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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Measurements to determine mixing state of black carbon emitted from the 2017/2018 California wildfires and urban Los Angeles" *by* Joseph Ko et al.

**Anonymous Referee #2**

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The manuscript presents measurements of refractory black carbon (rBC) mass and number loadings along with derived rBC mixing state properties (e.g., fraction of thickly coated rBC particles and coating thickness) for three events (air masses) that were encountered at a sampling station located Catalina Island (CA). The measurement campaign itself can best be described as a measurement opportunity. Emission sources were identified using HYSPLIT backtrajectory analysis coupled with inputs from the GDAS (Global Data Assimilation System) and HRRR (High-resolution Rapid Refresh) meteorological databases. Analysis was further augmented with data from local weather stations, local news reports, NASA MODIS (Aqua/Terra) imagery, and the California Department of Forestry and Fire Protection for spatial and temporal ex-



tents of sampled wildfire plumes. Armed with these datastreams the authors report on the correlation of rBC mass/number loadings and derived mixing state properties with emission source and estimated plume age. Examples of findings include the wildfire named "Camp Fire" that was ascribed as being responsible for a sample plume made of up thickly-coated rBC particles that were nominally a week old and slightly thinner coated particles (i.e., 36 nm and less) were ascribed to urban Los Angeles emissions. The authors also attribute biomass burning as a contributing source to rBC particles that were found to have a coating thickness $\sim$10 nm and were about a day old. While this work is highly-focused, it contains useful observations on rBC mass loading and mixing state that are of value to the community and thus should be published. However, this reviewer has profound reservations regarding three areas in this manuscript: (i) source attribution and estimated plume age; (ii) the research team's use of the rBC number size distribution data; (iii) and the discussions about increasing rBC diameter with atmospheric aging. Therefore, it is recommended that this manuscript undergo a major revision and be resubmitted.

Source attribution and plume age. With respect to source attribution, absence of a measurement of a biomass burning tracer (e.g., levoglucosan) have forced the authors to rely on HYSPLIT for emission source composition. For those flow patterns that are direct from source to measurement site, this approach is considered robust. However, for those trajectories that are more convoluted the robustness of this link degrades. Further, absent some measure of plume age (e.g., f44 fragment from an aerosol mass spectrum), the author's, again, rely on backtrajectories for plume age estimates. To be clear, the SP2 mixing state analysis is considered robust and the issue is with plume composition (source) and age. For example, this reviewer is astounded that the author's ascribe a biomass burn (BB) source to rBC coating thicknesses that are on the order of 10 nm and that the estimated plume is about a day old. To the author's credit, they seem to be aware of this when they acknowledge that their derived rBC coating thicknesses for a plume aged about a day is in contrast with several other published values (14 cited works). Their sole rebuttal reference to these 14 references is from

a paper by this same group authors. As highlighted in the 14 references and through direct experience BB -generated rBC becomes thickly coated (often well above 50 nm) very quickly (within the first couple of hours). This is due to the fact that wildfire plumes contain large OA (organic aerosol) mass loadings and are very rich in organic materials that can lead to SOA (secondary organic aerosol) production and condensable material onto an rBC particle. To say that BB plumes are contributing to the plume containing coating thicknesses that are more characteristic of urban plumes needs to be reassessed. Especially given that the preponderance of published data and new measurements (e.g., recently conducted WE-CAN and FIREx field campaigns) all show that BB events create very thickly coated particles very quickly. To be clear, this reviewer is not questioning the derived coating thicknesses, but rather the source attribution and estimated plume age. Therefore, the authors need to make a much more convincing case that the rBC particles sampled during L4 actually contain any biomass burning particles. As outlined above, this becomes a much harder argument to make due to the lack of compositional information that could quantify whether the L4 plume actually contained any wildfire emissions.

Staying with plume age, at the other end of the age spectrum, the authors argue that biomass burn plumes sampled during L3, and L8, L9, L10, are all nominally aged about a week. While the rBC particles will become thickly coated in the near field, as outlined above, coating volatility and subsequently photochemistry will likely cause the initially thickly coated rBC particles to lose material with age - through plume dilution and molecular fragmentation. This, again, gets at the robustness of the estimated plume age. As discussed above, for more direct flow patterns, the use of HYSPLIT is likely robust, but if the flow patterns are circuitous, and cross-over other potential emission sources, the possibility, indeed likelihood, of entrainment of other emission sources must be considered. If the authors feel that their ages are robust, then they should, more fully, discuss how to interpret their findings with the larger community of SP2-based mixing state literature. To this reviewer, this is one of the core findings of this manuscript and as such, needs to be addressed.



Finally, was any analysis conducted on whether the plumes sampled underwent any precipitation events that could have altered the microphysical make up of plume (e.g., washed out larger size, more thickly-coated particles)? [The authors are encouraged to read Taylor et al., (2014)Size-dependent wet removal of black carbon in Canadian biomass burning plumes ACP. 14 13755] on the size-dependent wet removal of rBC particles. Such wet removal could explain the lack of thickly coated rBC particles that were estimated to be about a day old (assuming the age estimate is robust).

rBC number size distribution. This reviewer has a major concern with applying a lognormal curve fit to the rBC number size distributions for which there is no obvious peak in the number size distribution data. The troubling application can be readily seen in figure 7 for L5 number size distribution where there is no peak in the number size distribution data, yet one is derived via curve fitting. This reviewer does not consider that L1 and L10 contain enough data to derive a robust lognormal fit. While not shown, based on Figure 8, presumably simpler fits were found for L2, L4, L7. The authors are reminded that the detection efficiency for the SP2 drops below unity for particles diameters 75 nm and smaller (authors are encouraged to read the SP2 detection efficiency paper by Schwarz et al., The Detection Efficiency of the Single Particle Soot Photometer AST, 44, 2010). Given that, it is not clear how meaningful the reported number size median rBC core diameters really are (see Figure 8). This reviewer questions the value of reporting fit-derived number size median core diameters that are less than 80 nm (which constitutes 6 out of the 10 reported values). This issue could very well help explain the observation reported by the authors (page 21, line 467- 468) that they “observe that changes in the mass median diameter are not consistent with the changes in number median diameter”. Perhaps this is due to the detection efficiency limitation cited above. This reviewer suggests that any discussions that use or make reference to those datasets for which there is no discernible peak in the number size data, be removed or, at a minimum, discussed with an open acknowledgement of the detection efficiency issue and how this will impact interpetation. Also, please reword the sentence (page 21, 469 - 471) “our results suggest that the number median diameter

could be a more useful metric when correlating core diameters to mixing state metrics since the SP2 measures characteristics of individual rBC particles on a number basis and the CT_BC is calculated for each measured particle." to reflect the impact(s) of detection efficiency issues with respect to smaller diameter rBC particles on the utility of the number median diameter metric.

Sticking with Figure 8 for an additional moment, the first reported blue bar for L1 has an amplitude consistent with $\sim$ 75 nm but reports a value above the bar of 53 nm. Please correct. Also, the author's reference a Table 3 (page 22, line 483 and again in the supplemental page 1), but this reviewer is unable to locate referenced table.

Increasing rBC diameter with atmospheric aging. On page 21 lines 460 - 471, the authors argue that the rBC core diameter increases with atmospheric aging through coagulation. Certainly the rBC core diameter will increase with age at the source (e.g., a wildfire) where particle concentration are sufficiently high (10ˆ4 - 10ˆ5 ccˆ-1) such that coagulation will occur on a time scale that is competitive with condensation. But as the plume dilutes, the kinetics of coagulation will decrease (rate goes as Nˆ2, where N is the number concentration). The highest rBC number concentrations cited (Figure 5, page 14) are $\sim$ 400 ccˆ-1. Homogeneous coagulation under these conditions would be over 600x slower than at 10ˆ4 cc-1. So, with the drop in particle concentration that occurs with age, it is not clear that coagulation will result in a measurable increase in rBC diameter. Given this, how can the authors explain the reported increase in rBC diameter with age? The studies that the author's cite that reference a coagulation mechanism, are analyzing data under high number concentration conditions than the authors encounter in the current study.

Other specific issues:

Page 1, line 18, 20. The passive voice exemplified by the use of the word "suspect". Are the author's hedging their bets? Suggest using a different - less passive - word.

Page 1, lines 23-25. The author's write "we conclude that an aging timescale on the



order of $\sim$hours is not long enough for rBC to become thickly coated under the range of sources sampled and atmospheric conditions during this campaign." This is misleading as several papers that have studied biomass burning (and those currently under review and data currently being analyzed) have (and are) showing that rBC particle become thickly coated very quickly. While this might be true for urban plumes, it certainly is not for BB (biomass burning) plumes. Please clarify.

Page 2, lines 43-44. The author's write "BC is emitted mostly as an "external" mixture, physically separated from other aerosol species." This is a bit misleading. It is very dependent upon when the plume is sampled. With respect to biomass burning, research has shown that rBC becomes coated within the first few minutes following generation - due to the chemical richness of the smoke plumes. Please reword to reflect this.

Page 3, line 74 and 75. The authors need to be very disciplined in their use of "mixing state", as one can be describing the aerosol mixing state (e.g., external vs internal) or the particle mixing state (e.g., coated or uncoated rBC). Yes, the authors sort of point this out on page 2 (lines 48-50) but then start interchanging "internal mixing state" with mixing state. For example, on the opening sentence of the cited paragraph, are the authors referring to the internal mixing state or the aerosol mixing state? Later in this paragraph, the authors reference internal mixing state of rBC (line 80). Please ensure consistency.

Page 3, lines 74 - 75. Here are two additional references to the use of microscopy with quantifying rBC mixing state that the authors are encouraged to consider: Adachi, K., Chung, S. H., and Buseck, P. R.: (2010) Shapes of soot aerosol particles and implications for their ef- fects on climate, J. Geophys. Res. Atmos., 115. Adachi, K., Moteki, N., Kondo, Y., and Igarashi, Y.: (2016) Mixing states of light-absorbing particles measured using a transmission electron microscope and a single-particle soot photometer in Tokyo, Japan, JGR.,121, 9153–9164.

Page 3, lines 80 - 83. Authors are encouraged to review (include) the work by Sedlacek

et al., who investigated the utility of the SP2 lagtime methodology [Investigation of Refractory Black Carbon-Containing Particle Morphologies Using the Single-Particle Soot Photometer (SP2) (2015) Aero. Sci. Tech., 49:872]

Page 3, line 83. The authors are encouraged to review (include) the work by Moteki and Kondo who have also contributed significantly to improving the quantification of the rBC mixing state [Method to measure time-dependent scattering cross sections of particles evaporating in a laser beam (2008) J. Aer. Sci. 39:348].

Page 9, lines 226 - 228. The authors might consider reviewing (including) the work by Sedlacek et al., who looked at the SP2 lagtime for a biomass burn plume. [Determination of and Evidence for Non-core-shell structure of particles containing black carbon using the single particle soot photometer (SP2). (2012) GRL. 39]

Page 10, Line 266. As highlighted earlier, please refrain from relying on a passive voice (e.g, “suspect”.

Page 12: The authors show the back trajectories for each day of the campaign. Why not put this figure in the supplemental and, instead, show those trajectories for the specific periods under discussion. This would make it easier to evaluate the HYSPLIT datasets.

Page 14 line 307. The authors reference Figure S9, but I think they mean S8?

Page 15, lines 337 - 344. The authors are encouraged to review paper by Subramanian et al., [(2010) Black carbon over Mexico: the effect of atmospheric transport on mixing state, mass absorption cross-section, and BC/CO ratios ACP 10] where attention is drawn specifically to figures 3, 12 and 13.

Page 22, lines 507 - 508. As highlighted above, this reviewer has concerns regarding the estimated plume ages.

Supplemental: page 1. As noted earlier, there is no table 3 in the main manuscript.



Supplemental: page 1, line 7. Suggest that the authors review Lund et al., [(2018) Short Black Carbon lifetime inferred from a global set of aircraft observations, npj Climate and Atmospheric Science 1, 31 doi:10.1038/s41612-018-0040-x]

Supplemental: page 7. This is a stylist comment. Would suggest using a different color to denote the sample location on Catalina Island. The currently used green color is hard to discern with the yellow star.

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