Atmos. Chem. Phys. Discuss., 15, C9875–C9888, 2015
www.atmos-chem-phys-discuss.net/15/C9875/2015/

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Light absorption properties of laboratory generated tar ball particles" *by* A. Hoffer et al.

A. Hoffer et al.

gelencs@almos.uni-pannon.hu

Received and published: 29 November 2015

Response to Interactive comment of Anonymous Referee #1 1.) "Not sure if this manuscript should go into ACP or AMT as it describes the production and characterization of an aerosol surrogate for TB and BrC."

During biomass burning, depending on the various parameters (e.g. oxygen supply of the burning, type and moisture content of the burned biomass), particles and compounds with different chemical and/or optical properties are emitted. Since TBs is emitted in large amount from biomass burning and this particle type is an important light absorber, the knowledge of its optical parameters (measured by appropriate techniques) is highly important to understand and to model the absorption of atmospheric

anthropogenic aerosols. The focus of the manuscript was placed on the optical properties of the tar balls and not on the generation of these particles, thus the paper is intended to be published in ACP.

2.) "The manuscript tries to distinguish itself, in my opinion excessively, from previous work by stating (e.g., P. 16216 L. 6-7; abstract and P.16217 L. 20-21; introduction) that "their [TB] absorption properties have been only indirectly inferred from field observations or calculations based on their electron energy-loss spectra [EELS]". I don't see a difference of "directness" between the method of this work and that of Chakrabarty et al. (2010) that is discussed in this manuscript. Chakrabarty et al. (2010) generate TB through smoldering laboratory combustion, characterize absorption, scattering, and size distribution and obtain complex refractive indices from inversion of these data. Very similar to this manuscript with the exception of the TB production method and the fact that Chakrabarty et al. (2010) use a more direct absorption measurement (photoacoustic), thereby excluding interferences from filter substrates. I'd also be a bit more critical of the results of Alexander et al. (2008) as EELS is not constrained by the same transition selection rules as optical spectroscopy and may therefore yield different results."

Yes, we tried to emphasize that the absorption properties of TBs were obtained directly for the first time in aerosol science. The reviewer also mentioned that these properties were measured either with non-optical methods (she/he would be more critical of these results) or those were inferred from field observations. Thus the direct measurement of the optical properties of a strongly absorbing particle type present in biomass smoke is highly important. Chakrabarty directly measured the optical properties of particles emitted from biomass burning, but important properties of the particles they analysed were different from those of tar balls. The particles he analysed were not perfectly spherical and the C/O ratio of the particles was 1:6, in contrast to the 1:10 value measured by Pósfai et al. (2004), and the former value was only an assumption (ibid.). This means that freshly formed atmospheric TB particles contain much less (by ∼40%)

oxygen than the particles Chakrabarty analysed. On the other hand, it well known that humic-like substances (HULIS) are also formed during biomass burning. HULIS is a water soluble compound, consequently, it would deliquesce at high relative humidity. According to Adachi and Buseck (2011) and Semeniuk et al. (2006) the freshly formed atmospheric tar balls are not hygroscopic, consequently their chemical composition is also different. Therefore, we maintain that the measurements described in our present paper represent the first direct determination of the optical properties of tar balls.

3.) "P.16217 L.8-9; introduction: ”Their sizes range from 30 to 500 nm in optical diameter as determined by TEM.” Unclear how TEM can determine “optical diameter”, I thought this would be done by optical methods yielding scattering, absorption, and extinction cross-sections and perhaps diameters for spherical particles. TEM diameters should maybe be characterized as projected area and geometric diameter.”

The sentence has been modified as follows: Their sizes range from 30 to 500 nm in geometric diameter as determined by TEM.

Response to Interactive comment of Anonymous Referee #3 1.) "My only real criticism is that the scope of the research is quite narrow. While interesting to know, do the light absorption properties of laboratory-generated TBs really matter that much? We are already capable of measuring the optical properties of real-world atmospheric (including biomass burning) aerosols. So do we need to know the specific properties of one component of these aerosols? It can be argued that this is important for modeling biomass burning aerosols, so I am willing to accept this as a driving force behind this study.”

Among the particle types produced by biomass burning, soot and TBs appear to be the particles with the longest residence times in the atmosphere, which in certain cases makes them important constituents of the aerosol at locations remote from the sources of particles. Thus, knowing the optical properties of TBs is useful for understanding and modeling the optical properties of aerosols on a regional scale, and even in the

global background atmosphere.

Specific Comments: 2.) "Pg. 16217, Line 1-2: Rephrase first sentence. A possibility is ‘Tar balls (TBs) are abundant in the global atmosphere and represent a particle type that is strongly emitted from biomass burning.”

The sentence has been rephrased as follows: “Tar balls (TBs) are ubiquitous in the global troposphere and represent a peculiar particle type emitted from biomass burning.”

3.) ”Pg. 16217, Line 4-6: ‘TBs can withstand the high-energy electron beam of the TEM.’ The only way these can be observed in the TEM is when they are illuminated by the high-energy electron beam and have been exposed to local beam heating and high vacuum. How do you know that the TBs have not changed in the TEM before you observe them? The authors state that morphological changes in the electron beam are not observed, but what if transformations or loss of volatile materials have happened before the particle was observed in the TEM. Was a cold-stage used to minimize beam heating? How can the authors be sure that volatile components do not leave the particle in the high-vacuum TEM environment. Have previous studies looked at these possibilities? If so, references should be provided.”

The tar balls generated in the laboratory showed similar behaviour under the electron beam as the atmospheric tar balls, as the morphology of the particles did not change while they were observed in the TEM. Contrary to TBs, other particles e.g. ammonium-sulphate cannot stand the high energy in TEM and evaporate during the investigation. Since there were no images taken from the particles before the TEM measurements, there is no direct information on the possible loss of volatile compounds. It is important to note, however, that after the tube furnace the particles were dried and diluted with dry air during particle generation. In order to simulate the processes relevant during TB formation in ambient conditions, the dilution ratio was high ($\sim$1:300). This ratio is high enough to prevent the condensation of volatile compounds e.g. methanol. On the other hand, the TBs were generated from wood and not from a mixture of synthetic compounds, thus, similar condensation (if any) might occur on the particles generated in the laboratory as on the ambient particles. In this study we have not used a cold stage but in some cases in previous studies on natural tar balls we did. The particles observed with and without the cold stage did not look any different. We also note that tar balls were observed using an environmental SEM (Hand et al. 2005), with no noticeable differences between the images taken by the ESEM and TEM. Even though some loss of volatiles in the vacuum of the TEM certainly cannot be excluded, we think that these losses are not significant.

4.) "Pg. 16218, Line 3: absorption Angstrom exponent Please define the acronym ‘AAE’ here which is used later on the page.”

The sentence has been changed to introduce the acronym: “The difference between the measured absorption between 370 and 880 nm was the highest in periods when TBs were the predominant particle type, suggesting that the absorption Ångström exponent (AAE) of TB was different from 1.”

5.) "Pg. 16219, Line 6-8: ‘By generating pure TB particles in the laboratory we have directly measured the optical properties of TBs. You have not actually measured TB particles, which are atmospheric particles. You have measured laboratory-generated particles which are very similar microscopically to TBs. Assuming these also have similar optical properties, then you have constrained the optical properties of TBs.”

Not only the morphology but also the chemical composition (the C/O ratio determined with the same methodology) of the laboratory generated TBs were similar to those of atmospheric TBs. Based on this similarity and based on the fact that the starting material for particle generation was wood tar that was produced by the pyrolysis of wood, a process that takes place during biomass burning, we believe we can call the generated particles “laboratory generated tar balls”. In this sense we obtained and investigated the optical properties of tar balls. The sentence has been modified to

indicate that the optical properties of laboratory generated TBs were measured: By measuring pure laboratory generated TB particles without the concurrent presence of other combustion particles, we have directly obtained the optical properties of TBs for the first time in aerosol science.

6.) "Pg. 16220, Line 7: ‘A PM1 cyclone (SCC2.229)’. Please list manufacturer.”

The manufacturer if the cyclone has been included in the sentence: “A PM1 cyclone (SCC 2.229, BGI Inc., US) was deployed at the outlet of the system to remove the large particles (the calculated cut-off was ∼500 nm aerodynamic diameter) from the gas stream.”

7.) "Pg. 16220, Line 14-16: ‘ the raw light absorption data were corrected according to Bond et al. (1999)’. The Bond et al. (1999) corrections were determined using a single wavelength PSAP instrument. Since the CLAP instrument was developed based on the PSAP (it is basically a multiple-spot PSAP) and the same filter and similar optics and detection methods are used, the Bond et al. (1999) correction scheme is used there also. There are two important things that must be accounted for when using the Bond et al. (1999) corrections for a CLAP instrument. One is a fundamental error in the filter area measurement of the original PSAP spot used in the original Bond study. This affects the loading correction. The other is how to handle measurements made at different wavelengths. Both of these are discussed in detail in the Comment by J. Ogren (Aerosol Sci Technol., 44:589-591, 2010). This work should be referenced, as it is likely (from the mention in the Acknowledgements section) that the data for this study were processed using the NOAA data processing utilities, which include the Ogren modifications to the Bond et al. (1999) correction scheme.”

The data has been corrected and processed using the NOAA data processing utilities. The suggested reference is included in the text: "The data were recorded with a time resolution of 5 s, the raw light absorption and scattering data were corrected according to Bond et al. (1999), and Ogren (2010) and Anderson and Ogren (1998), respectively.”

8.) Pg. 16222, Line 27: Define ‘ns-soot’.

Done: “Both HRTEM images and electron diffraction confirm that the particles in both samples are perfectly amorphous, lacking even the short-range order that is characteristic of nanosphere-soot (ns-soot) (Buseck et al., 2014).”

9.) "Pg. 16223, Line 12-21: ‘The uncertainty of the measurements of Particle Soot Absorption Photometer (PSAP) whose measurement principle is very similar to that of the CLAP is 20–30% (Bond, 1999). It was demonstrated that the presence of organic compounds (secondary organic aerosol, SOA) causes positive bias and enhances the uncertainty of the PSAP (Cappa et al., 2008; Lack et al., 2008). This effect has to be considered in the case of particles generated from tar which contain condensable organic compounds as well. Based on the above, if we consider that the CLAP overestimated the absorption of nigrosin by 25% and the scattering is also overestimated by 25 %, we obtain a refractive index of 1.65–0.29i and 1.77–0.27i for nigrosin at wavelengths of 550 and 652 nm, respectively.’ How specifically did the authors conclude that ‘the CLAP overestimated the absorption of nigrosin by 25%’? The Bond et al. (1999) study suggests an uncertainty in the PSAP measurements of 20-30%, but this could be in either direction (positive or negative). The Cappa et al. and Lack et al. papers show a positive bias in the light absorption measurement in the presence of significant amounts of SOA, but this effect is quite variable and depends on filter loading (i.e., transmittance). How do the authors know that there are lots of SOA particles on the CLAP filter leading to this bias? And even if there are, how do they arrive at the +25% value? This seems a bit arbitrary to me. Please explain your reasoning here in more detail.”

It is known that many parameters might affect the results of an inverse Mie calculation also used in our study. Beside the uncertainty of the optical instruments, the uncertainty of the size distribution measurement (the distribution was measured as a function of electromobility diameter), as well as the experimental conditions (e.g. the presence of volatile compounds like methanol) also contribute to the overall uncertainty

of the calculations. In order to evaluate the uncertainty of the measurement setup used during the experiments, the absorption and scattering coefficient as well as the number size distribution of nigrosin particles generated with the same method (dissolved in methanol and atomized with an ultrasonic equipment) as used for tar balls were measured. Using the inverse Mie calculation the index of refraction of nigrosin was obtained and compared to that reported in the literature (1.67−0.27i at 633 nm, Pinnick et al., 1973). The obtained index of refraction for nigrosin was reasonable (the real part was still overestimated by ∼6%, thus this was also considered when calculating the refractive index of TBs) only if the scattering and the absorption was corrected by 25%. We tried to explain the reason for these discrepancies but the bias is a consequence of many parallel effects, as mentioned above. We suggest checking the performance of similar measurements with a known compound (e.g. with nigrosin) every time before the measurements. The 25% discrepancy in the scattering and absorption coefficients might not always apply.

The following parts have been added and/or rephrased in the section dealing with measurement uncertainties:

Using inverse Mie calculation (Guyon et al., 2003, Hoffer et al., 2006) the index of refraction of nigrosin was obtained and compared to that reported in the literature Pinnick et al., 1973). It should be noted that many parameters might affect the results of an inverse Mie calculation. Beside the uncertainty of the optical instruments, the uncertainty of the size distribution measurement (the distribution was measured as a function of electromobility diameter), as well as the experimental conditions (e.g., the presence of volatile compounds) might also contribute to the overall uncertainty of the calculations. For example, according to Massoli et al. (2009),

When the measured absorption and scattering coefficient of nigrosin was decreased by 25% we obtained a refractive index of 1.65−0.29i and 1.77−0.27i for nigrosin at wavelengths of 550 and 652 nm, respectively. In this case the real part of nigrosin is slightly overestimated, as the index of refraction of nigrosin at 633 nm was reported to be 1.67−0.26i (Pinnick et al., 1973). By assuming that the absorption is similar at both 633 and 652 nm, Mie calculations using the refractive index of nigrosin (1.67−0.26i) and the measured size distribution yield scattering and absorption coefficients at 652 nm higher by ∼17% and lower by ∼2 %, respectively, as compared to those directly measured and corrected by 25%. These uncertainties are considered when interpreting the results. It is important to note that discrepancies in an inverse Mie calculation are a consequence of many parallel effects, thus our obtained biases might not always and generally apply.

10.) "Pg. 16224, Line 1: Please mention the wavelengths or wavelength range that the measurements in Table 1 represent. Also, please mention this in the Table 1 caption. Tables should be able to be interpreted on their own merit.

The following sentence is added to the table 1 caption: The AAE is calculated between 467 and 652 nm, the MAC and the refractive indices are for 550 nm.

“Oven temperature” is replaced with “tube furnace temperature” in the first row of Table 1.

11.) "Pg. 16224, Line 8: ‘mass absorption coefficients’. Do the authors mean MAE (mass absorption efficiencies) which appear to be what is listed in column 4 of Table 1. If these are the same, please use consistent naming in table and text.”

“MAE” has been changed to “MAC” in the 4th column of Table 1.: MAC (m2 g-1).

12.) "Pg. 16224, Line 9: ‘These values are similar to’. A roughly factor of two difference in MAC between TB and BC seems like a pretty big difference to me, but that depends on what you are comparing the difference to. It is small compared to the difference in MAC between TB and HULIS, which I guess is the point. These TB-like particles appear to be much closer to BC than HULIS in optical properties.”

To emphasize that the difference in the MAC between HULIS and TB is much higher than that between BC and TB, a sentence has been modified: These values are are

somewhat lower (by a factor of 2–10) than that characteristic for BC (âĹij 7 m2 g−1, Schnaiter et al., 2003; Clarke et al., 2004; Taha et al., 2007), but definitely much higher (by a factor of 25–100) than the mass absorption coefficient of HULIS (âĹij 0.032 m2 g−1, Hoffer et al., 2006).

13.) "Pg. 16225, last paragraph of section 5: Figure 3. is discussed in this paragraph but is never called out in the text.”

The sentence has been modified: “The optical properties of the generated TB particles were measured continuously while the tube furnace was gradually cooled from the temperature of ∼650°C (Figure 4).”

14.) "Pg. 16226, first half of the Conclusions section: Much of this discussion is about the importance of TBs in the atmosphere. This should have been discussed in the Introduction so that the reader knows why this study was performed in the first place. Typically new references are not presented in the Conclusions section. The Conclusions section should highlight the major findings of the study, and give numerical values or ranges for the important measurements. My recommendation is that the Conclusions section be re-written to present and summarize the major findings of the study without all of the background material on TBs in the atmosphere.”

The first part of the Conclusion section has been placed into the Introduction section. Numerical values and/or ranges for the important measurements are given in the Conclusion section:

Given the abundance of TBs in the global troposphere and their relatively high absorption efficiency over the entire solar spectrum (the obtained AAE between 467–652 nm is 2.7–3.4),

Somewhat surprisingly, their optical properties (the obtained mass absorption coefficient is 0.8–3.0 m2g−1 at 550 nm) suggest that they are not very far from BC or amorphous carbon, We suggest that TBs are on the dark side of brownness of aerosol carbon, but clearly out of the BC regime both in terms of their key absorption parameters (e.g. refractive index, the obtained value is 1.84-0.21i at 550nm and AAE) and for lack of fundamental properties (Petzold et al., 2013).

Response to Interactive comment of C. E. Chung 1.) "The description of tar ball generation, though it meets minimum criteria for a science paper, is very difficult to understand. A better explanation is needed, particularly because the employed methodology is quite new. A schematic diagram is desired. I see Tóth et al. (2014) included a figure for the instrumentation in their Fig. 1. A different and complementary figure will be very useful for this paper. In particular, various texts and Fig. 3 refer to "oily phase" and "aqueous phase". It is difficult to understand how liquid tar (product of dry distillation) can be in aqueous phase since liquid tar is some sort of oil. Also I recommend that the authors discuss the scientific meaning of separating the oily phase from the aqueous phase and dealing with the optical properties of each phase. Did the authors do this to address the variation of ambient tar balls (since some of the ambient tar balls might be formed from the oily phase while others from the water phase)?"

The applied methodology is not completely new, as it is very similar to that used in Tóth et al 2014. For particle generation an ultrasonic atomizer was used, which generated small droplets (a cloud) from the solution of the starting material in a plastic bottle. In order to regulate/maintain the temperature necessary to apply a heat shock more precisely, instead of a Bunsen burner a tube furnace was used. After the heat shock the particles were immediately dried and diluted. After this step the particles were measured with on-line instruments and sampled for off-line analysis as well. In spite of the fact that the main focus of the paper is the measured optical properties of the tar balls and not the particle generation, a figure about the experimental setup is included in the manuscript. The text in the experimental section has been also changed to help understand the particle generation procedure.

The obtained liquid condensate contained two phases. Maschio et al. (1992) also

found two liquid phases produced during conventional pyrolysis of various biomass. The authors used the term "aqueous phase" for the fraction containing "organo-oxygen compounds of low molecular weight", whereas the non-aqueous phase, which is also called bio-oil, contains insoluble organics of high molecular weight.

Since the chemical compositions of the aqueous and the oily phase obviously differ, the two phases were separated and investigated separately. The shapes of the particles generated from the oily phase were not perfectly spherical, thus the focus was put on the results of the aqueous phase. It is important to note, however, that it cannot be ruled out that using other experimental parameters (e.g. longer residence time after dilution of the heat shocked particles) TBs might also form from the oily phase of the liquid condensate.

2. "Table 1 and Fig. 3 talk about oven temperature. Since I could not understand the tar ball generation very well from section 2 (and section 2 mentions heating in multiple stages), I couldn't see the significance of discussing the effect of oven temperature.

Heat shock is necessary to generate TB particles from the liquid condensate obtained from biomass pyrolysis (Tóth et al., 2014). Since the heat affects the composition and therefore the optical properties of the generated particles, the investigation of this effect is important. Here I note that the AAE depends on particle size as well. Mie calculations (assuming monodisperse size distribution and using the index of refraction of TBs derived for different wavelengths) showed that the AAE decreases with increasing particle diameter above $\sim$150 nm. This means that the observed effect (the increasing AAE with decreasing temperature) cannot be the consequence of increasing particle size.

The following sentences have been added to the manuscript:

Tóth et al., (2004) showed that heat shock is necessary to generate TB particles from the liquid condensate obtained from biomass pyrolysis. Since the heat affects the composition and therefore the optical properties of the generated particles, investigation of the effect of temperature used for heat shock is important.

The results of Mie calculations (assuming monodisperse size distribution and using the index of refraction of TBs derived for different wavelengths) showed that the AAE of the generated particles decreases with increasing particle diameter above ∼150 nm. This means that the observed effect (the increasing AAE with decreasing temperature) cannot be the consequence of increasing particle size.

3. "The AAE in Alexander et al. (2008) concerns a single particle while the authors deal with an AAE of multiple particles with a size distribution. A more careful comparison is needed."

Since the AAE depends on particle size, the following part is added to the manuscript: Since the AAE depends on particle size, we estimated the AAE of the brown spheres investigated by Alexander et al. (2008) and that of our laboratory generated tar balls, assuming the same size distribution. For the calculations we used the size distribution of ambient tar ball particles measured by TEM in a rural background station (K-puszta) in Hungary (Pósfai et al., 2004), as well as the reported index of refractions (at 467 and 652 nm) of the brown spheres studied by Alexander et al. (2008) and those of the tar balls generated in the present study (see section 5). The AAE of the laboratory generated TB with an ambient size distribution was 2.4 in the wavelength range between 467 and 652 nm. This value is higher than that obtained for the brown spheres (1.3) in the same wavelength range.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 16215, 2015.

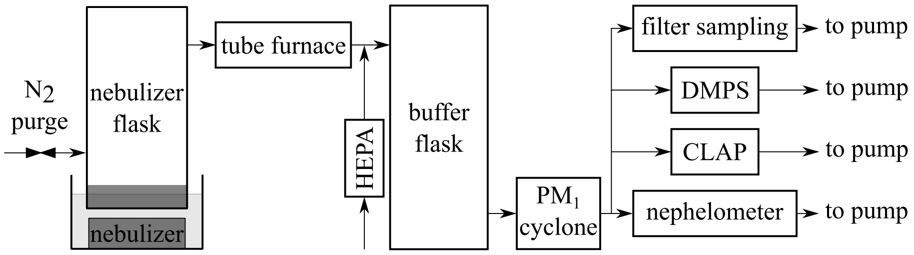

Fig. 1.