

Response to Reviewer #2:

We thank the reviewer for the thoughtful comments regarding, among other issues, potential biases in the BC measurements and in the absorption measurements. Certainly such issues are important to consider. Below we provide a point-by-point response in which we argue that the potential issues raised by the reviewer did not impact our observations and that our interpretations are robust. Our responses are in **blue** and the initial reviewer comments in **black**.

1. First major concern is the source of black carbon (BC) constituting the Class 6 particles. Per table 1, the fuels burnt constitute duffs, peat, dung - all of which have been found to smolder (low MCE values) and produce tar-balls or spherical brown carbon (BrC) aerosol with negligible/no BC, very high SSA, and AAE >6 in the 405-532 nm. For example: Chakrabarty et al. ((2010), ACP 10, 6363) observed and reported no BC from duff burning at Missoula FSL. More recently, peat collected from Alaska and In- donesia were burned in a Missoula FSL-replica chamber (Sumlin et al. 2017 and 2018 series of papers) and negligible BC was found. These fuels have been only observed to smolder (low-temperature fires) both in the lab as well in field. Consequently, the particle formation mechanism is distinct in these fires, meaning soot (BC) formation is not supported.

Response: The reviewer here is arguing that there is zero BC produced. Later (Comments 4) the reviewer questions whether the OA can be absorbing at 781 nm and suggests that there is a more notable enhancement of BC absorption at 781 nm at very large R_{coat} values. We find these arguments to be somewhat inconsistent. The very large R_{bc} values are determined for the systems where the total $[OA]/[BC]$ ratios are largest. These correspond to the much more smoldering burns. If there is no BC (as the reviewer suggests) then there can be no enhancement of BC absorption and, related, if the OA is not absorbing then there should be no absorption at all if there is no BC. Yet, we clearly observe absorption at 781 nm for the high $[OA]/[BC]$ systems (i.e., Class 6). Thus, we must conclude that, at minimum, there is either some small amount of BC for the Class 6 particles or the OA is somewhat absorbing at 781 nm. We believe our results suggest both to be true.

First, where the reviewer writes that Chakrabarty et al. (2010) “observed and reported no BC from duff burning,” we note that the cited paper states only that “A statistically relevant number of particles have been examined for morphology using SEM, and it was found that a high fraction (>95%) of all particles from each of the three samples were tar balls.” It is not stated what the other 5% of particles corresponded to. It is stated that thermal EC was measured for these same samples but “below detection limit.” However, this is, perhaps, not unexpected given that the total OA/BC mass ratios we derived were larger than 1000 for these very OA-rich particles. The amount of BC (or EC) is indeed, quite small, and depending on the detection limit of the OC/EC instrument used any EC present might not be quantified. Further, one would need fewer than 1 in 1000, or even 1 in 10,000, particles to be BC (assuming the same mass-per-particle) for our results to hold. The total number of particles analyzed by Chakrabarty et al. (2010) was not reported, but we believe it quite reasonable to think that 1 in 1,000 particles could have been BC-containing. Additionally, we note that the analysis of Chakrabarty et al. (2010) shown in Fig. 4 and Eqn. 3 seems to implicitly assume that there is a BC contribution, which they note resulted from “minor flaming combustion during the ignition of the fire.” Looking additionally to

Chakrabarty et al. (2016), who characterized emissions from Alaskan and Siberian peat, their Table 1 explicitly shows that BC is emitted. They report BC emission factors of 0.1-0.2 g kg⁻¹ fuel, compared to OC emission factors of 4-7 g kg⁻¹ fuel, corresponding to OA-to-BC ratios (assuming an OA/OC ratio of 1.6) of 32-176, which are smaller even than what we report. (We note that the actual results reported in Chakrabarty et al. (2016) contrasts with what is stated in Sumlin et al. (2017) where Sumlin (2017) state that for Chakrabarty (2016) “smoldering Alaskan and Siberian peat emissions contain BrC aerosols with no BC component.”) There are also the results of Bhattarai et al. (2018), who characterized smoke from combustion of three different peats. They used EC/OC analysis for EC concentrations, and a PASS-3 for absorption. The EF’s for EC are small (0.01-0.1 mg/g fuel), with OA/EC ratios of 154-522 (again assuming OA/OC = 1.6). Again, the amount of EC emitted is small, but not zero. For comparison, the [OA]/[BC] ratios we determined are even larger than this. The reviewer notes that Sumlin et al. (2017,2018) found “negligible” BC; it is not clear to us where this conclusion arises from since the reported measurement suite in Sumlin et al. (2017, 2018) did not include instrumentation for measurement of BC as best we can tell. Regardless, we are not arguing that there is a lot of BC here, and with an [OA]/[BC] > 1000 some might consider the amount of BC negligible. But, a “negligible amount” does not imply that BC is non-existent, and indeed there are literature results (e.g., Chakrabarty et al. (2016) and Bhattarai et al. (2018)) supporting the idea that there is a small amount of BC emitted from peat combustion.

Second, as to whether the OA is absorbing at 781 nm, we believe our observations are clear. If, as the reviewer contends, there is no BC present for these very OA-rich particles (which we do not think to be the case; see above) then there should be no absorption at 781 nm if they are not absorbing. Yet, the observed absorption at 781 nm was well above the detection limit. Thus, if there is no BC present the OA must be absorbing. (Also, if the OA is not absorbing at 781 nm, then the absorption at 1064 nm might be similarly small, and thus charring would not be expected.) But, as we argue, there is some small amount of BC present. Unless we are dramatically underestimating the amount of BC present in these very OA-rich particles then the magnitude of the derived MAC_{BC} values for these particular particles are too large (>100 m²/g in one case) to be reasonably explained through coating effects. Thus, again, the OA must be absorbing.

2. Could charring of organics by the SP2 and/or SP-AMS be responsible for enhanced rBC concentration erroneously showing up in particle classes, especially in Class 6? This needs to be addressed. Sedlacek et al. (Aerosol Research Letters 52:15, 1345- 1350) convincingly showed that initially near-IR transparent low-volatility compounds (fulvic and humic acid) particles at room temperature undergo chemical transformations as temperature is increased in a heated tube, creating new near-IR absorption transitions. They also say that this phenomenon enable SP2-induced charring of organic aerosol including tarballs (akin to Class 6 particles in this article). Sedlacek et al. observed around 5-10% mass loading of rBC in case of fresh OA/tar balls resulting from SP2-induced charring through near-IR light absorption. The reviewer is suspicious that the authors erroneously report rBC concentration corresponding to Class 6 particles due to this phenomenon and then draw their conclusions. Please provide substantive proofs that no soot photometer induced artifact is involved during the experiments, especially for Class 6 particles. If no evidence can be provided, please remove Class 6 particles from all plots which have [OA]/[BC] as the x-axis.

Response: The work of Sedlacek et al. (2018) is indeed important to consider. First, we believe it is very important to recognize that Sedlacek et al. (2018) only report that the SP2 detects fulvic acid and humic acid, BrC surrogates, as rBC when they are heated in a tube furnace to >500 degrees C. Their Fig. 2 shows that as this pre-heating temperature is reduced the likelihood of rBC detection is reduced. Indeed, it is implied in their paper (although not explicitly stated) that without heating neither fulvic acid or humic acid are detected as rBC in the SP2. In our experiments, the particles were not heated prior to detection with the SP2 (excluding the heating inherent in the particle generation). Thus, if our particles behave as fulvic or humic acid then we would not expect charring to be a concern.

Sedlacek et al. (2018) did also investigate charring of quite absorbing lab-generated tar balls, which is potentially of more relevance to our experiments than fulvic or humic acid samples. However, as they note “recent field observations suggest ambient tar balls may be less absorbing ($k \sim 0.02i$ at 532 nm) than laboratory tar balls,” with the latter having values around $0.2i$. Our median derived MAC_{OA} at 532 nm was $0.21 \text{ m}^2/\text{g}$, corresponding to an imaginary RI of around $0.007i$. Thus, our particles are more similar to field tar balls than lab-generated tar balls. Importantly, the tarballs investigated in Sedlacek et al. (2018) are not “akin to the Class 6 particles” as suggested by the reviewer. The reason for this is almost certainly the completely different particle production methods used in in our study versus by Sedlacek et al. (2018). Given the very different production methods, it is to be expected that the particle chemical properties differ, especially the graphitic content (which is likely of importance to any bias in the SP2 analysis).

3. The authors purport negligible absorption enhancement at 781 nm for R_{coat} values as large as 10 based on results from Figure 4c. My concern with this assertion is that the axes in these graphs are extremely skewed which can misrepresent the actual MAC_{BC} enhancements. The average E_{abs} for R_{coat} less than 10 is mentioned to be close to 1.2, but theoretical E_{abs} for longer wavelengths at these coating values are not expected to exceed 2 regardless (see Chakrabarty and Heinson, Phys. Rev. Lett., 2018). I believe that if the axes were not disproportionately skewed due to the extremely large MAC_{BC} values at the large OA/BC mass ratios (corresponding to Class 6 particles which in turn are due to the very small BC concentrations rather than large OA concentrations) we would be able to discern larger coating-induced absorption enhancements even at 781 nm. The conclusion that there is negligible coating-induced absorption enhancement based on visual comparison with a skewed axis is in my opinion is highly misleading. I notice that there are points in Fig 4c which have MAC_{BC} values larger than 10 which in turn would correspond to E_{abs} close to 2 which is significant in terms of absorption enhancements.

Recognizing the challenge of viewing things on multiple scales, we also included a version of this figure as Fig. S1, where results for each wavelength are shown on their own scale. We believe that there is also value in showing the results at the three different wavelengths on a common scale to visually illustrate the different behavior, and thus provided these two ways of viewing things. To the reviewers contention that we came to our conclusions based on “visual comparison with a skewed axis,” this is simply not true. We came to our conclusion based on explicit calculation of the E_{abs} values from the observed MAC_{BC} values and the extrapolated value at zero coating and interrogation of these calculated values

compared to the value determined from extrapolation to zero OA. As the reviewer notes, indeed there are MAC_{BC} values much larger than 10 in Fig. 4c at 781 nm. The reviewer implies that this results from a significant absorption enhancement. However, our observations are much more consistent with these large MAC_{BC} values resulting from OA absorption. As discussed above, even very weak absorption matters when the total $[OA]/[BC]$ is large. This is why there is a much stronger relationship between the MAC_{BC} and the total $[OA]/[BC]$ than there is with the $[coating]/[BC]$ ratio. Further, we note that the largest MAC_{BC} values correspond to E_{abs} values > 10 (from MAC_{BC} values $> 100 \text{ m}^2/\text{g}$). As the reviewer agrees, E_{abs} values from non-absorbing coatings on BC “are not expected to exceed 2”. Thus, we must conclude that the observable enhancement includes an important contribution from BrC absorption. Finally, we note that if, as the reviewer contends above (although we disagree with), the $[BC]$ are overestimated for Class 6 particles then the reported MAC_{BC} are underestimated for this class of particles, implying an even larger contribution from BrC. In any case, we have updated the manuscript to be more quantitative regarding the observed E_{abs} at 781 nm, adding the new text provided in our response to point 6 below.

4. The authors claim that the increased MAC_{BC} at 781 nm is due to OA absorption and not coating-induced. They need to cite relevant literature which demonstrates significant BrC absorption at longer wavelengths to back up this assertion.

While we believe our observations are clear on their own (see above discussion), we are happy to cite relevant literature. If the reviewer has any particular studies in mind, we would be happy to include them. Otherwise, we can include (for example) the classic paper of Kirchstetter et al. (2004), who report absorption by OC out to at least 700 nm, along with some others (Alexander et al., 2008; Phillips and Smith, 2017; Sengupta et al., 2018; Sumlin et al., 2018). We have added these to Table S3.

We also make the simple argument here: various studies indicate that absorption by BrC declines reasonably continuously with increasing wavelength. So, a thought experiment. If the $MAC_{OA,405nm} = 1 \text{ m}^2 \text{ g}^{-1}$ and the AAE = 5, simple extrapolation (assuming a constant AAE) yields an $MAC_{OA,781nm} = 0.037 \text{ m}^2 \text{ g}^{-1}$. This is small, but not zero and, when the OA concentration is much larger than the BC concentration, should be readily observable. If we instead assume the larger AAE values observed in our study, ~ 8.5 , the extrapolated $MAC_{OA,781nm} = 0.01 \text{ m}^2 \text{ g}^{-1}$. A key point is that when the OA abundance is sufficiently large even weak OA absorption can matter. This can be looked at one additional way. Consider that the absorption ratio between BC and OA is equal to $([BC]*MAC_{BC}/[OA]*MAC_{BrC})$. If the $[BC]/[OA]$ ratio is 10^{-3} (which we observe) then the OA absorption will be observable even if the ratio MAC_{BC}/MAC_{BrC} is 1000. Given an $MAC_{BC} \sim 4 \text{ m}^2/\text{g}$ at 781 nm, this means the MAC_{BrC} need only be $0.004 \text{ m}^2/\text{g}$ to matter at the largest $[OA]/[BC]$. We contend it is quite reasonable to think that some BrC is at least this absorbing at 781 nm. Such exceptionally small absorption might be true for some secondary OA, it seems less likely for OA from biomass combustion, which typically has larger MAC_{OA} values compared to SOA (see Lambe et al. (2013)).

5. In Figure 4, it does not make sense to include points for MAC_{BC} where the contribution of BrC to total absorption is much larger than that of BC. So, removing all points for Class 6 OA would make the plots in Figure 4 more informative. The BC concentration in Class 6 is very likely an artifact. The absorption enhancement at longer wavelengths have a weaker dependence on coating thickness than at shorter wavelengths as observed by Pokhrel et

al. (2017) cited in the manuscript, but it is still significant. I am unconvinced of the insignificance of coating-induced BC light absorption enhancement asserted by the manuscript or at least from the results as they have been presented right now.

First, as we discuss extensively above, the BC concentration is Class 6 is not likely an artifact, and thus removal of these points is not warranted. Second, we wish to clarify that nowhere do we conclude that the absorption enhancement is “insignificant.” We did, however, state it is “negligible,” and we believe this consistent with our observations. Perhaps this is parsing words, but we believe there is a difference between “negligible” and “insignificant.” The median E_{abs} (based on the ratio of MAC_{BC} values), excluding the values that are exceptionally large (>3 , and almost certainly dominated by OA absorption) was 1.14 and the mean was 1.17. These are “significantly” greater than one (in the statistical sense), yet still, in our view, “negligible.” However, we have revised the language in the paper to note that there is “only a minor coating-induced enhancement,” rather than a “negligible” enhancement and to make our statements more quantitative. Some of this was already discussed in Section 3.4.2, where we reported the mean E_{abs} at 781 nm. However, we have added an additional paragraph at the end of Section 3.4.1.

“Values for the absorption enhancement at 781 nm are calculated as the ratio between the observed MAC_{BC} in **Figure 4** and the derived $MAC_{\text{BC,pure}}$. The derived E_{abs} range from 0.96 to 27. Values greater than two occur only for the particles having particularly large $[OA]/[BC]$, > 400 . As E_{abs} values much greater than two at 781 nm are unlikely to result from mixing-induced enhancements, this again suggests that the OA is somewhat absorbing at this wavelength. For the burns where $[OA]/[BC] < 400$, the median $E_{\text{abs}} = 1.14$ and the arithmetic mean $E_{\text{abs}} = 1.19 \pm 0.14$ (1 σ). Given that some of this enhancement may result from BrC absorption at 781, these values can be considered upper-limits on $E_{\text{abs,coat}}$, and the small magnitude is consistent with our conclusion above that, while likely greater than zero, the mixing-induced enhancement is generally negligible. It is possible that the $E_{\text{abs,coat}}$ values when $[OA]/[BC] > 400$ are substantially larger. However, given the general lack of a dependence of the $MAC_{\text{BC},781\text{nm}}$ for $R_{\text{BC-coat}} < 10$ this seems unlikely.”

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