## Reply to the review by Anonymous Referee #3 for the manuscript, "Deposition of Brown Carbon onto Snow: changes of snow optical and radiative properties" by N. D. Beres et al.

We thank the anonymous reviewer for their thorough and thoughtful response and their recommendations to improve the manuscript. Below, questions and comments by the reviewer are in blue and the responses by the manuscript authors are in black.

Abstract:

I think a more useful result emerging from this work is the calculation of spectrally-resolved mass absorption efficiencies for TOC:absorption across 275-815nm. As noted below, the authors have not convinced me that this is purely a BrC MAE; in particular, BC is likely contributing to measured absorption. Nonetheless, given the paucity of observed values of spectral absorption by BrC, this dataset will be useful. As such, I think this aspect of the work should be highlighted in the Abstract.

The authors agree with the reviewer that the mass specific absorbance, $B_\lambda$, is a useful dataset for BrC-contaminated snow, though we respectfully disagree that this is "a more useful result" than the novel BrC deposition experiments and this closure study. We have included a statement in the abstract highlighting the $B_\lambda$ dataset.

The wording in line 23 of the Abstract needs to be modified so the focus isn't on the magnitude of the RF but the forcing per mass of deposited aerosol. I'd suggest editing to, e.g.: "The instantaneous radiative forcing per unit mass of total organic carbon deposited to the ambient snowpack was found to be 1.23 (+0.14/-0.11) W/me per ppm. This snowpack already contained light-absorbing impurities; in a completely lean snowpack the forcing per mass TOC deposited would have been 2.68(+0.27/- 0.22) W/m2 per ppm of BrC deposited."

The wording of the final lines of the abstract have been updated to better reflect the focus of these findings; The authors thank the reviewer for this suggestion.

Main paper:

1) The paper reads as if BrC will exist as an aerosol independent of other aerosol components (e.g. BC). In the ambient atmosphere BrC and BC pretty quickly become internally mixed. There are two aspect of this work that are likely not reflective of the 'real world', and which should be acknowledged: Here, the aerosol are generated in what sounds like fairly realistic peat-burning conditions (kudos to the team for this aspect of the work!). However, the aerosol are deposited to snow within minutes (or less), whereas in the real world most deposited aerosol will have had, at a minimum, hours to chemically evolve and mix. As widely documented, the chemical and optical properties of combustion aerosol – and the organics in particular – rapidly evolve in the first hour or few hours after emission. It needs to be acknowledged that real ambient aerosol that is deposited is likely internally mixed, so BrC "aerosol" doesn't really exist, whereas the aerosol deposited in this experiment is likely closer to an external mixture (e.g. pg. 3, lines 5-8 reads as if BrC "aerosol" exist in the ambient; these are likely mostly internally mixed aerosol with both BrC and BC). Second, and more important, is that ambient deposited aerosol is likely at least hours and mostly closer to days old, so the chemical composition and therefore optical properties of combustion aerosol, and the BrC component in particular, may be substantially different from the aerosol measured in the reported experiment.

The experiment outlined in our manuscript describes a process to isolate the optical and radiative effects of BrC aerosol on snow albedo. Previous studies (e.g. Chakrabarty et al. (2016) and Sumlin et al. (2018a, 2018b)) have shown large fractions of emitted aerosol from very similar combustion conditions as to our study are primary BrC aerosol – which is to differentiate from more chemically, optically, and physically aged or secondary organics that may absorb light. Here, we demonstrate the effect of these aerosols emitted from the combustion of a fuel that is found in regions physically adjacent to snow and ice regions that may or may not undergo long-range transport before depositing and affecting the radiative and optical properties of the snow. The exact extent and impact of depositions such as this has yet to be determined or estimated, but it is not outside the realm of possibility or reason for this investigation and future ones involving deposition studies with or without BrC aerosol.

2) pg. 8, lines 16-20 and It's noted that 700-860nm absorbance was subtracted from the measured signal, as a way of normalizing for drift.

a) What is the source of this “drift”? (instrumental?)

Yes, the source of the “drift” is instrumental, by which the spectrophotometric analysis may be affected. As outlined in Hecobian et al. (2010) and Sengupta et al. (2018), we subtract the light-absorption signal measured in longer wavelengths by the spectrophotometer (where we expect no influence from the experiment). This helps to account for instrument drifts during analysis periods and in between zeroing. We have added the word “instrumental” to the manuscript to clarify this.

b) The authors comment that this reduces the influence of any BC particle absorption since this is “fairly independent of wavelength across the UV-vis spectrum”. However, this isn’t really true: As stated in the paper itself, AAE for BC is ~1.0 – a slope of 1 in log-log space, not a slope of zero. So this is a sort of partial removal of BC signal, but not total. As the authors are trying to isolate absorption by BrC, a better approach would be to use the stated AAE of 1.0 for BC to subtract the estimated BC absorbance from the measured signal (starting with the assumption that all 700-860nm absorption is due to BC). Why not do this?

First, the reviewer is right in stating that our statement was incorrectly worded: the imaginary refractive index of BC is wavelength independent and the BC aerosol absorption coefficient is inversely proportional to the wavelength over the visible and near-visible spectral regions (AAC ≈ 1). This has been updated in our manuscript. Our statement is correct in stating that our baseline correction “reduces” the influence of any BC present in the liquid samples, but, yes, it does not completely eliminate the influence of any BC aerosol present in the sample.

If the residual absorbance in the 700-860 nm band would be solely due to BC it would, indeed, be best to model the BC absorbance over the whole spectrum. However, the residual absorption in the 800-860 nm band is caused by both instrumental drift and by BC absorption, and for our measurements, it likely that instrumental drift is dominant because very little BC is produced by the nearly exclusive smoldering combustion of peat. Had we been able to isolate the signal from the presence of BC only, we would have taken the approach as suggested by the reviewer. However, a conservative and, in our opinion, a best approach was taken to uniformly subtract the 700-860 nm absorbance signal which reduces the influence of any BC present.

3) pg. 9, lines 27-29: “In the UV, there was a stronger reduction (in albedo) than in the visible. . . At 700nm however albedo was reduced by less than 0.01, indicating very little BC added to the snowpack through the deposition experiments”. Perhaps I’m misunderstanding: Won’t this by definition be the case since the absorptance spectra were effectively zero’d out at 700-860n (pg 8, lines 16-20) for all spectra?

The sentence within the manuscript to which you refer (Pg. 9, lines 27-29) speaks specifically to the measured in-situ spectral albedo, which was not “effectively zero’d out” - it was in fact the table-top spectrophotometer absorbance measurements that were adjusted to account for instrument drift. This sentence that you refer to attempts to convince the reader that because the measured spectral albedo of the deposited area differed from that of the natural snowpack by less than 0.01 at 700 nm, there must be only a small amount BC aerosol added through the combustion/deposition experiment, especially considering the large amounts of BrC aerosol deposited. For example, if we use the SNICAR model to simulate the snowpack and sky conditions for the natural snowpack for Experiment 1 and add 65 ng of BC to the top 2.5 cm of snow, the spectral albedo at 700 nm (average of 695 and 705 nm values) will be reduced from 0.832 to 0.823, a difference of ~0.01. While we don’t quantify BC within our snow samples, the amount of BC deposited is dominated by the amount of BrC deposited (4,425 ng in the top 2.5 cm for Experiment 1!) and this can be seen optically through spectral albedo as well, mostly for values lower than 700 nm, where we expect the spectral response to be.

In general, I think the paper needs to do a clearer job of convincing me that what was measured was the spectral absorption of BrC, not a mix of BrC and BC.

While the authors don’t deny that there may be some BC aerosol mass present, there are many studies that the emission ratios of OC to BC are very large for smoldering combustion of peat fuels. We employ the same methods as previous studies that BC and BrC can be separately detected using optical methods (e.g., Bahadur et al. (2012), Kirchstetter and Thatcher (2012), Lu et al. (2015)). Additionally, our manuscript utilizes very similar combustion methods to previous studies that investigate the optical properties of emissions from the smoldering combustion of peat (e.g. Chakrabarty et al. (2016), Sumlin et al. (2018)). For example, Chakrabarty et al. (2016) list emission factors that are

20 to 110 times larger than those of BC. In our study, we find further evidence that there was not a great influence from any BC present in the deposited material, through the use of different optical measurements like snow reflectance and absorbance measurements of melted snow samples.

Similarly, “TOC” is used synonymously with “BrC”, when some of the organics in fact may not be light-absorbing (and therefore not BrC, by definition).

The reviewer is correct: the fraction of light-absorbing organic carbon versus non-light-absorbing organic carbon is not known to us for this particular fuel and combustion scenario and, for this study, we do not attempt to resolve it. However, throughout the optical measurements (snow surface albedo and spectrophotometric absorbance of melted snow samples), we consistently measure the same organic material without filtering. This way, we consistently use an “average” absorption of all organic compounds present and isolate those from the deposition experiment by using background subtraction.

4) Section 3.2.2 “Estimating changes in snow albedo and radiative forcing by BrC deposition” should be split into two sub-sections and renamed:

Pg. 13, line 10 through pg 14 line 17 is really describing how the observations were used to optimize the model so it produces the observed albedos.

Pg. 14 line 18 through pg 15 line 2 is really about the forcing *efficiency* per mass of deposited organics in a clean snowpack versus in the specific ambient snowpack where they did the experiment. Because the experiment was not producing realistic amounts of deposited aerosol (and was not intended to) the calculated “forcing” is not itself meaningful.

The authors agree that this separation of sections could help the reader understand the manuscript better. The manuscript has been updated to reflect this change.

5) pg. 14, lines 9-10: It’s highlighted that the difference in spectral albedo between the modeled and observed albedos was less than 0.15. However, isn’t this a result of the fact that BC and mineral dust amounts used in the model were specifically specified to reduce differences in the observed and modeled spectral albedos? This seems rather problematic, to then assert good agreement when it is built in by design!

Indeed, BC and mineral dust were added to the SNICAR natural/background snowpack in order to better match the measured “natural snowpack” albedo with a modeled one. This was done only for the “natural snowpack” before the deposited BrC was added within the model for comparison purposes.

The differences seen in the values to which you refer is when only after BrC is added to snowpack within SNICAR. In order to better test the derived BrC optical properties, we must make an assumption on the amount and type of impurities present before the deposition experiment. This is also done, of course, because BC and mineral dust mass were not measured. Similarly, the measured and modeled spectral albedo of the natural snowpack would not match in the 350 and 550 nm spectral range if light-absorbing OC (i.e. BrC) was not also added (note the “dip” in the measured albedo in this spectral range in Figure 3a and 3b for the natural snowpack). But, we didn’t have to make an assumption here; we measured the BrC (inferred through the TOC) in the natural snowpack and added it to the natural snowpack impurity values.

6) Section 3.2.3 Radiative forcing by impurities as a function of existing conditions. As noted above, it is not at all a new finding that forcing for a given deposited mass will depend on how dirty the snowpack was to begin with. Given that many studies have calculated forcing by assuming a totally clean ambient snowpack it is worth emphasizing this point, but it is not worth an entire page and figure (Figure 9) to show this, as it seems rather tangential to the rest of the work presented. I think it would be sufficient to reference earlier studies making this point, and to simply give the difference in forcing efficiency for the ambient snowpack versus for a clean snowpack.

The authors agree in the reviewer’s recommendation and appreciate their suggestion. We have removed this section and the corresponding figure.

7) I think the reported experiment could be improved upon in two ways. I'd ask the authors to consider whether they agree, and if so perhaps include these as areas for future work in the discussion at the end of the paper. (Note that this is not intended as a criticism of the work presented, only as ideas that were evident to me in reading the paper):
First, conducting the same experiment on a snowpack that is at and remains below freezing for the duration of the experiment would simply things. The authors do a good job of addressing how the above-freezing temperatures affected snow grain evolution and transport of aerosol in the snowpack. However, this did complicate their analysis – and the presence of liquid water may have affected the loss of particles in the snowpack and to the Whirlpak bags post-sampling.

Second, and more substantial: As noted above, the optical properties of organic aerosol in particular may rapidly evolves over the hours to day (or more) after emission in the atmosphere and in the high-actinic-flux environment of the snowpack. While the nature of the experiment is such that it would be logistically prohibitive to try and make a mixing chamber that would allow for in-atmosphere aging of the emissions before deposition, it would be feasible to monitor the evolution in snowpack spectral albedo over the hours to day+ following deposition. Because the experiment adds such a large concentration of absorbing impurities relative to the ambient snowpack impurities and relative to the amount of additional aerosol that would be deposited to the snowpack through natural processes over, e.g., a day, if the snowpack was below freezing (so aerosol is not being transported through the snowpack), the observed evolution in albedo could be largely attributed to the evolution in the properties of the deposited aerosol.

The authors agree that to further improve the understanding of BrC in snow and the changes it may cause to the optical, chemical, and physical properties of snow, much more experimentation and analysis is needed. This study provides a first look at how BrC aerosol produced using a relevant fuel may directly change the optical and radiative impacts of snow and ice, much in the same way that experimental studies of artificial BC deposition (and comparing to modeled results) have lent themselves to understanding how solely BC changes the optical and radiative impacts of the cryosphere, although BC is never the only impurity found in a natural snowpack.

The evolution of BrC in snow over different time scales is addressed in Section 4, where we discuss uncertainty in the study. In particular, the authors have conducted preliminary experiments of temporal changes to the snow reflectance and the degradation of absorption after deposition of primary BrC on snow over time, similar to studies showing photooxidation contributing to the loss of absorptivity over time of BrC aerosols in the atmosphere (e.g. Sumlin et al. (2017)). These unpublished results are interesting and require further testing to isolate the causes of this optical change over time.

SMALLER COMMENTS:
Pg. 5, lines 10-11: What was the diameter of the cylinder used for the deposition end of the apparatus? (see comment below on addition of this to Figure 1).

The approximate areal extent of aerosols deposited on the snow surface has been added to the paragraph containing the brief description of the deposition apparatus (page 5, line 9). The diameter (~50 cm) has been added to Figure 2.

pg. 5, lines 29-30: Small question: Is there a reason for selecting specifically a 25% increase in mass?

Yes. We chose combustion conditions – such as the fuel moisture content – to be the same or as similar as possible to previous studies (i.e. Sumlin et al. (2018)) that have carried out similar experiments. This way, we would be able to recreate the combustion conditions, apply some derived values from other studies – such as the size distribution of BrC aerosol, and (hopefully) recreate similar properties of the aerosol emitted for our purposes.

Pg. 6, lines 1-4: Over what surface area was albedo measured? Were any corrections required for, e.g., the shadow of the instrument itself? Any issues with fact that the deposition area is not infinite and you were using a cosine collector?

To the best of the authors' knowledge and abilities, the in situ measurements of snow albedo were performed without shadowing the deposition area while minimizing the distance between the deposition area and the optical fiber; however, as the reviewer has pointed out, the cosine response of the fore optic attachment includes reflectance information from outside the deposition area, albeit with less weighting for the large radius areas beyond the deposition area. While we don't quantify this effect within the manuscript, the authors thank the reviewer for our oversight in addressing this uncertainty in our measurements. Our section on uncertainties of this study (Section 4) has been updated to include the fact that a majority of the spectral information will be from within the deposition area and much less influence will be from the surrounding ambient snowpack.

pg. 11, lines 13-15: is there a reference to substantiate this assertion about the UV absorption of aromatic nuclei is at ~255nm?

In the updated manuscript, we have included two references to support this assertion.

9) pg 12, line 19: The AAEs given in Doherty et al. (2010) are for 450-600nm. AAE over this wavelength band might be quite different from that at the band of 330-400nm given here.

The values for $AAE_{400}^{330}$ reported in our manuscript are from Zhang et al. (2019) who, in their Fig. 6, report $AAE_{400}^{330}$ and not $AAE_{600}^{450}$. We assume Zhang et al. (2019) have adapted the Doherty et al. (2010) values to the wavelength range of 330-400 properly.

Figure 1: Overall this is a useful figure. I was, however, a bit confused by the box on the left side that simply says "Sumlin et al. (2018)". What is this supposed to represent? If it's the source of the BrC size distribution, just put "Sumlin et al. (2018)" inside that box.

The Sumlin et al. (2018) study lends two items to our manuscript, the size distribution of BrC aerosol particles used in this study as well as values of derived BrC imaginary refractive index, which we use only to compare against values derived through our methods; hence, there is a "T" split in the figure. There are two dashed lines in shown in the legend as well, indicating that the dashed box emphasizing that "Sumlin et al. (2018)" is from an outside study. The figure caption has been updated to clarify the figure and the use of outside studies.

Figure 2: Can you add the radius/diameter of the deposition area to this figure, please?

Figure 2 has been updated to include the approximate radius of the deposition area and has been scaled a bit to better represent relative lengths.

Figure 5 caption should state the R-squared at each wavelength (as shown in panel a for 275nm) is also given for each wavelength, and it should note at what wavelength resolution the mass-specific absorption is given.

Thank you for this suggestion; the figure caption has been updated.

Figure 7 caption should note that the real index of refraction is assumed to be a fixed value of 1.6 across all wavelengths. This is why both g and the mass extinction coefficient are so invariant (small gray area in panels b and c)!

Thank you for this suggestion; the figure caption has been updated.

Table 1: The air temp is given (footnote!) at a site 0.9km SE of the sampling site and at 2683m altitude. What is the altitude of the sampling site itself? Considerably different from 2683m? (Can you use the dry adiabatic lapse rate to estimate the sampling site temp if it wasn't measured, which would have been easy enough to do!)

The Tamarack Lake experiment site lies at an altitude of 2694m above sea level. The authors believe that the difference in altitude (~11 m) and linear distance (< 1 km) between the Mt. Rose SNOTEL site and the Tamarack Lake site does not represent a significant change in atmospheric or meteorological conditions; thus, the air temperatures provided are representative.

SUGGESTED SMALL EDITS:

Pg. 2, line 10: "cryosphere are a growing" –> "cryosphere is a growing"

Done.

Pg. 2, lines 20-22: Dang and Hegg (2014) should also be cited here.

Done.

Pg. 3, line 3: “toward shorter wavelength” –> “towards shorter wavelengths”

Done.

Pg. 3, line 25: add a comma after “(Ervens et al., 2004)”

Done.

Pg. 4, line 26: “presented in Fig. 1 to guide through the relationships” –> “presented in Fig. 1 as a guide to the relationships”

Done.

Pg. 7, line 24: “This method assumes there is little contribution to scattering to the overall extinction of light along the path.” These samples surely include insoluble particles, so there was some contribution from particulate scattering to the signal. Was the possible magnitude of this effect estimated? Would this constitute a positive bias in derived absorption?

The authors agree that the wording of this sentence may be a bit misleading in our intentions and assumptions made during our analyses. Indeed, the contribution to the scattered signal from insoluble particles is not quantified but is assumed to be low enough and present in both the snow albedo measurements after deposition and the absorbance measurements of the melted samples. Thus, any bias that is present in the measurements derived from scattered light is (assumed to be) accounted for. Additionally, visual inspection of the melted snow samples did not show any cloudiness, which would indicate scattering by a large fraction of insoluble particles. Instead, the uncertainty pertaining to insoluble particulates is present in the TOC analysis, where some insoluble OC may be unaccounted for (addressed in Section 4).

Pg. 9, line 25: “. . . in Fig. 3 alongside measured” –> “. . . in Fig. 3 alongside the measured”

Fixed.

Pg. 9, line 27: “In the UV, there was a stronger reduction than in the visible, up to ∼0.14 and ∼0-.21 at 350nm for Experiment 1 and 2, respectively (Fig. 3)” –> “In the UV, there was a stronger reduction in albedo than in the visible, of ∼0.14 and ∼0-.21 at 350nm for Experiment 1 and 2, respectively, relative to the natural snowpack albedo (Fig. 3)”

Fixed.

Pg. 10, line 23: “snow sampling sites, L1 TOC” –> “snow sampling sites, the L1 TOC”

Added “the”.

Pg. 10, line 26: “air pollution from mining. . .” –> “air pollution from the mining. . .”

Done.

Pg. 10, line 30: “concentration than Experiment 1” –> “concentration as Experiment 1”

Done.

Pg. 10, lines 31-32: delete “. . .for Experiments 2 than for Experiment 1 relative to the natural snow” (it’s not needed).

Done.

Pg. 11: "UV absorption band in presence of an aromatic.." –> "The UV absorption band in The presence of an aromatic.."

Fixed.

pg. 11, lines 29-30: I'm not sure what you're trying to say here with ". . .together with those of the nature snowpack, TOCsnow, as one dataset." Figure 5 only shows one dataset. ?

Reference to "one dataset" refers to the fact that the TOC concentrations from the natural snow and TOC concentrations from the deposition area snow are used together to derive the value of the specific absorbance, $B_{\lambda}$, instead of deriving a value of $B_{\lambda}$ for each individual set of TOC concentrations: one for $TOC_{snow}$ and one for $TOC_{BrC}$. This strengthens the derivation of $B_{\lambda}$ over the wavelength range to include more TOC/absorbance pairs for higher concentrations.

pg. 13, line 24: Figure 7 should be referenced at the end of the sentence at the beginning of this line.

Added.

Pg. 14, lines 9: the reference to Figure 7 should be to Figure 8.

Fixed.

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References:

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