC and BBA, and SOA and OM, then a table defining abbreviations might be worthwhile.

We have tried to be consistent in our use of these terms. BBA refers to any aerosol produced from biomass burning combustion, BC is light-absorbing carbon, and rBC is the operational definition of BC that is measured due to its ability to absorb IR light and incandesce/sublimate at high temperatures.

Similarly, we tried to be consistent in only using SOA when it refers to the organic carbon aerosol material in this experiment, since the only OM present was that produced by oxidation of a-pinene vapors. We use OM when it refers to observations or conditions that are insensitive to how it was formed. I.e. all SOA is OM, but not all OM is SOA. We now lay out our terminology used throughout the paper, on page 4:

"We confirm that significant SOA coatings on BC cause only small changes in the ion fragmentation patterns of elemental carbon (EC) in the SP-AMS. EC is defined as ions detected by mass spectrometry that consist of only carbon ions. We show that the infrared laser beam waist in the SP-AMS has a different effective beam width and therefore different detection efficiency for alkali metals versus rBC. The feasibility of quantitative measurements of organic matter (OM) by the LAAPTOF in complex and realistic particles containing inorganic salts, rBC, and SOA was also investigated. We demonstrate that there is a positive correlation between the LAAPTOF measured OM ion signal and to the SOA mass condensed on BBA particles. This is significant given the especially complex composition of BBA, and is highly encouraging for achieving mass quantitative single-particle measurements of other complex ambient particle matrices. In this work, we will use the term "SOA" to describe the condensed phase organic material that was formed from a-pinene ozonolysis. We will use OM to discuss all condensed organic matter, including mass that is primary or secondary in nature. Organic ions measured by mass spectrometry will be identified as OM because in this work we cannot strictly differentiate between primary and secondary organic material."

2 *Formulation of SP-AMS sensitivity to size and shape*

2.1 Definition of E_s and E_z

E_s has been defined as a shape-dependent collection efficiency in the present manuscript, which is slightly different to the usage suggested in the main text of Onasch et al. (2012).

The definition of E_s in Onasch2012 was subtly changed from its original meaning of collection efficiency due to particle shape. Onasch2012 actually defined E_s,new as the fraction of particles lost due to particle beam divergence causing particles to miss the vaporizer in the main text, and I think this change allows a clearer description of the present results.

However, in Table 1 of Onasch2012, E_s was defined as "size and shape related collection efficiency", which is more similar to previous definitions of E_s ($E_{s,old}$ = shape-related collection efficiency), not fully consistent with the first quoted definition, and overlaps with the definition of E_L (the fraction of particles lost during transit through the inlet and aerodynamic lens). A similar point has been made implicitly by the authors, who specifically wrote SP-AMS IR-beam particle collection efficiency when directly rel-evant.
To avoid confusion in this comment, I will define E_z similarly to E_s ,new, but specifying E_z as the collection efficiency of the SP-AMS laser vaporizer, for particles exiting the aerodynamic lens. Since E_z is obviously a function of aerodynamic diameter d_a, one may equivalently define it as $E_z(d_a)$, "the aerodynamic-size dependent collection effi-ciency of the laser, for a perfect lens". If $E_z(d_a)$ = 1, a plot of SP-AMS response versus d_a would mimic the transmission efficiency graphs for E_L shown in Liu et al. (2007; e.g. their Figs. 9 and 10). Conversely, the SP-AMS response if $E_z(d_a)$ = 1 would be flat after correction for lens transmission, by definition.

To begin, we have revised the manuscript to use the symbol E_{IR} to describe the fraction of particles that do not interact with the IR laser sufficiently to be detected.

We have revised the manuscript to include a discussion of the effect of aerodynamic lens transmission. In summary, we agree that the effect on particle transmission may be substantial for particles of small vacuum aerodynamic diameters. However, Fig. 9c/g shows that the largest increase in sensitivity occurs after the particles have been grown greater than 150 nm in d_{va}, the lower cut-off for the aerodynamic lens. Thus, any changes observed in detection efficiency would be due to E_{IR} alone.

To revise the manuscript, we begin by introducing the lens transmission effect in section 2.2. We analyze the potential effect of the lens transmission in section 3.2

(3.4). In general, we find that although the lens transmission certainly affects instrument sensitivity for some of the smallest particle vacuum aerodynamic diameters, the largest increase in sensitivity doesn't ensue until after the soot particles have grown to a d_{va} > 150 nm. Figure 9 has been modified to illustrate the point at which aerodynamic lens transmission becomes unity.

We have added the following discussion in section 2.2, on page 7:

"Both the SP-AMS and the LAAPTOF use the same aerodynamic lens inlet design (Huffman et al., 2005; Liu et al., 2007). The aerodynamic lens these instruments use efficiently transmit particles with vacuum aerodynamic diameters (d_{va}) between 150 nm and 700 nm. Particles smaller than 150 nm tend to be lost with the excess gas, while particles greater than 700 nm may be impacted on the lens' critical orifices. For the measurements presented here, some particles start smaller than 150 nm d_{va} and then grow into the ideal transmission regime. This is very important for mass-based measurements like the SP-AMS, but less so for individual particle analysis for the LAAPTOF. We will discuss how this affects our results in section 3.3."

We have also added to section 3.2 (3.4) on page 20:

"The ability of an aerodynamic lens, such as that used on the SP-AMS, to effectively focus a particle depends on particle morphology. Panels (c) and (g) in Fig. 9 illustrate the increasing response of the SP-AMS to coated rBC as a function of vacuum aerodynamic diameter. The increasing response is likely due to the product of the aerodynamic lens transmission efficiency and the overlap between the particle beam and the IR laser, E_{IR}. However, it appears that the largest increase in particle sensitivity occurs when the particle d_{va} increases beyond 200 nm. The lower size cutoff of the aerodynamic lens is 150 nm, as discussed in section 2.2 and illustrated by a black dotted line in Figures 9c and 9g. Any changes in sensitivity for d_{va} >150 nm are therefore minimally affected by particle lens transmission. The particles grow as more SOA mass is condensed, and the larger particles are focused more efficiently by the aerodynamic lens towards the center of the IR laser, resulting in a larger instrument ion signal response with both increasing particle size and increasing SOA mass."

2.2 Specific comments on shape and transmission issues

I think that changing from the current E_s to E_z as defined and discussed above, would improve this manuscript for the following reasons. These comments relate to the x-axes of Fig. 9.

We have revised the manuscript to reference the fraction of particles that interact with the IR laser as E_{IR}. The description of E_{IR} is as follows on page 7:
"The fraction of particles that pass through the IR laser and are vaporized (E_{IR}) has been shown to be the largest uncertainty for SP-AMS mass measurements using the IR laser. "

2.2.1 Changes in χ

A major reason why a shape-based definition of E_s can be misleading is that no realistic experiment ever measures particles of equivalent $d_{vol.-equiv.}$ but different shape (χ_v), which is the only scenario where E_s is directly meaningful.

Rather, as in the present study, most experiments measure soot as it is coated, so

$d_{vol.-equiv.}$ increases while χ decreases. So a plot of either one of these variables is difficult to interpret, especially for different initial particles (Figs. 9a,e,d,h in the manuscript).

To some extent these experiments do have different morphologies at different d_{va}s, but it turns out that the d_{va}s that were accessible before achieving sphericity were relatively insensitive with respect to E_{IR}. We discuss this limited effect of sphericity on E_{IR} in section 3.4, page 21:

> "As seen in panels (d) and (h), the shape factor decreases towards unity (χ = 1 for spheres) as the particles become more thickly coated with SOA. Although the particles become nearly spherical after a few coatings, they still need to grow to a sufficiently large diameter to be successfully focused into the IR laser beam of the SP-AMS. Neither particle shape nor diameter alone is sufficient to describe E_{IR}. Even at d_{va} = 250 nm there is a factor of two difference in response to particles with different dynamic shape factors. However, the largest increase in instrument response occurs after the particles are mostly spherical (χ < 1.2), which as we discussed in section 2.3 may describe the state of rBC particles in ambient biomass burning plumes after less than 1 hour of aging. This increase in instrument signal is driven by growth from condensation of additional SOA."

2.2.2 Lower limit of E_L

Liu et al. (2007) have shown that the transmission efficiency of the AMS lens, E_L, can drop off from unity for aerodynamic diameters < 150 nm and > 400 nm. Although the studied particles were labelled as 143, 187, and 220 nm in Fig. 9 (initial mobility diameters), all of these particles had d_{va} < 150 nm, as seen in Fig. 9G, and could have been outside of the E_L=1 range at t = 0.

As the authors likely know, a constant d_{va} for all d_m is the expected behaviour, as shown theoretically by DeCarlo et al. (2004; their Eq. 57) and in the laboratory by Slowik et al. (2004; their Fig. 4) as well as the present study (Fig. 9G).

To clarify Fig. 9 and strengthen its message, I would suggest (i) changing the mobility-diameter labels in Fig. 9A to initial-mass labels (femtograms), and

As stated above, in some cases the initial masses were very similar, such is the nature of fractal-like soot. We feel that the mobility diameter is the most effective label as this was the dimension in which they were experimentally classified.

(ii) measuring $E_L(d_a)$

, to establish the range of d_a where E_z is the main factor controlling the sig-nals in Fig. 9. Since the implicit goal of Fig. 9 is to explore whether or not E_z reaches a plateau for some range of d_{va}, it would be a great improvement to be able to rule out the effects of E_L.

We believe the literature values for E_L are sufficiently precise for us to be confident in our analysis. Most of the change in sensitivity occurs when particle d_{va} had grown above 150 nm and therefore E_L = 1 in those cases is a good assumption. To illustrate this, we have included the discussion in response regarding Section 2.1 above in the revised manuscript and adapted Figures 9c & d to include the dotted line that indicates the lower size cutoff of the lens transmission for d_{va} < 150 nm.

2.2.3 χ subpanel in Fig 9

On a related note, I would suggest removing the χ from Fig. 9 because (i) it is an approximate calculation (specifically, the approximation is $\chi_v \approx \chi_t$) whereas all other measurements in Fig. 9 are not, and (ii) I don't think it adds more to the plot than the d_{va}, which by virtue of being a measured quantity already includes χ_v.

We agree with the reviewer that the dynamic shape factor, χ, is an approximation and that it is also described by the measured quantity d_{va}. However, we also feel that it is important to point out that the particle shape is changing as a result of the coating, and that the particles are likely spherical by the time they start showing significant increases in sensitivity to either C_3+ or K. We believe that the achieved near-sphericity is not obvious and discuss the limited effect of shape on E_{IR} in section 3.4 on page 21.

3 ***Expected C^+_3 signals as a function of coating***

Figure 9 and its discussion imply that the C+3 signal (y-axis of Fig. 9) was expected to level off with increasing coating, as was observed by Willis et al. (2014). Of course, I agree – it would be extremely strange if this signal did not level off, since the SP2 literature makes it very clear that the evaporation/sublimation of an OM-coated rBC particle is a two-step process; first OM evaporates then rBC sublimates.
The manuscript currently concludes that the signal does not level off, and I am inclined to agree with this conclusion, but it is such a surprising conclusion in the context of the SP2 and AMS literature that it would be worth clarifying two things: first, the issue of E_L as noted in comment 2.2.2 above, second, normalizing each soot size to the actual mass of soot within the particle (instead of the initial C^+_3 signal as was done). The first point would remove a potentially important bias from Fig. 9G. The second point would allow the 3 selected mobility sizes to represent repeat experiments.

As addressed previously, it appears that the most significant change in total sensitivity occurs after particles have grown greater than 150 nm d_{va} and thus the large increase in sensitivity is entirely due to E_{IR}.

We believe the normalization to un-coated soot conditions is the most appropriate metric in Figure 9 for three reasons, and have included the following in section 3.4, on page 19:

> "First, the inherent variability in biomass burning limits how much one can expect uncoated soot particles to have similar amounts of K or BC. However, within a given coating experiment, the average composition of the soot particle core is guaranteed to be the same. Second, it allows for ready comparison of the data in Figures 9 and 10, which compares the changes in the two ions directly. Finally, the normalization is a small change relative to the effect induced by coating the soot particles with SOA, which is the focus of this work. Prior to normalization, initial wall-loss corrected values for C_3^+ (K^+) for nascent conditions agreed within 30% (20%), compared to the sometimes 300% (600%) change due to coating the particles with SOA."

To expand on the second point, the expected signal of C^+_3 is directly related to the true rBC mass concentration. One could rewrite Eq. 1 in Willis et al. (2014) as:

$$\mathrm{C}_{\mathrm{rBC,SP\text{-}AMS}} = \frac{I_{\mathrm{C}_3^+}/f_{\mathrm{C}_3^+}}{\mathrm{Q} \cdot \mathrm{IE}_{\mathrm{rBC}} \cdot \mathrm{E}_z(d_{va}) \cdot \mathrm{E}_L(d_{va})} \qquad (1)$$

where $I_{C^+_3}$ is the observed C^+_3 signal, $f_{C^+_3}$ is the fraction of rBC signal observed as C^+_3, Q is the SP-AMS flow rate, and IE_{rBC} is the ionization efficiency of rBC. The other two terms, E_z and E_L were defined above, and are the only terms that should be a function of coating here, since they are both functions of d_{va}.
If E_L is measured and IE_{rBC} is inferred as done by Willis et al. (2014), then $E_z(d_{va})$ could be reported directly by replacing $C_{rBC,SP\text{-}AMS}$ with $C_{rBC,SP2}$ above, and rearranging. Unless I am mistaken, this $E_z(d_{va})$ would be a universally applicable correction factor for the SP-AMS in laser-only mode. If E_L cannot be measured for some reason, one could plot the right hand side of

$$\mathrm{E}_z(d_{va}) \cdot \mathrm{E}_L(d_{va}) = \frac{I_{\mathrm{C}_3^+}/f_{\mathrm{C}_3^+}}{\mathrm{Q} \cdot \mathrm{IE}_{\mathrm{rBC}} \cdot \mathrm{C}_{\mathrm{rBC,SP2}}} \qquad (2)$$

against d_a and at least overlay a literature curve for E_L, which would clarify the current Fig. 9G since the reader could then interpret the lower and upper limits of d_a with extra caution. (In case it's not clear, I'm focussing on Fig. 9G since that is the subpanel which should be generalizable to other studies.)

Extending this reasoning to determine the difference of E_z for potassium vs. rBC would not necessarily require knowledge of IE_K (Drewnick et al., 2006) but only the assumption that IE_K is constant. Perhaps filter-based quantification of K would help.

Experimental details prohibit the analysis described above. First and foremost, there was a flow splitting artefact that resulted in inconsistent subsampling of the aerosol. As a result, we cannot at this time correlate the absolute mass concentration from the SP2 with the mass concentration measured by the SP-AMS. Furthermore, the fact that our ion signal increased throughout our experiment prevents us from assuming that $E_{IR} = 1$ at the end of the experiments. As a result, we rely on relative changes and mobility measurements which are not dependent on absolute mass concentrations that would be affected by sampling artifacts for monodisperse aerosol.

We have included the following to address this within the manuscript at the beginning of Section 2.3, on page 9:

> "During these experiments, there was evidence of subsampling in the aerosol sampling lines, resulting in different particle concentrations reaching some instruments. As a result, we do not compare the absolute concentration of aerosol species measured by the various instruments. Instead, we perform our analysis based on particle size measurements that are unaffected by the flow-splitting issues due to the monodisperse aerosol used here."

4 *Other comments*

4.1 Endless increase in K sensitivity

The apparently endless increase in sensitivity to K should be further discussed, especially with respect to Willis et al. (2014)'s results where the collection efficiency for organics (not K) coated on regal black (not nascent soot) appeared to level off with coating mass ratios of ~3.
Could the increase in sensitivity to potassium have been related to its being surface ionized from organics rather than BC? (I'm envisioning a potassium salt crystal attached to a BC particle.) Both surface and material would matter during surface ionization. Some mention of the Saha equation or Carbone et al. (2015)'s work might also be relevant here (e.g. p12.24). This or some other physico-chemical effect, rather than particle beam focussing into the laser, might explain the apparently continuous increase in sensitivity. (I am only suggesting a brief discussion of this.)

Note also Ghazi and Olfert's (2015) data where particle sphericity at OM-to-rBC mass ratios of 5 are reported. (So as not to contradict the d_{va} *discussion above, I mean to suggest that sphericity should be the point at which whatever interactions causing the increased sensitivity to K reach their limit; nothing to do with* E_z*.)*

We thank the reviewer for bringing this work to our attention. We have included the following discussion on page 22:

"This is different from what is expected based on the results of Willis et al. (2014). When Willis et al. coated Regal Black with OM in the form of DOS, they observed that both OM ions and EC ions reached a maximum enhancement after coating the Regal Black with a thick coating of BES (OM mass:EC mass > 3.) Although we cannot rule out the effect of E_{IR}, the continued increase merits investigation of other causes for increased ion signals with additional SOA coating.

The continuous increase in K^+ ion signal may potentially be explained by changes in the thermal ionization efficiency, described by the Saha-Langmuir equation [Vandburg and Ionov, 1973]. This equation states that the probability of thermal ionization of a species will increase if the surface it vaporizes from has a higher work function or reaches a higher temperature. One explanation is that the highly oxygenated SOA possesses a higher work function than the rBC, and thus as the particle is coated it may generate potassium ions more efficiently. However, it seems unlikely that K would vaporize before all the SOA, as is seen in similar, albeit ambient pressure, IR laser systems (Moteki and Kondo, 2007; Schwarz et al., 2010; Stephens et al., 2003). An alternative explanation is that thicker SOA coatings may cause the particle to penetrate deeper into the Gaussian profile of the IR laser beam before the K vaporizes and it subsequently vaporizes from a hotter surface, thus generating more ions thermally.

With respect to the increasing C_x^+ signal with increasing coating thickness, a potential explanation includes the fragmentation of SOA to contribute significantly to C_x^+ mass. As stated in Section 3.4, laser-off measurements of the SOA showed that C_3^+ accounted for 0.08% of the SOA mass. With an OM mass increase of ten times the BC present in a particle, and assumed relative ionization efficiencies for rBC and OM of 0.2 and 1.4, respectively, the perceived increase in EC that would be attributed incorrectly would be 1.1%. This is much smaller than the observed relative increase in C_3^+ for OM:BC > 3, ~63% for the change in the last two data points for d_{mob} = 220 in Figure 9a. Furthermore, with the increased fraction of particles being vaporized by the IR laser, it has been shown that fragmentation would decrease, thereby decreasing the contribution of SOA to C_3^+. Alternative explanations may include instrument differences and variability in IR laser beam width."

We will include a reference to Ghazi and Olfert (2013) when discussing our coated particle's sphericity in Section 3.1 on page 12:

"The SOA coating mass would then be 25.7 fg of OA mass per particle, and would result in a mostly spherical particle. Although we cannot say the particle coating observed by Schwarz et al. (2008) consisted entirely of OA mass, the volume equivalent of any secondary component such as sulfate would also result in a spherical particle shape, with a SOA to BC mass ratio greater than > 3.2 (Ghazi and Olfert, 2013). As shown before, because the particle shape and size influences the particle beam profile and the beam width at the IR laser, the shape factor influences the total rBC signal detected by the SP-AMS."

4.2 Figure 7

[a] How confident are you that interference from OM ions is not an issue in the quan-tification of these C^+_x ions?

[b] When C^+_9 was not observed unless particles were coated, was the expected C^+_9 signal well above the detection limit? (i.e., can you exclude improved absolute signals as an explanation for the appearance of these higher-x C^+_x ions?)

Response to [a] and [b]:
Review of the mass spectra shows that OM ions may reduce the certainty with which we can quantify the C_x^+ where x is greater than 5. This is due to the low absolute signal for $C_{>5}^+$ ions, and also the abundant signal at the same nominal m/z from OM ions at high SOA loadings. However, the residual at those m/z's is reduced by including the C_x^+ ions in the peak fitting, and thus we feel this observation merits discussion. We've included the following revision to the manuscript to expand the possible interpretation of the trends on page 15:

"We propose three possible explanations for these trends: 1) SOA coating changes the fragmentation pattern of EC to reduce the C_3^+ signal, thereby enhancing the apparent ratio of other EC ions relative to it; 2) SOA generates significant signal for $C_{>3}^+$; or 3) The abundant signal at the same nominal masses as $C_{>5}^+$ causes the HR peak fitting to incorrectly attribute some signal to $C_{>5}^+$. Although the addition of the higher C_x^+ fragments appear to reduce the residual, the peak fitting without them is still very good (residual <0.05 %). Furthermore, the signal at C_1^+-C_5^+ is much higher and better resolved in the peak fitting due to fewer available peaks to fit. Although the causes of these trends are not clear, the trends themselves show that soot source apportionment by the SP-AMS might be most meaningful for rBC that has been thermally denuded to remove any coatings as this would remove any effect of OM on the C_x^+ ratios measured from the rBC."

4.3 LAAPTOF quantification

4.3.1 linear response

After the positive comments about the linear response of the LAAPTOF in the abstract, I was surprised by the complexity of Fig. 12. The response to 187 nm particles was linear, while the response to the other 2 sizes was definitely not! I do not think Figure 12 can be fairly described as "linear" and I would say that this word does not belong in the abstract nor conclusions, except with a strong caveat. Also, how many particles were used for this graph? Are statistical errors negligible (error bars)?

The abstract has been reworded as follows:

> "The average organic matter ion signal measured by the LAAPTOF demonstrated a positive correlation with the condensed SOA mass on individual particles, despite the inhomogeneity of the particle core compositions."

We have also included error bars indicating the standard error to Figures 12 and 13 and their captions. The number of particles used in the analysis is given in detail in section 3.2 (3.4) page 24. The following line (underlined) has been added to clarify the limited number of particles:

> "All data points represent the average of at least five particles with a minimum of 100 Hz of total EC ion signal at *m/z* +24, +36, +48, and +60, representing C_{2-5}^{+}. This excludes any homogeneously nucleated SOA particles and low-signal particles from the analysis. 160 particles of the 454 total particles detected met the above criteria. A linear regression fit of all LAAPTOF OM ion signal as a function of SOA mass per particle results in a $R^2 = 0.72$ (OM signal (Hz) = 75(fg SOA) + 167)."

4.3.2 complex SOA

p19.25: "despite the complex nature of the SOA coating"

Comment 1: is alpha pinene SOA complex from the perspective of 193 nm LDI? From what perspective? I would suggest that it is rather chemically homogeneous in terms of intramolecular structure.

aPinene SOA contains many types of organic compounds, from carboxylic acid monomers and high-molecular weight compounds (Zhang et al., 2015). Compared to other surrogates for OM, the use of SOA with a mélange of functional groups and gamut of molecular weights is an important step towards atmospherically relevant organic matter. This is especially true in the context of previously used less complex SOA surrogates such as single compounds (BES and DOS), and condensed fuel vapors. We have included the following discussion to clarify our meaning on page 24:

> "187 nm soot cores results in a highly linear fit with a $R^2 = 0.998$ (OM signal (Hz) = 120(fg SOA) + 179). SOA contains hundreds or thousands of organic compounds, with a broad range of molecular weights, degrees of functionalization, and optical properties (Zhang et al., 2015). Despite the complex

nature of the SOA coating and biomass-burning aerosol core, we observed a strong linear relationship."

Comment 2: Jeong et al. (2011) and Healy et al. (2013) found a good correlation be-tween OM signals in SP-LDI-MS and reference measurements, contrary to laboratory studies suggesting a high sensitivity to impurities, so it seems that complex OM mix-tures are more-easily rather than less-easily quantified. This might be discussed here. Citations to these two papers are also missing from p7.11.

We have included these relevant references. We have also included a discussion of how this work shows the feasibility of single-particle mass quantitative measurements. The text was revised as follows on page 24:

"It is important to note that although other LDI-SP-MS studies have found a good correlation between OM signal and reference measurements, this work shows that an even better correlation can be obtained if the analysis can be informed by the chemical information provided by the mass spectra. In this case we show that, with some improvements in excimer laser homogeneity, it may be possible for an algorithm to isolate rBC-containing particles and identify the necessary function to convert OM signal into SOA mass per particle."

4.3.3 charring

The word "charring" is used at p20.6,21; p21,4 to describe the formation of C^+_1 from OM during LDI. My feeling is that charring is associated with combustion and combustion timescales, and that a word like "decomposition" brings to mind the rapid molecular reactions that are likely involved in LDI.

We have revised the manuscript based on your suggestion.

4.3.4 variability

p20.13: "Despite the variability in the soot core composition..."

As commented in the General section, it would be nice to see quantitative information on how the authors observed this variability and on exactly what varies (relative K absence/presence of species, etc).

Electron microscopy measurements have shown that combustion particles are variable with respect to morphology and content of inorganic species (Li et al., 2003; Pósfai and Buseck, 2010). Furthermore, we observe a wide distribution of particle vacuum aerodynamic diameters for the uncoated soot, despite seeing a narrow distribution of BC mass from the SP2 (see Fig. 3). This suggests that the morphology of the nascent soot before being coated is variable. However, >97% of the individual particles contained measurable BC, as was measured by the SP2.

We have included the following text on page 11 to include this discussion:

"Electron microscopy studies of aerosol particles have shown that biomass burning can result in a wide range of particle compositions and morphologies (Li et al., 2003; Pósfai and Buseck, 2010). For this work, based on our measurements it appears that that most of the particles initially consisted of mostly BC, with trace primary organic material and inorganic material, including potassium salts. The particles maintained their initial core composition mass as SOA was condensed onto them. This made the particles increasingly homogeneous in terms of composition and shape. Single particle measurements by the SP2 showed that >97% of the particles detected by light scattering contained >0.7 fg of rBC. In cases where the uncoated, non-BC containing particles were too small to be detected by the SP2 via light scattering, the fraction of BC-containing particles was monitored after the particles were grown with SOA to detectable sizes. The fraction of BC-containing particles did not change, except in cases where there was substantial and obvious new particle formation. We believe that the largest variability in particles was with regard to the amount of potassium in a particle and with respect to particle shape. We do not have an estimate of variability in individual particle potassium content. Variability in particle shape is observed by the broad distribution in vacuum aerodynamic diameters. As the particles became coated, and therefore more uniform in shape and composition, the vacuum aerodynamic diameter distribution narrowed. The coating of fractal-like soot with organics has also been shown to cause structural collapse of the particle, potentially affecting its light absorption cross section (Cross et al., 2010; Ghazi and Olfert, 2013; Park et al., 2004)."

Second, how was variability in particle composition differentiated from variability in LAAPTOF performance?

In this work, variability in particle composition is constrained as described above. We do not attempt in this work to isolate the effects of particle variability with those induced by variability in the excimer laser fluence. This is discussed further in response to the next point.

Third, shot-to-shot variability is mentioned on p20.8, but how significant is this? How was it observed? And can it not also be invoked at p19.23 to explain the poor linear regression?

The measured shot-to-shot standard deviation from the average was ~20%. However, the excimer beam also has a Gaussian profile and is much larger than the cross-section of the particles (100 um x 300 um beam profile). Wenzel et al. (2004) for example showed that spatial homogenization of the LDI pulse greatly reduced the variability in measured mass spectra from standard compounds. Thus a large degree of the variability is inherent to the instrument, but can be accounted for by averaging over many similar particles. We believe that these compounding variabilities are in part addressed by averaging over many particles, but also suggest that in light of these considerations the linear regression on p23.10 is encouraging for further investigation. This would include calibrating with aerosols of more constrained composition, analyzing a larger number of particles, and/or using a UV laser with a more homogeneous spatial profile.

We have included the following text to emphasize the assumed variability in soot particles on page 25:

> "We sampled biomass-burning particles that contained potassium salts, which ionize readily, as well as strongly light-absorbing rBC (Gross et al., 2000). This represents the complex composition of realistic aged BBA. Initial particles were composed mostly of black carbon, with initially variable shapes, and with an unknown distribution of potassium salts per particle. Despite the variability in the soot core composition of individual particles, a positive correlation between the amount of SOA mass per particle and the LAAPTOF ion signal from oxidized organics was still observed from these mixed rBC and inorganic salt particles, when averaged over the many particles we sampled."

5 *Minor comments*

5.1 p2.37

Here I would say "compositional" rather than "chemical" information.

We have changed the manuscript according to your suggestion.

5.2 p3.3 and p17.9

p3.3 and p17.9 mention a "laser beam waist" without defining "waist". I understand it to mean the effective beam area as the beam is viewed from the perspective of an incoming particle? I'm not sure if the definition of "waist" matches this.

We have changed the term "laser beam waist" to "laser beam effective cross-section".

5.3 p3.11,42

Here the phrases "conventional aerosol mass spectrometer" and "normal operation" are ambiguous since the AMS has not yet been defined, and since this paper also discusses LDI-SP-MS.

The following text (underlined) has been included in the manuscript on page 3:

> "The SP-AMS is a variant of the conventional aerosol mass spectrometer that includes an intracavity infrared (IR) laser that can vaporize light-absorbing refractory material. A conventional AMS includes a 600 °C heater to vaporize aerosol particles in a vacuum before ionization . Refractory is an operationally defined term describing any material not vaporized by the heater in a conventional AMS."

We changed the term from "normal operation" to be less ambiguous:

> "The vapors produced by the IR laser are ionized by the same electron source used when vaporization is performed only with the 600 °C heater."

5.4 p3.13-15

Please reword these lines to allow for the caveat that the AMS can also see potassium, e.g. Drewnick et al. (2006), though not so well as the SP-AMS.

We have revised the manuscript as follows on page 3:

> "Two species of interest are difficult and impossible to detect, respectively, with a conventional AMS: potassium and refractory black carbon (rBC). Refractory is an operationally defined term describing any material not vaporized by the 600 °C heater in a conventional AMS. Potassium and rBC are chemical species that are used as inert, non-volatile tracers for biomass burning (Andreae, 1983; Hennigan et al., 2011; Lee et al., 2016)."

5.5 p3.36

I'd suggest giving "sequential vaporization" an expository sentence, here or later, given its central importance to your message.

We have modified the text to include the following on page 3:

> "We will show that as BBA is coated with OM, the SP-AMS ion signal response to the mass of potassium and BC increases. Furthermore, we will show that the SP-AMS response to potassium increases more rapidly than that for rBC for equivalent amounts of OM coating, despite the species being internally mixed. We believe that this is in part due to the ability of components with low ionization energy to be ionized directly upon vaporization (Carbone et al., 2015; Drewnick et al., 2006). However, most chemical components in the SP-AMS undergo sequential vaporization followed by 70 eV electron ionization of the neutral vapors. This allows for extensive but reproducible molecular fragmentation and subsequent classification and detection of the resulting ions in the high-resolution time-of-flight mass spectrometer."

I'd also suggest changing "only the vapors" to "the neutral vapors."

We have changed the manuscript according to your suggestion.

5.6 p4.9

Please provide the wavelength, laser fluence, and expected/designed/estimated aero-dynamic size transmission range of the LAAPTOF in the Experimental section.

The aerodynamic size transmission is expected to be similar to that of the SP-AMS, given that they have the same inlet design described in Liu 2007. We have added the following text to the manuscript on page 7:

"Both the SP-AMS and the LAAPTOF use the same aerodynamic lens inlet design (Huffman et al., 2005; Liu et al., 2007). The aerodynamic lens these instruments use efficiently transmit particles with vacuum aerodynamic diameters (d_{va}) between 150 nm and 700 nm. Particles smaller than 150 nm tend to be lost with the excess gas, while particles greater than 700 nm may be impacted on the lens' critical orifices. For the measurements presented here, some particles start smaller than 150 nm d_{va} and then grow into the ideal transmission regime. This is very important for mass-based measurements like the SP-AMS, but less so for individual particle analysis for the LAAPTOF. We will discuss how this affects our results in section 3.3."

The description of the LAAPTOF laser wavelength, power, and fluence are now included in section 2.2, page 7. The text has been changed as follows:

"The particle is then ablated and ionized with an 8 ns pulse from a VUV 193 nm excimer laser (EX5, GAM Laser, Inc.) that is triggered immediately by the second particle light scattering event. The VUV pulse travels coaxially up the particle beam and hits the particle in the ion extraction region, coincident with and orthogonal to the second light scattering laser beam. During these experiments, the 405 nm scattering lasers were not operational, and instead we free-fired the excimer laser at 10 Hz with an average laser pulse energy of 2.0 mJ, and an average laser fluence of ~1.1×10^5 J m^{-2}. We set and periodically confirmed the VUV laser power using a laser power meter (EnergyMax, Coherent, Inc.)."

5.7 p5.1

Another essential difference between spark-generated EC (which should not be called soot, as it is a very different material) and flame-generated soot is the microstructure of the carbon, which causes it to have, for example, different optical properties (Gysel et al., 2012) and so would interact differently with 193 nm and 1064 nm light.

Thank you for raising this point. We agree and have revised the manuscript as follows on page 5:

"Spencer and Prather (2006) used graphite spark-generated elemental carbon (EC) with condensed unleaded fuel to calibrate the ATOFMS LDI-SP-MS and found a linear relationship between the ratio of summed select OM cation signals to summed select elemental carbon cation signals, as the mass of OM condensed on the EC was increased. However, as pointed out by Gysel et al. (2012), EC from graphite spark discharge has different optical properties than combustion soot. Before such analysis can be used with confidence on realistic combustion BBA and complex SOA, two key differences between soot and BBA must be addressed, namely the variable morphology of BBA and the presence of inorganic salts."

5.8 p5.16

Both biomass-burning and engine-exhaust soot may be fractal-like, if the combustion conditions are of the right efficiency. So why would biomass-burning particles have a higher surface area than engine exhaust soot? I would actually expect a lower specific surface area due to slightly larger primary particles.

With respect to specific surface area, that is correct. However, the biomass burning particles do tend to be larger, and thus have more surface area, even if they have the same specific surface area. We have clarified the text as follows on page 11:

"Relative to engine exhaust soot, <u>biomass-burning particles are typically larger and contain more non-carbonaceous components</u>, such as inorganic salts (Bond et al., 2006; Li et al., 2003; Reid and Hobbs, 1998)."

5.9 p5.24

"electrical mobility" − > "mobility"

We have changed the manuscript according to your suggestion.

5.10 Figure 2

The last sentence in the legend could be clarified by mentioning d_{va} only.

We have changed the manuscript according to your suggestion.

5.11 p9.12 – σ

I wasn't clear where this effective beam width σ was from (Willis et al. 2014?). Also, it should depend on the absolute laser power of an SP-AMS, which is not a controlled variable at present.

We have added the citation for Willis et al. (2014) and mentioned that the IR laser effective beam width will depend on IR laser power on page 11:

"If the attenuation is low, then some of the particles will miss the laser and the refractory material will not be detected. The IR laser intensity was measured by Willis et al. (2014) to have a Gaussian distribution with a $\sigma \approx 0.18$ mm, although this may vary with IR laser power. As the beam-width probe is wider than the effective width of the IR laser for rBC, anything less than complete attenuation of the measured ion signal when the beam-width probe is at the center position indicates that some of the EC mass on particles containing rBC will not be detected. Therefore, E_{IR} will be < 1 (Willis et al., 2014). However, as we will show, vaporization of potassium occurs with a larger effective IR beam width, and thus E_s is larger for potassium than rBC."

5.12 p9.33

There is a publication using the SPLAT from PNNL which discussed this broadening in detail (in terms of line widths), and might be worth citing here.

We have included a citation for Zelenyuk et al. (2008) on page 9.

5.13 Section 2.4

It would be here helpful to state the mass of BC for comparison to the mass of OM. Also, instead of assuming a density of OM for Schwarz's coatings, it would be clearer to compare volumes since the present experimental results could be converted to volume.
(The latter is not intended as a request.)

We have included the BC mass on page 12:

> "They determined aged ambient particles with a BC core mass equivalent diameter of 200 nm (BC mass of 8.4 fg) had a coating thickness of 79 nm ~1 hour after emission from the biomass burning source."

We feel that the current discussion in units of mass allows for the ready comparison with Figures 9a & 9e.

5.14 p11.11

The caveat "by mobility" is not needed (or?).

We have changed the manuscript according to your suggestion.

5.15 p12.1

The fragmentation table is mentioned here as though it is highly complicated, perhaps you could alter the text to emphasize that only CO^{+}_{2} and C^{+}_{1} are inferred from a frag table in this case (or?), to strengthen your point.

We have expanded the text as follows on page 13:

> "Highly resolved ions were classified into a species and are displayed at unit mass resolution according to the fragmentation table therein. With respect to this dataset, the fragmentation table was only used to adjust the apportioning of CO_2^+ and C_1^+ ions. To account for CO_2+ in the gas-phase vs particle phase, the fragmentation table was adjusted using HEPA filter measurements. To account for C_1^+ that may result from the fragmentation of non-refractory OM components, the fragmentation table specifies that the amount of C_1^+ attributed to rBC is limited to $0.625*C_3^+$, the ratio observed for the rBC calibrant, Regal Black (Onasch et al., 2012)."

5.16 p12.14

Please mention that $C2H3O+$ also represents other anhydrosugars (Lee et al. 2010).

We have clarified the manuscript as follows on page 14:

"We also observed the highly oxygenated ions $C_2H_3O_2^+$ (*m/z* +60) and $C_3H_5O_2^+$ (*m/z* +73), which are common tracer ions for biomass burning. However, $C_2H_3O_2^+$ was less than 0.5% of the total organic signal for nascent soot, much less than what has previously been reported in BBA measurements (Aiken et al., 2010; Corbin et al., 2015; Cubison et al., 2011; Hennigan et al., 2010, 2011; Lee et al., 2010). This is likely due to low cellulose content in the bark that we burned, resulting in less formation of the anhydrosugars including levoglucosan compared to burning wood (Branca et al., 2007)."

5.17 p13.14

f_{44} wasn't mentioned before. Also, if laser-off measurements are generally available, the ratio of OM with laser on to off would be very interesting.

Given the already extensive nature of the manuscript, we refrain from extensive comparisons of the "organic" mass spectra. We include the observed *f44* for completeness, but don't wish to speculate on the contribution of refractory CO_2^+.

5.18 p13.17
Fullerenes are not rBC!

C60 sublimates at 600 C – it's not refractory.

A citation to the HRTEM literature would be relevant here.

We have removed the reference to fullerenes so as not to imply they are refractory. And have included the discussion of HRTEM literature on page 15, shown below:

"Attribution of rBC in the SP-AMS mass spectrum would be straightforward if graphitic material had a consistent fragmentation pattern and if all elemental carbon fragments (the C_x^+ family) arose only from rBC. However, studies using high-resolution transmission electron microscopy have shown that rBC can have varying degrees of disorder that result from formation conditions. Onasch et al. (2015) showed the IR laser in the SP-AMS may cause restructuring of the rBC due to annealing. Annealing has been observed in other graphitic particle systems using high resolution transmission electron microscopy and a pulsed laser (Vander Wal and Choi, 1999; Vander Wal and Jensen, 1998). It is also well known that organic aerosol produces C_1^+ and C_2^+ fragments following electron ionization (Alfarra, 2004; Corbin et al., 2014), but we have evidence that SOA either produces larger C_x^+ fragments or that it changes the rBC fragmentation pattern."

p13.25

"particle mobility" – > "size", since not just mobility size is used.

We have changed the manuscript according to your suggestion.

5.20 p17.1-8

I'm not clear on what was actually done here. Was the beam-width probe repeatedly moved into its central position throughout the coating experiment? It sounds like it was held constant, but that seems unlikely.

We've adjusted the text on page 20 as shown below:

"Panels (b) and (f) show the attenuation of the K^+ or C_3^+ ion signal normalized to SP2-measured rBC that resulted from moving the beam-width probe into the center of the particle beam."

5.21 p17.19

Referring to the extensive discussion above, "depends on particle size and shape" should be changed to a well-defined size, d_{va}.

In regard to the discussion that follows, we have opted to use the term "morphology". We will then discuss the size, shape, and ultimately the inclusive term d_{va}. The revised text reads as follows on page 20:

"The ability of an aerodynamic lens, such as that used on the SP-AMS, to effectively focus a particle depends on the particle morphology."

5.22 Figure 9a

The selected soot sizes are given in "soot core" sizes. Since the SP2 measures only soot cores, I had thought volume-equivalent SP2 information was being given initially, but actually these are mobility sizes (I think). Given the confusion between d_{ve}, d_{va}, and d_m in this manuscript I would suggest changing to m_p in femtograms here; which is also important to know the coating mass ratio for comparison to the x axis.

Copying our response from 1.1.1i above regarding this issue:
In some cases the initial masses were very similar; such is the nature of fractal-like soot. We feel that the mobility diameter is the most effective label as this was the dimension in which they were classified. We have however included in Figure 9e the initial BC masses.

We have revised the Figure caption as follows:

"**Figure 9.** SP-AMS-measured biomass-burning ion signals for C_3^+ (top) and K^+ (bottom) for three mobility selected core particle sizes versus four different metrics. These signals are corrected for particle wall-loss using SP2-measured rBC, and then normalized to values obtained from the uncoated nascent soot. Symbols are colored/shaped by their initial soot core mobility diameter (SP2-measured BC mass per particle), prior to SOA coating, where red triangles = 143 nm (1.2 fg), teal squares = 187 nm (2.0, 2.3 fg, two replicate experiments), and purple diamonds = 220 nm (3.9 fg). The nascent particles are indicated by black dots, and the lines connect them with the data points following subsequent SOA coatings. The left panels (a and e) display the normalized ratio of the SP-AMS-measured C_3^+ and K^+ ion signals, respectively, to the SP2-measured black carbon mass concentration as a function of the mass of SOA per particle. The SP-AMS-measured ion to SP2-measured rBC mass ratio is normalized to the uncoated soot values. Panels (b and f) display the attenuation of the SP-AMS ion signal caused by the beam-width probe in the center of the particle beam; greater attenuation indicates a more collimated, narrow particle beam, as expected for particles that are larger and/or more spherical. Panels (c and g) display the mode mobility diameter of the particles that produced either the C_3^+ or K^+ ion signal. Panels (e and h) display the particle dynamic shape factor; particles start as less spherical ($\chi > 1.0$) and move towards sphericity ($\chi = 1$) as more SOA mass is added. The measurement uncertainties are indicated by the vertical error bars and represent the standard deviation of one-minute AMS integration time from the ten-minute averages presented by each symbol."

5.23 Figure 9 legend

The sentence including "SP-AMS:SP2" seems to be a relic of an older draft.

We have clarified the Figure 9 caption to correct this, as shown in the response above to 5.22.

5.24 p19.14

"even with a high SOA:rBC mass ratio > 9"

Could you provide some context, e.g. citation to a paper like Ghazi and Olfert's?

In section 2.4 we cite Schwarz et al., who measured the SOA:rBC > 3. Although Ghazi and Olfert did investigate even thicker coatings on flaming soot, they did so in a laboratory. We have included the following text to provide context in the metric of mass of SOA-to-BC ratio:

"Although we cannot say the particle coating observed by Schwarz et al. (2008) consisted entirely of OA mass, the volume equivalent of any secondary component such as sulfate would also result in a spherical particle shape, with a SOA to BC mass ratio greater than > 3.2. As shown before, because the particle shape and size influences the particle beam profile and the beam width at the IR laser, the shape factor influences the total rBC signal detected by the SP-AMS. "

5.25 p21.21

In the conclusions, the authors cite Lee et al. (2016) as an example of how the present manuscript can help to improve the quantitative interpretation of SP-AMS measure-ments – I would suggest citing all of the other relevant SP-AMS papers here (which can be found via the citations to Onasch et al. (2012)).

We have expanded the papers cited, although we do not consider this list to be exhaustive. The findings here could be applicable to any measurements of BC by the SP-AMS.

It might also be worth mentioning, somewhere, that some atmospheric studies found a good correlation between SP-AMS-estimated and reference rBC concentrations. This good correlation could be interpreted as implying a constant rBC size distribution for those studies.

We have added the following text on page 26 to discuss this:

"Although these measurements explored thick SOA coatings and large particle sizes, we did not observe a plateau in instrument response to potassium or black carbon as the coating was increased. These findings have important implications for obtaining quantitative mass measurements, and can help to better inform the analysis and interpretation of SP-AMS measurements of the emissions and specifically aging biomass-burning aerosol (Corbin et al., 2015; Dallmann et al., 2014; Fortner et al., 2012; Lee et al., 2016; Massoli et al., 2015). We would like to add however, that although changes in dva may result in varying E_{IR}, SP-AMS measurements of rBC have been shown to correlate with reference measurements (Fortner et al., 2012; Willis et al., 2014). This suggests that the changes in secondary aerosol mass required to cause big changes in E_{IR} for BC did not happen on the timescale of those measurements."

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Interactive comment on “Effect of secondary organic aerosol coating thickness on the real-time detection and characterization of biomass burning soot by two particle mass spectrometers” by Adam T. Ahern et al.

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In the Conclusions, the authors state contrary to Corbin et al. (2014), we did not observe the characteristic fullerene-rich signal they previously reported for fuel-rich combustion. As an author of that study – and not as a reviewer – I would like to take the opportunity to comment publicly on the nature of those fuel-rich combustion samples.

After Corbin et al. (2014) was published, a paper by Maricq (2014) appeared where particles produced by a CAST burner were studied by mass spectrometry. Maricq operated his CAST burner in a manner that is considered comparable to our study, and his results indicated that the composition of the fuel-rich CAST burner soot was representative of a quenched combustion, such that soot graphitization reactions were frozen prior to the formation of normal flame soot.

Therefore, we now do not consider the "fuel-rich" CAST samples to be representative of fuel-rich combustion as relevant to biomass-burning, since it seems that the quenched flame, rather than the fuel-to-oxygen ratio, was essential in controlling that sample’s composition. In contrast, the results of Maricq support the view that the fuel-lean sample of Corbin et al. (2014) is representative to typical flame soot BC. Nevertheless, BC particles dissimilar from flame soot might still be relevant to atmospheric science (Fortner et al., 2012).

We thank Joel Corbin for bringing this work to our attention. We have changed (underlined) the Conclusions as follows to address this:

“Mass spectral analysis with the SP-AMS also revealed that increased SOA coatings on the biomass-burning soot changed the relative abundance of elemental-carbon clusters. Specifically, as the particles became more thickly coated with SOA, the ratio of $C_{>3}^+$ to C_3^+ increased. The degree of change for the ratio of C_4^+ to C_3^+ was smaller than the precision suggested Corbin et al. (2014) for identifying soot-particle source types using ratios of the elemental carbon ion family, C_x^+. However, the observed ratio of C_4^+ to C_3^+ was inconsistent with that previously observed from unquenched combustion (Corbin et al., 2014; Maricq, 2014). This reinforces the need for thermal denuding of ambient soot samples before attempting source analysis using EC ratios.”

Response to Referee #2:

General comments:

The manuscript reports the performance of two commercially available real-time aerosol mass spectrometers, soot-particle aerosol mass spectrometer (SP-AMS) and laser ablation aerosol particle time of flight mass spectrometer (LAAPTOF), based on the observations from a series of chamber experiments. Soot particles generated by wood burning was used as a source of black carbon core for the a-pinene SOA coat-ing experiments. Single particle soot photometer was used to quantify refractory black carbon (rBC) mass. This manuscript mainly focuses on the interpretation of SP-AMS measurements, providing valuable information to improve our understanding of collec-tion efficiency of SP-AMS, and provide useful data to demonstrate quantitative aerosol mass measurement using LAAPTOP. The data analysis is comprehensively performed and the manuscript is well written. However, there are a few points directly linked to the major conclusion of this paper that required further justification (please see ma-jor comments below). Overall, I highly recommend this manuscript to be published in Atmospheric Measurement Techniques after addressing the specific comments below.

We would like to thank the Referee for their thoughtful commentary and assistance in refining our message. We have discussed the major and minor comments in detail, and included our corresponding revisions of the manuscript, below. The Referee's comments are in italics, followed by our response. Additions or modifications to the manuscript text are <u>underlined</u>.

Major comments:

1 *SOA fragmentation: Section 3.1, page 13 and line 19-14: It is unclear whether the a-pinene SOA mass spectra obtained with a conventional AMS using a thermal vaporizer operated at 600 degree Celsius is from the "IR laser off" measurements in this study or from the literature. Variations of SOA composition produced from different chamber conditions are commonly observed and AMS mass spectra of SOA can be somewhat instrument dependent. This type of comparison would be more valuable if those mass spectra were obtained from the same chamber experiment and AMS. Furthermore, what is the possible reason to give less fragmentation for those organics are vaporized by the IR laser? If the proposed argument is correct, it is expected to observe gradual changes in fragmentation pattern of organic as a function of SOA coating thickness on BC surface (i.e. narrower particle beam and hence more SOA vaporized by the thermal vaporizer instead of the IR laser). Please discuss.*

We will respond to the points in the order that they were raised:
i) The SP-AMS mass spectra in Section 3.1 were collected with the IR laser on. We have clarified this in the Figure caption as follows:

"**Figure 6.** Stick integrated high-resolution mass spectra from the SP-AMS for nascent (top) and thickly SOA-coated soot (bottom). <u>Mass spectra were collected with the IR laser on</u>, and have been normalized by total rBC mass as measured by the SP2 to account for particle wall-loss. Peak bar colors correspond to the assigned chemical components for each unit *m/z* ion peak, based on analysis of the high-resolution mass spectra. The nascent soot spectrum is rich in refractory black carbon, inorganic ions, and organic fragments. The spectrum from the SOA-coated soot, on the other hand, is dominated by the OM from the secondary organic aerosol. However, increased sensitivity to larger EC fragments from rBC in the coated particles is obvious."

ii) As shown by Canagaratna et al. (2015) using VUV-SP-AMS, the organic molecules that are vaporized with the IR laser evaporate at their respective boiling point and thus are less energetic than those that vaporize from the 600 °C heater. We have included a discussion of this in the text, and reference Canagaratna et al. (2015), as follows:

> "Canagaratna et al. (2015) used near-threshold VUV ionization with a SP-AMS to confirm that ionization via the IR laser resulted in significantly less fragmentation for pure species, relative to when vaporized by the 600 °C heater."

iii) The reviewer's interpretation that a gradual change in OM fragmentation patterns would be expected with increasing SOA coating is correct. This would be an interesting investigation due to a number of variables that change throughout the experiment. Changes in the organic mass spectra would vary due to changes in the fraction of particles interacting with the laser. The mass spectra could also change due to the changing SOA composition with subsequent a-pinene injections. We believe that a compositional comparison would be more appropriate to analyze in a separate publication and is beyond the scope of this already long first manuscript exploring SP-AMS measurements of well-constrained BC particles coated by SOA.

1 *rBC fragmentation: Section 3.1, line 8-12 and Figure 7: Quantification of Cx ions, especially those greater than C6 with relatively weak signals (from Figure 6), may be influenced by organic fragments that overlap with Cx ions in the peak-fitting of high resolution mass spectra. The influence can become more significant as the SOA mass associated with BC increased. Please discuss this possible uncertainty on the observed trend in Figure 7.*

Review of the mass spectra shows that OM ions may reduce the certainty with which we can quantify the contribution to the measured ion signal from C_x+ EC ions where x is greater than 5. This is due to the low absolute signal for C_x when x > 5, and also the abundant signal at the same nominal m/z from OM ions at high SOA loadings. However, the residual (the amount of signal that remains for after subtracting the optimized sum of a given set of ions at a nominal *m/z*) at those m/z's is reduced by including the C_x+ ions in the peak fitting, and thus we feel this observation merits discussion. We've included the following revision to the manuscript to expand the possible interpretation of the trends on page 15:

"We propose three possible explanations for these trends: 1) SOA coating changes the fragmentation pattern of EC to reduce the C_3^+ signal, thereby enhancing the apparent ratio of other EC ions relative to it; 2) SOA generates significant signal for $C_{>3}^+$; or 3) The abundant signal at the same nominal masses as $C_{>5}^+$ cause the HR peak fitting to incorrectly attribute some signal to $C_{>5}^+$. During HR peak fitting, the user decides whether to include an ion based on the residual signal. The residual signal is the amount of measured signal that is not reproduced by the fitted HR ion species. Although the addition of the higher C_x^+ fragments appear to reduce the residual signal, the peak fitting without them is still very good (residual <0.05 %). Furthermore, the signal at C_1^+-C_5^+ is much higher and better resolved in the peak fitting due to fewer available peaks to fit. Although the causes of these trends are not clear, the trends themselves indicate that soot source apportionment by the SP-AMS might be most meaningful for rBC that has been thermally denuded to remove any coatings as this would remove any effect of OM on the C_x^+ ratios measured from the rBC."

1 *Page 17, line 20-23 and Page 18, line 11-14: This argument is based on the assumption that all particles are homogeneous and completely internally mixed but it seems unlikely the case for the monodisperse particles used for the SOA coating experiments. As shown in Figure 3 (top panel), the size-selected particles have a wide range of dva and the size distributions of potassium and rBC are not completely overlapped to each other. A recent field work has demonstrated non-uniform mixing of potassium in the aged biomass burning emissions (Lee et al., 2016). Please clearly state the assumptions used in the data analysis and briefly discuss how may this uncertainty affects the final conclusion of the paper.*

With respect to the assertion that the different rate of change in K and EC signals reveal different effective IR beam widths, the most important fact is that, as stated on p16.7-8, turning off the IR laser greatly decreases the K signal to less than 1% of the signal observed with the laser on. This shows that the large change in the K signal was a result of being internally mixed with rBC. Furthermore, as stated on page 10, the SP2 measurements throughout the experiments showed that > 97% by number of the biomass burning aerosol used in this experiment contained > 0.7 fg of rBC, and therefore the particles were able to sufficiently absorb the IR laser and vaporize any non-refractory material.

With respect to our assumptions about the particle composition, we have included the following text on page 11:

"Electron microscopy studies of aerosol particles have shown that biomass burning can result in a wide range of particle compositions and morphologies (Li et al., 2003; Pósfai and Buseck, 2010). For this work, based on our measurements it appears that that most of the particles initially consisted of mostly BC, with trace primary organic material and inorganic material, including potassium salts. The particles maintained their initial core composition mass as SOA was condensed onto them. This made the particles increasingly homogeneous in terms of composition and shape. Single particle measurements by the SP2 showed that >97% of the particles detected by light scattering contained >0.7 fg of rBC. In cases where the uncoated, non-BC containing particles were too small to be detected by the SP2 via light scattering, the fraction of BC-containing particles was monitored after the particles were grown with SOA to detectable sizes. The fraction of BC-containing particles did not change, except in cases where there was substantial and obvious new particle formation. We believe that the largest variability in particles was with regard to the amount of potassium in a particle and with respect to particle shape. We do not have an estimate of variability in individual particle potassium content. Variability in particle shape is observed by the broad distribution in vacuum aerodynamic diameters. As the particles became coated, and therefore more uniform in shape and composition, the vacuum aerodynamic diameter distribution narrowed. The coating of fractal-like soot with organics has also been shown to cause structural collapse of the particle, potentially affecting its light absorption cross section (Cross et al., 2010; Ghazi and Olfert, 2013; Zhang et al., 2008)."

We have also included the following revision to clarify the discussion on page 20:

"If an internally mixed particle containing potassium and rBC passes through the center of the laser, two processes will take place. rBC will become vaporized and ionized, and potassium will be thermally ionized. Since turning off the IR laser reduced the potassium signal to <1% of that when the laser was on, we know that the observed changes in K signal result from rBC particles internally mixed with some K. Thus, our measurements show that particles may pass through the potassium thermal ionization region of the IR beam but miss the smaller rBC vaporization region."

With respect to Lee et al. (2016), it is possible that the biomass burning emissions they measured included a wider variety of fuels and combustion conditions resulting in more variable biomass-burning aerosol composition and properties. It is also conceivable that for single-particle measurements, the area where a particle interacts with the IR laser beam may cause a sampling artefact that may resemble external mixing.

4) Figure 11 and Figure 9: More discussion is required to interpret the continuous in-crease of K and C3 signals as SOA mass increased. In particular, it is expected that Cx and K signals become saturated when BC particles are thickly coated and become spherical shape if particle beam width is the major factor that governs overall collection efficiency (Willis et al., 2014). However, the mobility diameters of size-selected particles may fall in the dva region (i.e. < 150 nm) that the lens transmission efficiency of particle is less than 1. This may explain why the experiments with smaller BC cores show steeper slopes in Figure 9a and e. Please discuss if the effects of lens transmission efficiency can be ruled out in this study and how may this uncertainty affects the final conclusion. Furthermore, what is the major purpose of Figure 11? I think Figure 9 already provides the same information in a more quantitative manner. Please clarify.

This important issue was also raised by Referee #1, and we include our response and corresponding revised text regarding this issue below:
We have revised the manuscript to include a discussion of the effect of aerodynamic lens transmission. In summary, we agree that the effect on particle transmission may be substantial for small vacuum aerodynamic diameters. However, Fig. 9c & 9g shows that the largest increase in sensitivity occurs after

the particles have been grown greater than 150 nm in d_{va}, the lower cut-off for the aerodynamic lens. Thus, any changes observed would be due to E_{IR} alone.

To revise the manuscript, we begin by introducing the lens transmission effect in section 2.2. We analyze the potential effect of the lens transmission in section 3.2 (3.4). In general, we find that although the lens transmission certainly affects instrument sensitivity for some of the smallest particle vacuum aerodynamic diameter, the largest increase in sensitivity doesn't happen until after the soot particles have grown to a d_{va} > 150 nm. Figure 9 has been adapted to illustrate the point at which aerodynamic lens transmission becomes unity.

We have added the following discussion in section 2.2, on page 7.

"Both the SP-AMS and the LAAPTOF use the same aerodynamic lens inlet design (Huffman et al., 2005; Liu et al., 2007). The aerodynamic lens these instruments use efficiently transmit particles with vacuum aerodynamic diameters (d_{va}) between 150 nm and 700 nm. Particles smaller than 150 nm tend to be lost with the excess gas, while particles greater than 700 nm may be impacted on the lens' critical orifices. For the measurements presented here, some particles start smaller than 150 nm d_{va} and then grow into the ideal transmission regime. This is very important for mass-based measurements like the SP-AMS, but less so for individual particle analysis for the LAAPTOF. We will discuss how this affects our results in section 3.3."

We have also added to the following to section 3.2 (now 3.4) on page 20:

"The ability of an aerodynamic lens, such as that used on the SP-AMS, to effectively focus a particle depends particle morphology. Panels (c) and (g) in Fig. 9 illustrate the increasing response of the SP-AMS to coated rBC as a function of vacuum aerodynamic diameter. The increasing response is likely due to the product of the aerodynamic lens transmission efficiency and the overlap between the particle beam and the IR laser, E_{IR}. However, it appears that the largest increase in particle sensitivity occurs when the particle d_{va} increases beyond 200 nm. The lower size cutoff of the aerodynamic lens, as discussed in section 2.2 and illustrated by a black dotted line in Figures 9c and 9g. Any changes in sensitivity > 150 nm are therefore minimally affected by particle lens transmission. The particles grow as more SOA mass is condensed, and the larger particles are focused more efficiently by the aerodynamic lens towards the center of the IR laser, resulting in a larger instrument ion signal response with both increasing particle size and increasing SOA mass."

We believe that the high time resolution portrayed in Figure 11 highlights the fact that the increase in K and C_x are still increasing despite the particles being thickly coated. If during the transition between the averaged points we had achieved E_{IR} = 1, the high-time resolution data in Figure 11 would show a plateau. We have included the following text to elaborate on this unexpected finding:

"This is different from what is expected based on the results of Willis et al. (2014). When Willis et al. coated Regal Black with OM in the form of BES, they observed that both OM ions and EC ions reached a maximum enhancement after coating the Regal Black with a thick coating of BES (OM mass:EC mass > 3.) Although we cannot rule out the effect of E_{IR}, the continued increase merits investigation of other causes for increased ion signals with additional SOA coating.

The continuous increase in K^+ ion signal may potentially be explained by changes in the thermal ionization efficiency, described by the Saha-Langmuir equation [Vandburg and Ionov, 1973]. This equation states that the probability of thermal ionization of a species will increase if the surface it vaporizes from has a higher work function or reaches a higher temperature. One explanation is that the highly oxygenated SOA possesses a higher work function than the rBC, and thus as the particle is coated it may generate potassium ions more efficiently. However, it seems unlikely that K would vaporize before all the SOA, as is seen in similar, albeit ambient pressure, IR laser systems (Moteki and Kondo, 2007; Schwarz et al., 2010; Stephens et al., 2003). An alternative explanation is that thicker SOA coatings may cause the particle to penetrate deeper into the Gaussian profile of the IR laser beam before the K vaporizes and it subsequently vaporizes from a hotter surface, thus generating more ions thermally.

With respect to the increasing C_x^+ signal with increasing coating thickness, a potential explanation includes the fragmentation of SOA to contribute significantly to C_x^+ mass. As stated in Section 3.4, laser-off measurements of the SOA showed that C_3^+ accounted for 0.08% of the SOA mass. With an OM mass increase of ten times the BC present in a particle, and assumed relative ionization efficiencies for rBC and OM of 0.2 and 1.4, respectively, the perceived increase in EC that would be attributed incorrectly would be 1.1%. This is much smaller than the observed relative increase in C_3^+ for OM:BC > 3, ~63% for the change in the last two data points for d_{mob} = 220 in Figure 9a. Furthermore, with the increased fraction of particles being vaporized by the IR laser, it has been shown that fragmentation would decrease, thereby decreasing the contribution of SOA to C_3^+. Alternative explanations may include instrument differences and variability in IR laser beam width."

Minor comments:

2 *Introduction: It is recommended to change the subtitle of Section 1.1 to "Characterization of carbonaceous aerosol by SP-AMS" and add another subtitle to Page 4, line 9 for LDI-SP-MS.*

We have followed your suggestion.

2 *Section 2.4 and Figure 4: It is more appropriate to put the text and figure to the Section of Results and Discussion.*

This was suggested by Referee #1 as well. We agree and have moved this text and figure to the Results section.

2 *Figure 8 and page 15, line 15: OM fragment at m/z 43 (C2H3O+) was not clearly observed in Figure 8. Is this fragment frequently observed in other particles?*

This OM fragment at *m/z* 43 was observed in 10 of the 160 total particles used in this analysis. It was not used for this analysis because introduction of the additional noise at that *m/z* was larger than the effect on total OM signal by including *m/z* 43.

Technical corrections:

1) Page 9, line 23: AMS chopper has 2% throughput.

Thank you, this has been fixed.