Manuscript: Mixing state of refractory black carbon aerosol in the South Asian outflow over the northern Indian Ocean during winder (Kompalli et al.,)

Review of the Revised Manuscript

The authors have done a very good job addressed the concerns raised by this reviewer - as well as Reviewer #2 - as outlined in their responses. This reviewer was happy to see that the BC number fraction did drop (nominally by 3x) highlighting the limitations of relying solely on the SP2 to detect non-refractory aerosol particles. Also, the authors reevaluated the role of self-coagulation. The reviewer appreciates the author's efforts of clearly delineating bulk coating thicknesses versus individual BC particle coating thicknesses. Finally, this reviewer was pleased to see that the suggestion of examining the ratio of non-refractory coating to overall non-refractory aerosol mass.

The manuscript is stronger for the extra effort of the authors and underscores the true value of the peer-review process: more accurate and better articulated science. The manuscript is now recommended for publication.

Review manuscript

The manuscript details the analysis of SP2 data collected aboard a research ship as part of the ICARB-18 campaign with a focus on the microphysical properties of refractory black carbon (rBC)-containing particles. As the authors point out, the SP2 detects individual rBC particles through laser-induced incandescence thereby providing mass loadings and size/mass distributions. By combining the incandescence channel with the co-located SP2 scattering channel, the mixing state of individual rBC particles can also be probed. Their analysis reveals that outflow regions are characterized by higher rBC loadings and more thickly coated rBC-containing particles with a decrease in coating thickness in the oceanic regions. Studies such as this are essential in filling in measurement and information gaps in the South Asian region and thus are important for improving our quantitative understanding of the radiative forcing impacts of BC aerosols in this region. Despite the over use of very long sentences, the manuscript is clearly written. The manuscript shares a lot similarity - with a couple of notable exceptions - to that published by Brooks et al., who conducted an aircraft-based study of northern India.

This Reviewer has a concern that the authors are, in some instances, over interpreting data collected by a single instrument and, in doing so, drawing potentially incomplete (or erroneous) conclusions - as exemplified by their use of rBC number fraction (which is discussed below). Therefore, it is recommended that the manuscript be revised as per comments below and resubmitted. To be clear, the findings contained in this manuscript are of good value and need to be published, but in its current state, the manuscript is not quite ready.

As alluded to above, 90% of this manuscript - based on rough estimate of pages dedicated to measurement type - involves only data collected by the single particle soot photometer (SP2). (The remaining 10% is on aerosol composition via an ACSM.) While the SP2 in an incredibly sensitive instrument towards rBC particles and its mixing state, it is not sensitive to changes in rBC aggregate morphology - that is rearrangement of a fractal aggregate to one that is more collapsed - and it suffers from limited detection sensitivity towards pure scatterers (i.e., non-BC particles).

First a comment on rBC morphology. For a given mass, the SP2 will report the same incandescence intensity independent of the rBC particle fractal dimension. Therefore a statement such as "The

observed narrow range of mean NMD (0.10-0.11 µm) and MMD (0.19- 0.20 µm) over the entire region (Fig. 3c and 3d) reveals that the prevailing BC over the entire study region has a mixed-source origin and the particles are aged during the long advection leading to transformation processes (such as collapsing of the BC cores)" is very misleading [page 10, lines 11-12]. The authors again put forth a similar line of reasoning in the conclusion [page 23, lines 4-5] "BC size distributions indicated highly mixed BC sources, likely including a combination of fossil fuel and solid fuel sources, along with the restructuring of the cores of the aged BC particles." The authors present no supporting data that there is any restructuring of the cores and thus cannot conclude that such processes are taking place. Indeed, there is lab studies which suggest that aggregate restructuring occurs through capillary condensation at the interstitial locations between primary particles and thus such restructuring would occur very early in the coating process. The authors are encouraged to review the work by the Khalizov group (e.g., Invanova et al., AST 2020 and references therein).

As highlighted above, this reviewer has a major issue with the authors operational definition of the "fraction of particles containing rBC" (which the authors define as the sum of the number concentration of BC and non-BC scattering particles detected by the SP2). Using the SP2 to measure the number concentration of non-BC will severely bias the derived number fraction of rBC particles because the scattering channel has a severely limited detection range (i.e., ~200 nm - 400 nm). In contrast, the incandescence channel has a nominal detection sensitivity range, in terms of a mass equivalent diameter, from about 80 nm to ~ 500 nm. In short, the SP2 severely undercounts pure scattering particles and therefore deriving a rBC number fraction using the SP2 scattering data will bias the rBC number fractions high and could very well mask the impact(s) that <200 nm non-BC particles might exert in differing regions. One would think (hope) that the instrument suite deployed aboard the research ship during the campaign had a CPC measurement, which would provide an excellent measurement of aerosol number concentration for particles ranging in diameter from ~ 10 nm to 1000 nm, thereby greatly improving the utility of examining the rBC number fraction. Given the presence of higher anthropogenic emissions nearest the coast, it is not unreasonable to expect sub-200 nm pure scattering particles to be abundant. If no CPC, or equivalent measurement, is available then the discussion of variation in fraction of particles containing rBC is meaningless and thus should removed.

The authors report the observation of exceptionally thickly coated particles. Brooks et al., from which the current manuscript is nominally modeled after, reported on the rBC mixing state in northern India during the pre-monsoon and monsoon seasons. Using their Figure 6 "pre-monsoon (IGP)" plot it is estimated that a 130 nm BC core had a nominal coating thickness is ~110 nm. A similar back-of-the-envelope estimate from the current manuscript's Figure 6 suggests a coating thickness of ~250 nm (the authors are strongly encouraged to adjust the scaling of the color mapping in Figure 6 so that more variation in the coating distribution might be seen). This difference in coating thicknesses for a 130 nm core represents about a 4.5x difference in coating volume. This is a big difference and as such, this Reviewer finds it a bit of stretch for the authors to simply state that "…the present study…..are comparable to the values reported in pollution in-plume air mass regions elsewhere (e.g., Cheng et al., 2019; Brooks et al., 2019)." [page 14, lines 19-20] Given this large difference, surly the authors could offer some discussion on why such a difference exists; that is, why are their rBC coatings so much thicker? Indeed, their reported coating thicknesses exceed what is observed for wildfires, which are known to rapidly create thickly coated rBC particles. This is perplexing and interesting finding that begs the question of why is there such a big difference, yet, no further discussion is provided by the authors beyond a cursory comparison with Brooks. The authors are encouraged to think about this finding and perhaps provide a more detailed discussion to help explain why the coating thicknesses found in this study are some much greater than that found by Brooks and in wildfires.

The authors report the organic contribution to the coating as being responsible for ~ 40% near the coast and in the remote ocean, accounting for a little over 20%, as inferred from the ACSM. What is the influence of having a mixture of sulfate and organics on the refractive index assumed in the coating calculation? Additionally, while a density of 1.7 g/cc is reasonable for sulfates, it is high for organics (1.4 g/cc). Perhaps authors could conduct some sensitivity calculations to see if these factors exert influence on the derived coating thicknesses.

The authors are sometimes using the term "aging" in a very confusing and, potentially, misleading way. For example, the authors write [page 14, lines 4-7] "While the larger BC particles are scavenged rather quickly, the smaller, less-aged, and relatively less-coated BC particles (occasionally, even bare soot particles) can persist in the outflow and be transported to the remote marine regions." This is misleading - more thinly coated BC particles are not necessarily "less-aged". Particles can undergo photolysis or heterogenous oxidation that can bring about fragmentation leading to material loss as particles age leading to thinner coatings or larger diameter particles can be preferentially scavenged leaving behind smaller and more thinly coated particle. So to label a smaller, less-coated BC particle - even bare soot particles - as less-aged is wrong. Correct this.

Do the authors have access to optical property measurements, specifically aerosol light absorption? If they do, they are strongly encouraged to roll that into this study so as to make this a more complete analysis.

Finally, it seems to this reviewer that the authors have additional data mining that they could do. Given their bulk coating mass-to-core ratio and the mass loadings of non-refractory aerosols via the ACSM, it might prove very interesting to examine the ratio of non-refractory coating to overall non-refractory aerosol mass. Using the bulk mixing ratio of coating mass over rBC mass (Table 3) along with the rBC mass for the SEAS leg (Table 3) and the reported NR-PM mass in Figure 7, a back-of-the-envelope calculation suggests that about ~40% of the NR-PM mass is bound to BC particles, whereas for the EIO leg this ratio drops to ~ 15%. This suggests the preferential loss of coating and also suggests that the rBC number fraction of particles does change significantly (as per this Reviewer's comments above on this subject).

Specific issues.

Page 3, line 5. "Produced by the incomplete (low-temperature) combustion of hydrocarbon fuels…" "Low temperature" is subjective, please quantify or remove.

Page 3, line 20. "The sources of BC are highly heterogeneous." What do the authors mean by "heterogenous"? There are three sources of BC: fossil fuel, biomass burning (wildfires and agricultural burns), and biofuel combustion. Please clarify what you mean by heterogeneous.

Page 3, line 20. "It has a long atmospheric lifetime." Compared to what? Certainly not CO2, which has a nominal lifetime of 100 years. The authors are encouraged to read the paper by Lund et al., (npj Climate and Atmospheric Science (2018)1:31) who report nominal BC lifetimes < 6 days. Please clarify what you mean by long atmospheric lifetime.

Page 8, lines 20-21. "….E_{sca} is helpful in identifying the nature of sources." This is only true under the assumption of no material loss via oxidative and/or photochemistry that could either alter overall particle size and/or the refractive index of the coating.

Page 9, lines 13 and 15. “folds” should be singular. Please change.

Page 10, lines 12-18. The authors write “….the NIO-E region depicted slightly larger mean MMD (~0.20 µm) due to frequent larger values (35 % of the measurements showed MMD> 0.20 µm) compared to all the other regions (Fig. 3d). This is a result of either of two possibilities: (i) Self-coagulation of rBC cores due to enhanced atmospheric aging, which increases the rBC core diameters (at the same time, sedimentation of larger particles resulting in a large reduction in number concentration and mass concentration); (ii) The second and less likely possibility of a sizeable contribution (though not dominant) from solid fuel sources (biomass/crop residue/coal burning) in the upwind regions to the observed BC concentrations which were transported by the air masses traversing through the eastern coast of India and the Bay of Bengal” In figure 2c, the nominal rBC number concentration is ~200 /cc. Since coagulation goes a N^2, such a low concentration indicates that the rate of coagulation will be very slow. The authors should do a calculation to ascertain whether such low concentrations can result in enough self-coagulated rBC particles within the time frame of there measurements to account for ~ 35% of the measurements in this region showing MMD> 0.2 um. Also, this Reviewer is quite surprised that there is very little discussion about the possible impacts of cloud processing of rBC particles that this might have on this observation (not to be confused with scavenging).

Page 15, lines 14-17. Do the authors have access to any independent measurements of size distributions beyond solely relying on the SP2? As pointed out above, independent measurements of the microphysical properties would help in buttressing interpretations and, in some cases (e.g., rBC number fraction) enable a robust analysis to be performed.