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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Brown carbon in tar balls from smoldering biomass combustion" *by* R. K. Chakrabarty et al.

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Comment: In this paper, the authors report the observation of spherical tar balls emitted from smoldering combustion of two fuels. The authors experimentally determine the optical properties of these tar balls and infer brown carbon (BrC) as a primary component of the tar balls. The imaginary refractive indices of BrC are estimated and then applied in the sensitivity calculation of the radiative forcing efficiency (RFE) by compared with traditional organic carbon with no absorption at visible and UV wavelengths. They conclude that accounting for the absorption by BrC leads to an increase in aerosol RFE and therefore suggest the importance of the inclusion of optical properties of the tar balls into future radiative forcing models. This paper takes a useful approach toward understanding the optical properties and radiative forcing of brown

carbon from smoldering biomass combustion, however, the sample size discussed in this manuscript is too small - only includes three samples of two different wood types - to convince the community that tar balls with similar properties also exists in other smoldering biomass combustions. The authors need to provide more data from reproducibility tests and other samples to support their findings and therefore draw the attention from the research community that optical properties of tar balls should be included in the radiative forcing models. Furthermore, the estimation of kBrC has to be verified. Overall I recommend the publication of this paper after consideration of the specific comments as stated below.

Reply: We thank the reviewer for taking the time to thoroughly review this manuscript. We have made a number of changes in the revised manuscript thanks to the reviewer's input.

Comment: Page 6280, line 2, can the authors be more quantitative about "large-scale production of spherical, carbonaceous particles", i.e., how much percentage of spherical carbonaceous particles were found in their samples?

Reply: As per the suggestion made by Reviewer #2, "large-scale" has been replaced with "laboratory" in Page 6280, line 2 of the revised manuscript.

Comment: Page 6280, line 4, can the authors be more specific on the "real-time measurements", e.g., spectrally varying AAC, refractive index and so on?

Reply: Specifics regarding the "real-time measurements"– spectrally varying AAC and imaginary part of the refractive indices – are added to Page 6280, line 4 of the revised manuscript.

Comment: Page 6280, line 9, this manuscript is talking about absorption in the visible and nearvisible range (405nm, 532nm and 780nm), but the statement here is that "...accounting for UV absorption by brown carbon leads to a significant increase in aerosol radiative forcing efficiency and increased atmospheric warming". This "UV

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absorption" is mentioned twice in the abstract and also elsewhere in the conclusion. 405nm could be considered as a near-UV range, but I don't think it is within the UV range, so the UV absorption should not be emphasized in this manuscript.

Reply: Emphasis on "UV absorption" in Page 6280, line 9 has been replaced with "near-UV absorption".

Comment: Page 6280, line 10, the authors should be careful to say this is a "significant" increase in aerosol radiative forcing efficiency. This sentence is also confusing by saying "increased atmospheric warming" since it seems like brown carbon is warming the atmosphere while actually the net effect of brown carbon is cooling the atmosphere.

Reply: On Page 6280, line 10, the word "significant" has been removed, and "increased atmospheric warming" has been replaced with "increased light absorption".

Comment: The authors say we should consider brown carbon optical properties or we get the RFE wrong. What are RFE of other substances? How much of a change is this RFE compared to that of prevalent substances such as sulfate and black carbon?

Reply: The reviewer is requested to refer to "Dinar, E., Riziq, A. A., Spindler, 5 C., Erlick, C., Kiss, G., and Rudich, Y.: The complex refractive index of atmospheric and model humic-like substances (hulis) retrieved by a cavity ring down aerosol spectrometer (crd-as), Faraday Discuss., 137, 279–295, 2008" for a detailed sensitivity study of RFE of bulk Humic-LIke-Substance (HULIS – a class of spectrally absorbing organic compound in aerosols and believed to be the generic constituent of Brown Carbon) with sulfate and soot. Their sensitivity study emphasizes the increasing importance of the absorbance by HULIS when compared with the optical properties of sulfate and soot at the UV range compared to the visible, although absorption in the visible should not be neglected. As a follow-up and complement to their study, we performed a sensitivity analysis of our measured optical properties of brown carbon particles with traditionally accepted properties of organic carbon in this study.

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Comment: Page 6280, line 24, brown carbon does absorb some solar radiation in the blue and near UV ranges, however, I am suspicious to say that this absorption is strong.

Reply: The word “strong” has been removed from Page 6280, line 24.

Comment: There are two main terms in this manuscript as stated in the title: brown carbon and tar balls. The authors should first give a clear definition and introduction of these two terms at the beginning of this manuscript and cite more literatures about the tar ball identification in Page 6281, line 13.

Reply: On Page 6280, lines 23-25 have been re-worded to convey a clear definition of brown carbon in the manuscript. A line (with relevant citations) defining the general characteristics of tar balls in context of this manuscript has been added after line 13 on Page 6281.

Comment: Page 6281, the third paragraph, the authors need to explain how representative are PPduff and AKduff of general combustion. What type of combustion would this represent and how prevalent is it? Following this point, in page 6282, the first paragraph, the authors need to address the question of to what extent does their experimental methodology actually mimic a "real" burn.

Reply: PPDuff and AKDuff constitute two of the nine major duff species found in boreal and Northern American forest regions of the Northern Hemisphere. Together, these nine types of duff species contribute between 46 and 72% of all wildland fire carbon emissions in a given year. The unique combustion facility was designed to mimic “real-world” combustion scenarios with appropriate dilution of the combustion emissions and fuel arrangement to approximate combustion conditions found in prescribed forest burns. The authors have added the aforementioned description in the first paragraph in page 6282 of the manuscript.

Comment: Page 6282, line 13, the authors may state briefly what the modified combustion efficiency is. Was this also measured during the sampling?

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Reply: Yes, modified combustion efficiency (MCE) was measured during this experiment by a collaborating group from the Colorado State University. For readers' convenience and taking into account of Reviewer #2's suggestion, we have added a brief definition and citation for MCE on paragraph 1 of page 6282.

Comment: Page 6285, line 1, did all or most of the single particles analyzed under SEM look like near-sphere? What is the proportion of these near-sphere tar balls of all the particles from the emission? It would be more convincing if the authors could state the proportion of tar balls or provide a SEM image in which a large part of near-sphere particles were observed in addition to the SEM image for a single particle. Whether the particles are spherical or not directly relates to the validity of the use of Eq (1) to retrieve particle size-number concentration and the use of Mie theory to calculate the refractive indices.

Reply: Yes, almost all particles (>95%) from smoldering combustion of PPDuff and AkDuff looked like near-spheres. A sentence mentioning this proportion has been added on Page 6285, after line 1.

Comment: Page 6285, the first paragraph, the authors should clarify which statements are based on the analysis in this study and which are cited from other literatures. For example: How did the authors identify that the smoke particles in this study are homogeneous tar balls? Did the author just inferred this from other literatures or there was actually a way to identify this in this study?

Reply: Bright-field imaging combined with carbon and oxygen mapping of the particles confirmed the homogeneity of tar balls in study. Similar observation have been reported by our group in "Chakrabarty, R. K., Moosmüller, H., Garro, M. A., Arnott, W. P., Walker, J. W., Susott, R. A., Babbitt, R. E., Wold, C. E., Lincoln, E. N., and Hao, W. M.: Emissions from the laboratory combustion of wildland fuels: Particle morphology and size, J. Geophys. Res., 111, D07204, doi:10.1029/2005JD006659, 2006" and by another group in "Pósfai, M., A. Gelencsér, R. Simonics, K. Arató, J. Li, P. V. Hobbs, and

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P. R. Buseck (2004), Atmospheric tar balls: Particles from biomass and biofuel burning, J. Geophys. Res., 109, D06213, doi:10.1029/2003JD004169". Further, unlike soot particles – containing aggregates of spherules that consist of concentrically wrapped graphitic layers– tar balls are amorphous and show no electron diffraction patterns or continuous rings when viewed under an electron microscope.

Comment:The authors mentioned that the EDX analysis shows that tar ball particles consist primarily of carbon and oxygen with an average molar ratio of about six. Is this a result from EDX analysis in this study?

Reply: Yes. EDX analysis was performed for this experiment confirming our previous observations of carbon to oxygen ratio $\approx$ 6 from "Chakrabarty, R. K., Moosmüller, H., Garro, M. A., Arnott, W. P., Walker, J. W., Susott, R. A., Babbitt, R. E., Wold, C. E., Lincoln, E. N., and Hao, W. M.: Emissions from the laboratory combustion of wildland fuels: Particle morphology and size, J. Geophys. Res., 111, D07204, doi:10.1029/2005JD006659, 2006".

Comment: If the EDX analysis was performed in this study, since polycarbonate filters which primarily contain carbon were used for SEM-EDX analysis, how can the authors differentiate the carbon of tar ball particles from the total carbon detected by EDX which also includes the carbon from the filters?

Reply: Differentiation was done by subtracting the EDX signal of a blank polycarbonate filter from the total EDX signal obtained from both the tar balls and the filter.

Comment: Page 6282, line 5, can the authors provide the concentrations of particles going through all the instruments? If the concentration is much higher than ambient concentration, some gaseous-phase carbon would condense on particulate phase and thus was taken into account here. However, this carbon may not exist in the particulate phase any more in the ambient atmosphere. How do the authors think the optical properties obtained in this manuscript can represent the real condition when this kind of brown carbon is in the ambient atmosphere? Is the increase of radiative forcing

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really significant for AMBIENT brown carbon?

Reply: The concentration of particles coming out of the smoke chamber was split isokinetically before going through all the instruments. The average concentration was much higher than ambient concentration. However, contrary to the reviewer's beliefs, it is very unlikely that the condensed-phase carbon on a particle would cease to exist in particulate phase under ambient conditions. The most current understanding of tar balls formation mechanism suggests that during smoldering combustion large molecular weight, low-volatility organic compounds (LVOC) are released dominantly, and then rapidly condense into growing particles that may undergo polymerization with OH radicals in water droplets resulting in accumulation mode particles. The LVOCs remain in particulate phase even under vacuum conditions of an electron microscope as observed by the authors and other research groups in the past. Hence, we are certain that brown carbon containing compounds retain their particulate phase under ambient conditions, and contribute to increase of radiative forcing.

Comment: Page 6286, line 13, the authors should cite more original papers which did measure AAC of brown carbon. Moreover, WSOC mentioned here is kind of distracting. How does WSOC relate to brown carbon?

Reply: The authors are not aware of any reference reporting directly the AAC of brown carbon aerosol. A number of recent studies have suggested that optical properties of brown carbon aerosols may be due to WSOC compounds and humic-like substances (HULIS) constituting the aerosol. WSOC contains polycyclic-aromatic, phenolic, and acidic functional groups. HULIS is defined through an extraction procedure of WSOC and HULIS aerosols and have been measured to have an AAC of 6-7. Therefore, the authors have cited the references which have reported the AAC of WSOC and HULIS.

Comment: Page 6287, line 4, in the concept of "SSA Angstrom exponent", the authors are trying to have an Angstrom (which is the ratio of two things) for another ratio (SSA), which is confusing. I suggest the authors present the Angstrom for absorption and

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scattering separately and compare them for different wavelengths, which has a much more physical meaning rather than having such a convoluted value.

Reply: The SSA values have been added in the last paragraph on Page 6286 of the manuscript. The authors feel that the need to include the scattering angstrom coefficient (SAC) information in the manuscript as well. The importance of the parameter SAC in the satellite data-retrieval and modeling community is evident from Figure 2 of a very recent paper"Russell, P. B., R. W. Bergstrom, Y. Shinozuka, A. D. Clarke, P. F. DeCarlo, J. L. Jimenez, J. M. Livingston, J. Redemann, O. Dubovik, and A. Strawa (2010). Absorption Angstrom Exponent in AERONET and Related Data as an Indicator of Aerosol Composition. Atmos. Chem. Phys., 10, 1155-1169". In this manuscript, we have defined a useful criterion for detecting brown carbon in aerosols – a negative SAC.

Comment: Page 6287, line 9, was the negative SSA Angstrom coefficients observed for brown carbon in other literatures?

Reply: As per the best of the authors' knowledge, the negative SSA Çžngström coefficients for brown carbon containing aerosols have not been reported in any peer-reviewed publication. Apart from being a novel measurement of this parameter, the authors feel that future observation of the negative SSA Çžngström coefficients may become a useful criterion for identification of brown carbon in aerosols.

Comment: Page 6287, line 18, the authors need to explain more on Equation (3) and the estimation and kBrC. To my understanding, kBC and kBrC is not the actual imaginary refractive indices for black carbon and brown carbon, while they are the refractive indices after considering the volume fraction of BC and BrC in the sample. This means kBC and kBrC are dependent on the volume fraction of BC and BrC. This point should be clarified in the manuscript. Otherwise, the dotted line in Fig 4 representing kBC may confuse the reader with the actual imaginary refractive index of pure BC which is around 0.74.

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Reply: Taking into consideration of the reviewer's suggestion, Equation 3 has been modified to reflect the volume fractions of BC and BrC used for calculating the refractive indices. Accordingly, Figure 4 caption has also been modified to stress the refractive indices retrieval of the volume fractions of BC and BrC in the three samples studied.

Comment: Could the author give the estimated fraction of BC and BrC based on the calculation using Eq (3)? kBrC was applied to estimate the RFE, if kBrC is just the imaginary refractive index considering a certain fraction of BrC, I suspect the actual imaginary index of pure BrC would be higher (maybe not that much though). How do the authors think about this part of uncertainty in the estimation of REF?

Reply: Assuming the commonly used imaginary refractive index for BC to be 0.5 ("Bond, T. C., and Bergstrom, R. W.: Light absorption by carbonaceous particles: An investigative review, Aerosol Sci. Technol., 40, 27-67, 2006."), the estimated volume fractions of BC are – 0.25% (AKDuff),0.64% (PPDuff2) and 1.1% (PPDuff1); while the estimated volume fractions for the remainder, OC containing BrC, are – 99.75% (AK-Duff),99.32% (PPDuff2) and 98.9% (PPDuff1). Given the insignificant amount of BC volume content, the actual imaginary index of pure BrC would be within $\sim$1% of our calculated imaginary index of BrC, and hence, would not affect the estimation of RFE.

Comment: The authors state that the BC content in PPDuff2 is less than that in PP-Duff1, indicating a higher BrC content in PPDuff2. Could the authors explain why two different BrC contents can result in the same BrC component of the imaginary refractive index?

Reply: The change in the BC content from PPDuff 2 to PPDuff1 is below the detection limit (less than 1%), resulting in similar BrC component of the imaginary refractive indices.

Comment: Could the authors explain more about the validation of Lorentzian function applied here? Can the authors provide support from the literatures that the Lorenzian function is valid to be applied here?

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Reply: We are not using the actual Lorentzian function, a near resonance approximation of the Kramers-Kronig relation for the damped simple harmonic oscillator, but a "Lorentzian-like" function (as expressed in the text) that doesn't include the linewidth term and is written in wavelength, not in frequency space. While having data for three wavelengths is state-of-the-art for in-situ measurements of the light absorption coefficient it does not provide enough data points (i.e., only three) to fit the multiple parameters of more sophisticates line shape models. We have added a reference (Demtröder, 2003) that discusses the Kramers-Kronig relation for the damped simple harmonic oscillator and the Lorentzian approximation.

Comment: As stated at the beginning, the sample size discussed in this manuscript is very small. The measured data and modeled curve of imaginary refractive indices fit very well with each other in Fig. 4, but just for the data from very few samples without any reproducibility tests. This raises the questions that whether the RFE calculated later in this manuscript be representative for the brown carbon emitted from real smoldering biomass combustion in a certain region or even globally, and thus may weaken the statement of the importance of including brown carbon into radiative forcing models. The authors need to provide data from reproducibility tests and more samples to support their findings.

Reply: The authors would like to point the reviewer to our previous pilot study carried out in the combustion chamber at FSL, Missoula to characterize the particle morphology of smoldering emissions from Duff and other wet wildland fuels – "Chakrabarty, R. K., Moosmüller, H., Garro, M. A., Arnott, W. P., Walker, J. W., Susott, R. A., Babbitt, R. E., Wold, C. E., Lincoln, E. N., and Hao, W. M.: Emissions from the laboratory combustion of wildland fuels: Particle morphology and size, J. Geophys. Res., 111, D07204, doi:10.1029/2005JD006659, 2006". The current study was a follow-up on our first observations of tar balls during the pilot study from similar duff fuels. Altogether in both of these field campaigns, the authors have repeatedly observed tar balls being emitted from duff fuels and other smoldering combustion of wildland fu-

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els, thereby confirming the reproducibility of our observations. For a detailed overview of the various burns conducted during this field campaign, the reviewer may refer to "McMeeking, G. R., Kreidenweis, S. M., Baker, S., Carrico, C. M., Chow, J. C., Collett, J. L., Hao, W. M., Holden, A. S., Kirchstetter, T. W., Malm, W. C., Moosmuller, H., Sullivan, A. P., and Wold, C. E.: Emissions of trace gases and aerosols during the open combustion of biomass in the laboratory, J. Geophys. Res., 114, D19210, doi:10.1029/2009JD011836, 2009". Utmost care was also taken during this study for our laboratory burns to mimic "real-world" burn, such that the research findings find use in the radiative forcing modeling community. The in-situ optical measurements were performed using a state-of-the-art IPN, which is a 3-wavelength photoacoustic spectrometer integrated with a nephelometer. Measurement of additional optical data points in the wavelength space was hindered due to the lack of a better real-time instrument than the IPN used for this study.

Comment: Page 6288, line 24, the authors may explain how the calculated kBrC is applied in Eq (4) to calculate the RFE.

Reply: kBrC affects directly the values of SSA and β in Equation 4 used to calculate shortwave RFE. A sentence has been added on page 6289 after Equation 6 mentioning the use of kBrC in equation 4.

Comment: Page 6295, Table 1, are the values of scattering and absorption coefficients averaged over the whole sampling period?

Reply: The values of scattering and absorption coefficients are averaged over four minutes for each of the two sampling times.

Comment: Page 6295, 6296, Table 1 and Table 2, the authors need to rearrange the layout the tables to make the values of refractive index be easily read. Table 2, column 3, the unit of RFE was separated into two lines.

Reply: The layouts of Table 1 and Table 2 have been modified for better readability in

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the revised manuscript.

Comment: Page 6298, Fig. 2, if the EDX analysis is not a result from this research, it may not be appropriate to state here. Or the authors should add the citations.

Reply: EDX analysis was performed for this experiment confirming our previous observations of carbon to oxygen ratio $\approx$ 6 from "Chakrabarty, R. K., Moosmüller, H., Garro, M. A., Arnott, W. P., Walker, J. W., Susott, R. A., Babbitt, R. E., Wold, C. E., Lincoln, E. N., and Hao, W. M.: Emissions from the laboratory combustion of wildland fuels: Particle morphology and size, J. Geophys. Res., 111, D07204, doi:10.1029/2005JD006659, 2006".

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 6279, 2010.