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Interactive comment on “Formation and evolution of Tar Balls from Northwestern US wildfires” *by* Arthur J. Sedlacek III et al.

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In this paper, Sedlacek et al. present a set of measurements and analysis to understand formation and properties of tar balls (TB) in biomass burning plumes on the US. The paper is very well written, and for the most part, clear. Considering the difficulty in extracting specific information on different particles from biomass burning plumes, the papers present a set of very compelling new data on the TB physical properties and their evolution. I, therefore, strongly support the publication of these results, as I think they will be very useful to the community. I only request a few minor clarifications and small changes as discussed next.

General comments: 1. In the abstract, the authors suggest that the index of refraction

found for the TBs is m=1.56-0.02i, but I did not find this value to be really discussed in the paper. The last figure of the paper shows a comparison with different index of refraction values published in the literature. The use of the Chakrabarty et al. and the Hand et al. index of refractions seems to bracket the measured values, but why was the Hand value for k=0.02 chosen for the abstract is not clear to me. In addition, which one of the two Chakrabarty et al. values given in table 2 were used in the last figure? My point is that the abstract seems to imply a rather specific index of refraction value, while I think the range between the two works mentioned above probably would be a more realistic assertion.

The authors agree with the Reviewer. Our intention is to show that the BBOP data are consistent with TBs having a refractive index with a low imaginary component, but not consistent with the two high imaginary components in the literature. Abstract wording (line 18) changed to read: “Mie calculations are consistent with weak light absorbance (i.e., m similar to the literature values 1.56 – 0.02i or 1.80 – 0.007i).” Similar changes have been made in text (e.g., we added “or 1.80 – 0.007i” to line 276).

2. I would consider some small reorganization or at least some referencing to specific sections in some cases where some concepts/quantities are mentioned before an explanation is given on how they are calculated or defined. An example is the TB mass fraction, but I will mention that more directly in the specific comments next.

We have carefully read through the manuscript and, with the help of the both Reviewers, identified locations where action was needed (e.g., line 171).

Specific comments:âĂÍ- Line 69: is this a commercial impactor?

Yes. The impactor sampler was made by Arios Inc., Tokyo, Japan. Text has been added to clarify this.

- Line 76: “had the same qualitative trends. . .”, in what sense? I do not fully understand this statement.

The authors agree that the wording is confusing. The sentence has been modified to read: “Ns-soot volumes as determined from 2D TEM images using fractal parameters from Adachi et al (2010) were in agreement with that derived from SP2 measurements of refractory black carbon (rBC).”

- Line 100: Why is the SP-AMS calibrated with regal black and the SP2 with fullerene? Does it matter that two different types of particles are used for calibration?

The reviewer asks a very good question. First, however, we will point out that the data used from the SP-AMS in this work derives from the ammonium nitrate calibration of non-refractory particulate matter (NR-PM), here dominated by organic aerosol particles, and a relative collection efficiency obtained by comparing the laser on NR-PM to the laser off NR-PM. Under SP-AMS laser off conditions, the SP-AMS operates as a standard AMS with a resistively heated tungsten vaporizer, which is calibrated with ammonium nitrate particles (Canagaratna et al., 2007). Under SP-AMS laser on conditions, the dominant NR-PM signals in the biomass burning plumes were still derived from the standard tungsten vaporizer. Direct comparisons between the two sampling modes indicate that the laser on mode increased the measured NR-PM organic mass loading due to several factors, including (1) different collection efficiencies between the two different vaporizers, (2) inadvertent heating of the ion formation chamber and tungsten vaporizer above their typical values, and (3) potential different sensitivities between ions formed from the two vaporizers (Onasch et al., 2012; Willis et al., 2014; Lee et al., 2015). Given the incomplete understanding of these different influential factors, we determined and applied separate collection efficiency (CE) factors for the NR-PM signal obtained during laser on (0.76) and laser off (0.5) modes.

Getting back to Reviewer #2 specific question, given the lack of a comprehensive understanding of black carbon particle chemical and physical properties, it is very common for different measurement techniques to rely on different calibration standards. In the current case, Onasch et al., (2014, 2015) and Corbin et al. (2015) explored the refractory carbon cluster ion distributions measured for different black carbon particle

types, including Regal black and fullerene soot, which are manufactured carbon blacks, and atmospherically relevant soots from diesel and biomass burning. Both the diesel and the biomass burning ion distributions were more closely replicated by Regal black particles than fullerene soot particles. The major differences here pertain to Cx+ ion signals for clusters greater than C5+; fullerene soot generates significant large carbon cluster ions, whereas Regal black does not exhibit these ion signals.

The amount of incandescent light collected by a SP2 instrument also varies by soot particle type. As has been discussed in the literature (Moteki and Kondo, 2010; Gysel et al., 2011; Laborde et al., 2012; Baumgardner et al., 2012), fullerene soots tend to give calibration curves that better represent ambient soot particles than particles like Regal black. Therefore, within the SP2 community, fullerene is widely used as a calibration standard (Baumgardner et al., 2012). These differences relate to the amount of incandescence light collected for a given mass of particles. More graphitic or refractory particles, such as graphite and carbon blacks heat to higher temperatures prior to vaporization/oxidation than either fullerene soot or ambient soots.

As indicated above, these differences in black carbon calibrations are interesting and complex, but do not directly relate to the results presented here.

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- Line 115: “using the laser-off CE = 0.5 as the presumed ambient NR-PM loadings” maybe a verb is missing as in: “using the laser-off CE = 0.5 to calculate the presumed ambient NR-PM loading?

We agree that the wording was awkward. We have changed the sentence to read, “Counting each transect pair as a data point and using the laser-off mode corrected with CE = 0.5 as the best estimate of ambient NR-PM loading, we obtain an average laser-on mode CE = 0.76 (1σ = 0.10) with CE values that range from 0.63 to 0.88 for a given transect pair.”

- Line 125: “enhancement” with respect to the background? How was the background determined?

The background, which was readily apparent, was determined during sampling times in between plumes. These small changes in background mattered little for most in-plume measurements as we sampled close to the fires during BBOP and the concentrations were typically much higher than in background surround air.

- Line 171: This is an example of when a concept, I believe, is discussed before it is defined. The question the reader might have is: how was the mass ratio calculated? This is discussed later, but here is confusing. Either postpone this discussion, or define the ratio before, or at least refer to the section where the mass ratio is clearly defined. The same issue appears in line 182.

We appreciate the Reviewer’s comment about using a term/concept before formally defining it and how this could create difficulties. We have changed in line 176 the text “TB/ns-soot mass “ to “TB/ns-soot number ratio”. In responding to this comment, it became clear that we should have used the number ratio instead of mass ratio given that we were discussing the TB/ns-soot number ratio in this paragraph.

In line 182, the sentence currently reads: “The downwind increase in TB mass is due to an increase in number concentration rather than a change in particle size (green 25th, 50th, and 75th percentile lines in the lower panel of Figure 6).” This sentence is merely saying that an increase in TB mass contribution in the plume is due not to individual particle size growth, but instead, due to increased number of TB particles. The authors feel that the sentence is clear on this point and that there is no new concept that is being presented. Unrelated this to comment, the authors have elected to make a small stylistic change to Figure 6: use of shading to define the 25th to 75th percentile range. Manuscript text that referenced this figure has been updated to reflect this stylistic change.

- End of sentence on line 188: I think they refer to figure 6.

Yes, the Reviewer is correct, and this has been changed.

- Line 206: I think it would be useful to explain how R is calculated, given that what was measured (at least reported earlier) is the number fraction. To calculate the mass ratio a few assumptions (e.g., the bulk mass density) and different measurement of the soot morphology especially needs to be made, I would guess. Again, this becomes clear below, but here is a bit obscure. I would move the mass ratio definition earlier on, or at least I will clearly refer here to the section where it is defined.

We defined R as the ratio of TB mass to ns-soot mass. We have added (highlighted in bold) the following to the end of the sentence at line 206: “TB fractional contribution to total mass is denoted by fTB and we define R as the ratio MTB/Msoot derived from TEM and SP2, respectively.”

- Line 248: “The results presented here raise the question as to how best to describe TBs.” One “to” too many, I believe.

The authors appreciate the extra care about the grammar shown by the Reviewer: the extra “to” has been removed.

- Line 274: Maybe refer back to equation 1a so it is clear what the four components are.

We have added (highlighted in bold) the following text to the end of the sentence in line 274 “. . ...where i labels the four aerosol components in our calculation (see equation 1a)”.

- Lines 275-276: It would be good to have error bars associated with the SSA estimates from the measurements. In addition, I guess Mie was used for soot as well, which might underestimate the SSA of that component, although maybe that’s not a real issue owing to the fact that the Mie underestimation is mostly in the scattering

Error bars have been added to the SSA estimates derived from the measurements.

- Figure 4: y-axis label, “Age” seems an odd term here. I would think “Age” should have dimensions of time, while the quantity plotted is probably dimensionless. Same on the x-axis label of figure 6, although in this case there is the term “photochemical” in front, at least.

The Reviewer is correct. The x-axis label has been changed to photochemical age. Defined in text as – Log10 ([NOx]/[NOy]), which is dimensionless.

- Figure 8: As mentioned earlier, error bars on the measured data (green curve) would help interpret which literature value(s) of the index of refraction is(are) consistent with the measurements. Caption, for Chakrabarty et al. in table 2, are reported two different index of refraction values, which one was used here? In addition, why one or the other?

We have added error bars to the experimentally-derived SSA estimates as discussed in response to the Reviewer’s earlier comment. As highlighted in Table 3, we used at TB refractive index (RI) of 1.8 – 0.007i from Chakrabarty in our calculated SSAs. While we could have added an additional SSA curve on figure 8 – to reflect the other TB RIs – the objective of this figure was to bound our experimentally-derived SSA estimates using four published RIs whose imaginary component span two orders of magnitude.

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