

Response to the Anonymous reviewer #1

1/ The introduction requires an update of the cited literature. In the meantime, another IPCC report was published and the assessment of the role of black carbon in the climate system by Bond et al. (Bond et al., 2013) became available. Both documents may contribute new details to the radiative effects of biomass burning products and thus a thorough discussion is recommended.

Tar ball particles are not considered to belong to BC since they do not meet at least 3 criteria (out of the 5) characteristics of BC. Nevertheless, the introduction on BC absorption is still relevant, since aerosol shortwave absorption is highly uncertain in global climate models. Therefore the introduction is revised in several points concerning climate forcing of BC based on the most recent literature as follows:

It should be noted, however, that unlike CO₂ that absorbs only in the infrared spectral range, atmospheric BC directly absorbs sunlight (both incoming and reflected) over the entire solar spectrum with an exceptionally high specific efficiency (mass absorption coefficient $>5 \text{ m}^2\text{g}^{-1}$ at 550 nm). On a per mass basis BC is 360,000–840,000 times more efficient in terms of instantaneous energy absorption than carbon dioxide (Jacobson, 2002), and its 100-year global warming potential (GWP) is 910 (uncertainties $-90\% +100\%$) (Bond et al., 2013).

and

Unfortunately, there is no standard method for the atmospheric measurement of BC, optical and thermo-optical methods are those that are most frequently used (Andreae and Gelencsér, 2006; Petzold et al., 2013). Due to the combination of different factors the assessment of the global climate forcing of BC is loaded with very high uncertainty (best estimate $+1.1 \text{ W m}^{-2}$; 90 % uncertainty bounds of $+0.27 \text{ W m}^{-2}$ to $+2.1 \text{ W m}^{-2}$ (Bond et al., 2013).

2/ The manuscript claims a good agreement between the properties of tar balls produced with the proposed method, and tar balls collected in the atmosphere. However, the degree of agreement is not presented but only mentioned (e.g., Section 3.1, 3rd paragraph; Section 3.2, last sentence). As an example, in Section 3.1, the optical diameter of produced particles and their good agreement with atmospheric particles is mentioned. However there is no proof for the claimed agreement. Here it is strongly recommended to present size distributions of particles produced in the lab and collected in the atmosphere. Data are obviously available, otherwise average diameters and diameter ranges couldn't be stated.

As requested, in the revised version we included a figure and amended the text as follows:

The observed size distribution of the in-vacuo optical diameters of the laboratory-generated particles collected on grids is shown in Figure 3, together with those of ambient tar ball particles determined using the very same method (Pósfai et al., 2004). There is fairly good agreement between the two size distributions, and the mean size (300 nm) is well within the

range reported for atmospheric tar balls (30–500 nm) by others (Pósfai et al., 2003; Fu et al., 2012; Adachi and Buseck, 2011).

3/ Same point as above but now, even more serious, about the ageing of particles described in the entire fourth paragraph of Section 3.1. This paragraph is entirely descriptive and lacks a justification of arguments. It presents results only in the last sentences whereas the majority of the paragraph describes knowledge from literature. Although this paragraph discusses an important point of the study, namely the simulation of particle ageing by the applied “heat shock”, a justification of this approach as an ageing simulator by intercomparison of results is missing.

As requested, a paragraph was added to justify the application of heat shock to the laboratory-generated tar droplets as follows:

The ‘raw’ particles collected without a heat shock were mostly liquid droplets whereas those which underwent ageing (heat shock at 600 °C) were clearly solidified. Tar ball particles observed in the atmosphere were all solids as seen in their compact spherical morphology that is preserved upon impact on sampling grids. In the burning of biomass ejected tar droplets cannot escape into the atmosphere without passing through a high temperature zone of variable height and temperature. This fact lends strong support to our experimental approach that uses heat shock to simulate this basic process occurring during biomass burning. Indeed, this heat shock was clearly needed to produce rigid spherical particles very similar to atmospheric tar balls.

The lengthy literature review on possible chemical transformations was shortened and the following reasoning was added to this section:

It is possibly the last stage of ageing that is relevant in both our experiments and atmospheric tar ball formation. Unfortunately, no direct justification is possible since atmospheric observations of tar balls are concerned only with the “end-products” of formation, whereas experimental observations of tar ageing are always performed in bulk. However, there is one indirect implication from a recent study demonstrating that tar can polymerise and form char already inside the pores of the burning biomass at higher temperatures (Pattanotai et al., 2013).

4/ The description of the experimental methods is incomplete and could be better arranged. The first paragraph of the results section presents the rationale for the taken approach. It would be better placed at the beginning of the experimental section. With this paragraph at the beginning of Section 2, the complete approach can be easily described. A more quantitative description of the production of tar (including a sketch of the used apparatus) followed by the current version of the particle generation approach and the description of the TEM methodology would present a straightforward storyline of the study.

The experimental section was rearranged and supplemented as requested, the rationale for the taken approach was put in front (moved from the Results and discussions section). The order of the subsections was changed. The pyrolysis section now precedes the particle generation, as logically follows from the experimental setup. The description of dry distillation setup became more quantitative by giving more details as follows:

About 170 g of dry chops was subjected to the dry distillation process yielding liquid tarry condensate of about 35 ml. The temperature was raised at rate of about 25 °C min⁻¹ up to 530 °C as measured with a thermometer (Testo 925 K-type thermocouple thermometer).

Distillation lasted about 20 minutes. The products of dry distillation were collected in 40 ml vials, separated into tar and water phases at and an approximate volume ratio of 1:3. It is well established that a high water yield might cause phase separation (Oasmaa et al., 2010). Precipitation of solids was not observed. Due to their high reactivity and instability the distillation products were used for particle generation within few days after their production.

As also requested, the following was added to TEM measurements:

The morphology and elemental composition of the particles were studied in bright-field TEM images obtained using a Philips CM20 TEM operated at 200 kV accelerating voltage. The possible presence of an internal structure was checked in high-resolution electron micrographs. The electron microscope was equipped with an ultra-thin-window Noran Voyager detector that allowed the energy-dispersive X-ray analysis (EDS) of the elemental compositions of individual particles. A dolomite (CaMg(CO₃)₂) standard was analysed to obtain sensitivity factors ("k-factors") for the quantitative thin-film analyses of C and O. Spectra were acquired for 60 s, with the diameter of electron beam adjusted to include the individual tar ball particles.

5/ The presentation of the chemical composition of particles in Section 3.2 requires more detail. Since obviously at least 15 particles have been analysed, it would be good to see all results and not only the average values and their range. And is there any information on the chemical composition of particles previous to the "heat shock" ageing? This section also requires discussion of data from the literature.

As requested, all data are now reported in a new table. Observations on the composition of the raw particles are also reported and reference to literature is also made as follows:

Some of these particles contained other elements (K, S, Si) at most in trace amounts if at all, which corresponds to previous observations of atmospheric tar ball particles (Pósfai et al., 2003; Pósfai et al., 2004; Adachi and Buseck, 2011; Niemi et al., 2006). The carbon-to-oxygen ratios of the tar ball particles after thermal shocking are listed in Table 1. The C/O ratios varied between 6 and 18, the average was about 10. The carbon-to-oxygen ratios of liquid tar droplets and aggregates were found to be much more variable and spatially inhomogeneous ranging from close to one (hydrocarbon-like species) up to the high bound value of solid tar ball particles. This is possibly due phase separation processes such as volatilization and condensation as well as the variable water content of the droplets formed from aqueous emulsion.

6/ The nomenclature used in the manuscript deviates significantly from the recommended terminology for reporting BC data (Petzold et al., 2013). An adaptation of the recommended terminology is suggested.

The introduction was modified as follows:

Unlike atmospheric gases BC is not a single chemical species but a distinct type of carbonaceous material having very strong specific light absorption over the entire solar spectrum (Petzold et al., 2013). Further common characteristics are its fractal-like chain aggregate structure, high thermal stability, insolubility in any solvents and specific microstructure (ibid.).

In addition, 'soot' was replaced with BC throughout the manuscript in accordance with the most recent recommendations. It should be noted that there is no full agreement in the definition of BC between two recent comprehensive papers (Bond et al. 2013 and Petzold et al., 2013).

MINOR COMMENTS

1/ Abstract: The abstract is more written like a summary; rewriting including more details on results is recommended.

The Abstract was rewritten as follows:

Atmospheric tar balls are particles of special morphology and composition that are fairly abundant in the plumes of biomass smoke. These particles form a specific subset of brown carbon (BrC) which has been shown to play a significant role in atmospheric shortwave absorption and thus climate forcing. Here we suggest that tar balls are produced by the direct emission of liquid tar droplets followed by heat transformation upon biomass burning. For the first time in atmospheric chemistry we generated tar ball particles from liquid tar obtained previously by dry distillation of wood in an all-glass apparatus in the laboratory with the total exclusion of flame processes. The particles were perfectly spherical with a mean optical diameter of 300 nm, refractory, externally mixed, and homogeneous in the contrast of the TEM images. They lacked any graphene-like microstructure and exhibited a mean carbon-to-oxygen ratio of 10. All of the observed characteristics of laboratory-generated particles were very similar to those reported for atmospheric tar ball particles in the literature, strongly supporting our hypothesis regarding the formation mechanism of atmospheric tar ball particles.

2/ Page 33092, line 21: the sentence “: : : radical polymerisation with OH radical : : :” is not clear, please rephrase.

Rephrased as follows:

...low volatility products of biomass pyrolysis undergo polymerization in multiphase reactions...

3/ Page 33093, line 13: replace “glass tube of 200 mm long” by “of 200 mm length”.

Done.

4/ Page 33095, line 26: remove one word “that”.

Done.

5/ Page 33097, line 22: It suggested to rephrase “: : : exclusion of flame processes.”

Done.

6/ Fig. 2: It would be beneficial to show the TEM images with the same scale to allow for an easy intercomparison of particle sizes.

Since we wished to show in a single figure several features that are observable at different spatial scales, such as an overview of the sample before heat shock and the amorphous material of individual tar balls after heat shock, we found it impractical to present all panels on a single scale.

Response to the Anonymous reviewer #2

1. Page 33091, lines 15-17: Where does this estimate come from? A very recent study (Liu et al., GRL, doi:10.1002/2013GL058976, 2014) provides estimates of the direct forcing by brown carbon (in addition to in-situ measurement results), which should be mentioned and cited here.

It is from the Chung et al. 2012 paper, it is now indicated in the text. The suggested paper is also cited here.

2. Page 33094, section 2.2: This section would fit better in the beginning of the experimental part of the paper, at least in terms of chronological sequence.

Done. See answer to point 3 of reviewer #1 above.

3. Page 33097, lines 17-18: Please, provide evidence for this similarity, e.g., by showing some composition data from ambient tar ball particles, and discuss this comparison in more detail, including references to literature data.

Done. See answers to the reviewer #1 above.