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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.

R. K. Chakrabarty et al.

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Comment: Chakrabarty et al present optical measurements and modeling on particles produced from the smoldering of a variety of duffs. The authors assert that "tar balls" are the major particle type emitted from duff smoldering. The authors also state that "tar balls" are composed of "brown carbon". From this assertion, they have used Mie theory to retrieve optical properties in order to calculate a radiative forcing efficiency. These results are of use, but I think more evidence is needed to support the various assumptions used in this study. Furthermore I would encourage more effort (such as a sensitivity study) by the authors to show that their estimates are reasonable. Having the advantage of being able to read the other reviewer's comments, I am pleased to see that they hit on many of the same points that I have. Therefore, the points below

should be addressed before the manuscript is accepted for publication.

Reply: We thank the reviewer for taking the time to review this manuscript. A number of suggested changes by the reviewer are reflected in the revised manuscript.

Detailed Comments

Comment: Title and introduction: Personally, I do not like the use of the non-scientific terms "tar ball" and "brown carbon" because of their poorly defined meanings. "Brown carbon" is slightly better because it connotes weak absorption in the visible region. Even better would be "light absorbing carbon (LAC)". In the end, there is graphitic carbon (soot) and organic carbon; the organic carbon can have a range of optical properties from non absorbing (traditional OC) to weakly absorbing (brown carbon, tar balls etc. . .). Please give a detailed, precise, and succinct definition of brown carbon and tar balls.

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: P 6279, Author List: Claudio Mazzoleni's name needs an "i" at the end of it.

Reply: The typo has been corrected in the revised manuscript.

Comment: P 6280, line 2: Since these are laboratory studies, I disagree with calling this observation "large scale". Since this is the field of geosciences, I would think "large scale" refers to global or continental scale. I think it would be unique if tarballs were produced in the laboratory, so changing "large scale" to "laboratory" might help this paper stand out.

Reply: "Large-scale" has been replaced with "laboratory" in Page 6280, line 2 of the revised manuscript.

Comment: P 6280, lines 7-12: The author draws the distinction between “brown carbon” and “traditional” organic carbon. Technically, I don’t believe that there is any difference between organic carbon and brown carbon. Brown carbon is organic carbon. What has changed is the traditional view (by the atmospheric geosciences community) that organic carbon does not absorb light. Therefore, I suggest a re-wording here.

Reply: The second sentence of the abstract has been re-worded to reflect the suggested changes by the reviewer.

Comment: P 6280, lines 24-25: I haven’t seen convincing evidence of brown carbon having k>0.01. Compared to soot (k 0.5), I wouldn’t call this “strongly absorbing”. However it may still be important due to the large observed mass concentrations of organic species. Suggest re-wording this sentence.

Reply: Taking into consideration of both the reviewers’ suggestion, the word “strong” has been removed from Page 6280, line 24.

Comment: P 6281, line 1: I don’t get how the 88

Reply: The reviewer is requested to refer to the reference cited - “Bond, T. C., Streets, D. G., Yarber, K. F., Nelson, S. M., Woo, J.-H., and Klimont, Z.: A technology-based global inventory of black and organic carbon emissions from combustion, J. Geophys. Res., 109, D14203, doi:10.1029/2003JD003697, 2004.”for the details.

Comment: P 6281, line 7: I found it surprising that a duff could smolder for more than a month. This is interesting. Please provide a reference for this.

Reply: A reference (Rein, G, Smouldering combustion phenomena in science and technology. Int. Rev. Chem. Eng. 2009, 1, 3–18.) has been added to line 7, Page 6281.

Comment: P 6285, line 2; Figure 1: Since the entire analysis presented in this paper depends on the assumption that all particles were homogeneous, spherical tar balls, I think more evidence is needed to show that all of the particles in these samples were

indeed homogeneous spheres. This point could be made by showing that they have examined a statistically relevant number of particles, and that some high fraction of those particles was a “tar ball”. I suggest that the authors show several images of tar balls particles from each sample. I have personally seen images of the pine duff sample and am not convinced that every particle is a homogeneous sphere.

Reply: Almost all particles (>95%) from smoldering combustion of PPDuff and AK-Duff looked like spheres under an SEM. Together with the analysis from our previous study (please refer to 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), we have looked at the shape of $\sim$150 particles corresponding to each of the two duff species. An additional micrograph of tar ball emitted from PPDuff has been added to Figure 2. A sentence briefly stating that a statistically relevant number of particles have been examined, and that high fraction (>95%) of those particles was “tar balls” has been added on Page 6285, after line 1.

Comment: P 6285, line 18: I wonder how chemically similar tarballs are between studies and even between sampling times in the same study. Biomass burning composition has been shown to undergo chemical reactions with plume age as a result of photochemical oxidation, which may change optical properties (Capes et al., 2008). Some discussion of how this relates to the results in this paper should be discussed.

Reply: The burns investigated in this study were conducted in a sealed chamber at the FSL combustion facility, Missoula, Montana. There were no windows/inlet in the chamber to allow in sunlight. However, there was very minimal artificial lighting inside the chamber. The lighting conditions inside the chamber were designed to prevent photochemical oxidation/reactions of the particles due to sunlight. Hence, the authors strongly believe that the particles residing inside of the chamber during a two-hour long burn were least interfered by sunlight, thereby minimizing the possibility of any

photochemical oxidation.

Comment: P 6285, line 19: BC particles may also be compact (collapsed).

Reply: Agreed. However, collapsed soot particles would still show off concentrically wrapped graphitic layers under an electron microscope. On the contrary, tar balls are amorphous and show no electron diffraction patterns or continuous rings when viewed under an electron microscope.

Comment: P 6286 line 4: Suggest the start of a new paragraph here.

Reply: This suggestion has been taken into account in the revised manuscript.

Comment: P 6286, line 24: The explanation of SSA should be given earlier, along with its definition (lines 18-19).

Reply: This suggestion has been taken into account in the revised manuscript.

Comment: P 6287, line 13-20 and Figure 4: From Figure 4, it is seen that the magnitude of kBC is less than 0.01. The refractive index of pure BC is generally around 0.5 (Bond and Bergstrom, 2006). What the difference between these two values? If the value of k is not the refractive index intrinsic to the material, I suggest denoting this by “effective” or “retrieved”. I understand that the Mie derived refractive index is apportioned to black carbon and brown carbon (eq 3). Are the imaginary refractive indices reported here somehow related to their mass concentration? If so, it would make the analysis much more clear to explicitly state this. Along these lines, it was stated earlier in the manuscript that BC was below the detection limit (line 21-23). Therefore, is it really valid to assume there is BC in the sample? Based on the derived refractive index, what is the concentration of BC? If there is BC in the sample, is it really appropriate to assume a homogeneous sphere (or is it even a tarball in the first place?)? Is equation 3 even valid for the case of the heterogeneously internally mixed BrC/BC particle? Please show error bars on Fig 4a so the reader can see how significant the refractive index is at the longer wavelengths.

Reply: kBC and kBrC are not the actual imaginary refractive indices for black carbon and brown carbon. They are the refractive indices after considering the volume fraction of BC and BrC in the samples. Taking into consideration of both the reviewers’ suggestions, 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. The authors would like to point out to the reviewer that elemental carbon (EC) (and not BC) was measured below the detection limit (line 21-23) – this has been corrected in the revised manuscript. 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 were – 0.25% (AKDuff),0.64% (PPDuff2) and 1.1% (PPDuff1); while the estimated volume fractions for the remainder OC containing BrC were – 99.75% (AKDuff),99.32% (PPDuff2) and 98.9% (PPDuff1). Given the insignificant amount of BC volume content and the spherical SEM images of the particles, the authors feel the assumption of a homogeneous sphere to be a valid and well-justified one. The error measurements have been reported in the first paragraph of Page 6286. Needless to say, the error values of the refractive index at longer wavelengths are insignificant compared to the retrieved values, and hence, the authors feel no real need to highlight them in Fig 4a.

Comment: P 6287, line 18: I wouldn’t call the refractive index “data” since it was calculated. Please change this.

Reply: This sentence has been modified.

Comment: P 6288, line 1-3: Were there any measurements of inorganic species (such as nitrates or ammonium)? How might these inorganic species affect the optical properties? This may also be related to the statement that the derived refractive index is a function of time (p 6287, line 11-12).

Reply: Electron Dispersive Spectroscopy (EDX) analysis of tarballs from this study showed no inorganic constituents. Hence, the authors cannot provide any speculation as to how the retrieved refractive indices might have been affected by the presence of inorganic species.

Comment: Table 2: I think it would be useful to include the SSA in the table.

Reply: The SSA values have been added in the last paragraph on Page 6286 of the manuscript.

Comment: Table 2: The real part of the refractive index seems very high (almost 1.9). How do these values compare to literature values of organic carbon (or "brown" carbon, HULIS, tarballs, etc)? These values really make me question how accurate the retrievals are. How sensitive are the results presented in this paper to the refractive index? How sensitive is the refractive index to uncertainties in size distribution, shape and inhomogeneities?

Reply: The retrieved real part of the refractive indices are in good agreement with recently reported results (please refer to: i) Hoffer, A., Gelencser, A., Guyon, P., Kiss, G., Schmid, O., Frank, G. P., Artaxo, P., and Andreae, M. O.: Optical properties of humic-like substances (hulis) in biomass-burning aerosols, Atmos. Phys. Chem., 6, 3563–3570, 2006.; and ii) Hungershoefer, K., Zeromskiene, K., Iinuma, Y., Helas, G., Trentmann, J., Trautmann, T., Parmar, R. S., Wiedensohler, A., Andreae, M. O., and Schmid, O.: Modelling the optical properties of fresh biomass burning aerosol produced in a smoke chamber: Results from the efeu campaign, Atmos. Chem. Phys., 8, 3427–3439, 2008.). The measurement errors in the real part of the index of refraction (arising from the uncertainties in size distribution, shape and inhomogeneities) were calculated to be around 4.1% and that in the imaginary part were approximately 13.6%.

Comment: Figure 2 and related discussion: Takahama et al has asserted that tarballs may contain Fe. Was this observed? Would this be expected (from elements in soil?)?.

(Takahama et al., 2008)

Reply: EDX analysis of tarballs from this study showed no Fe. The authors are in no position to make any generalized educated guess/speculation regarding tarballs which are emitted from soil to contain Fe.

Comment: Figure 3: Since absorption and scattering are more intimately related to surface area, I suggest showing the surface area distributions.

Reply: The surface area distribution is an important information for particles large enough to scatter in the geometric regime (scattering cross section is proportional to the particle surface area). However, the number size distribution in this study peaks at about $\sim$70nm suggesting that a large majority of particles scatter either in the Rayleigh regime (scattering cross section is proportional to the sixth power of particle radius) or in the Mie regime (i.e., smaller particles than in the geometric regime). Any particle in the Rayleigh regime is a volume absorber, while in the Mie regime the size dependence is more complicated. Hence, the authors feel that showing the surface area distributions would add little or no value to the final results and findings of this paper.

Comment: Figure 4: All text on this figure is too small. Why is there no data for Pine duff 1 in figure 4a? Y-errorbars should be shown.

Reply: The data for PPDuff 1 was collected four minutes after ignition of the fuel. During this sampling time, the IPN at 405 nm was not operating. Page 6286, line 2 mentions the error involved in the retrieved refractive indices – "Using the method of quadrature sum of the individual errors, the measurement errors in the real part of the index of refraction were calculated to be around 4.1% and that in the imaginary part were approximately 13.6%". Given the small error values of the retrieved refractive indices, the authors feel no real need to include Y-error bars in Figure 4.

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