**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Modelling the optical properties of fresh biomass burning aerosol produced in a smoke chamber: results from the EFEU campaign" *by* K. Hungershöfer et al.

K. Hungershöfer et al.

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We want to thank Tami Bond for her detailed comments and suggestions. Our replies to her review are given below. Text changes compared to the ACPD version are also indicated.

Comment 1: Authors spend quite some time (p 12659) describing how differences in combustion and other parameters can affect optical properties etc. If this is so then the conditions of this burning (not just the fuel) should be well described.

Response: We agree. The following text was added to Section 3.1 (Experimental results) including information from the video recording during the combustion experiments.

During the SAVA20a experiment, 580 g of savanna grass and 716 g of acacia were burnt, where the latter was only used to ignite and maintain a sufficiently stable burning process. The largest amount of the acacia was combusted in the initial stage of the experiment (ignition at 11:15; emission into the container starting at 11:17) and the video recording showed that it was nearly completely burnt before 11:29 when the measurements started. Hence, we consider experiment SAVA20a to be representative for savanna grass. The temporal development of the fire can be summarized as follows: Each time after a handful of dry grass was put into the fire, large flames appeared, but decreased within 20 to 40 seconds and then some new grass was added. Occasionally some small acacia pieces were also put into the fire to sustain the combustion. Hence, for most of the time this experiment was characterized by a rapid change between flaming and smouldering burning conditions - resulting in a mixed phase combustion for each of the two-minutes averaging intervals. During the MUSA23a experiment 948 g of musasa (pieces of a medium sized branches) was burnt. The video recording showed small flames for most of the experiment except after occasional rearrangement of the fuel, which produced moderate flames. After a period of a few minutes the flames decreased and more smoke was visible so that again the experiment was dominated by mixed phase combustion.

Comment 2: Authors then make the assumption that composition is invariant through-out combustion (p12664 line 10). They soon find that this assumption does not let them predict the optical properties during flaming periods. This should be no surprise, given the background discussion they provided! Why make such a limiting assumption? Authors claim they will assess 'the influence of particle size on the observed variability in the scattering and absorption coefficients' (line 12 same page). If another major variable exists (such as chemical composition) then no such statement can be made.

Response: There are two reasons for making this admittedly unrealistic assumption: 1) No time-resolved chemical composition measurements were performed, i.e. only average values were available. 2) Since particle size and chemistry are the two single

most important parameters for scattering/absorption, holding the chemistry (refractive index) constant allows the exploration of whether the observed changes in scattering/absorption are due to changes in particle size or chemistry. The good agreement between modelled and measured optical properties shows that the changes in particle size explain most of the variability in scattering/absorption except for a few minutes at the very beginning, where deviations from the mean chemical composition obviously have occurred due to changes in combustion conditions.

The cited statement 'the influence of particle size on the observed variability in the scattering and absorption coefficients' was our attempt to provide the rationale for our 'constant' refractive index approach as explained above. We have reworded this section to make this issue more clear.

old: For both internal mixing types, the chemical composition was presumed to be the same for all sizes and constant over the whole duration of the experiment. Hence, for a given experiment temporal changes in the modelled optical properties are solely due to changes in the particle size distribution not due to variations in the chemical composition. This allows an assessment of the influence of particle size on the observed variability in the scattering and absorption coefficients.

new: The chemical composition was presumed to be the same for all sizes and constant over the whole duration of the experiment, because no time-resolved chemical composition measurements were performed and differences in size-resolved chemical composition are irrelevant for our analysis. Hence, for a given experiment temporal changes in the modelled optical properties are solely due to changes in the particle size distribution not due to variations in the chemical composition. This allows an exploration of whether the observed changes in scattering/absorption are due to changes in particle size or chemistry.

Comment 3: Elemental carbon and/or absorption is said to be of interest here. Analytical technique is described as thermographic (C-mat Stroehlein). The Stroehlein

instrument measures only total carbon. Some thermal separation must have been done. Its assumptions should be described.

Details on the thermographic method were added in Section 2.1 (Measurements) as stated below.

old: A Berner type impactor with five size bins (0.05-0.14, 0.14-0.42, 0.42-1.2, 1.2-3.5, 3.5-10 um) was employed to determine size-resolved particle mass and apparent elemental carbon (ECa) mass fraction using a microbalance (Mettler Toledo, OH) and a thermographic method (C-mat 5500, Stroehlein, Germany), respectively. We use the term apparent elemental carbon (Andreae and Gelencser, 2006) here to indicate that this species was not directly measured, but inferred from the carbon fraction that was oxidised above the temperature threshold of 650 °C (Iinuma et al., 2007).

new: A Berner type impactor with five size bins (0.05-0.14, 0.14-0.42, 0.42-1.2, 1.2-3.5, 3.5-10 um diameter) was employed to determine size-resolved particle mass using a microbalance (Mettler Toledo, OH). Additionally, a thermographic method was applied to these impactors to determine the organic carbon (OC) and apparent elemental carbon (ECa) mass fraction using a C-mat 5500 instrument (Stroehlein, Germany), where OC and ECa are defined as follows: OC is the CO_2 fraction evolving under nitrogen at 650 °C with CuO as a catalytic reagent and ECa is the evolving CO_2 fraction evolved under oxygen at 650 °C. The term 'apparent elemental carbon' is used in this study, because this species is operationally defined and does not correspond to a rigorously definable chemical species (Andreae and Gelencser, 2006) A detailed discussion of the OC/ECa method used here and the non-negligible influence of higher molecular weight compounds on OC-ECa separation is presented in Iinuma et al. (2007). A comprehensive comparison of this method with other OC/ECa methods can be found elsewhere (Schmid et al., 2001).

Comment 4: Description of step 2 (p 12663) is very confusing. Scattering and absorption are measured (two parameters). In step 1, real and imaginary refractive index are

derived - OK because two unknowns are derived from two measurements. Then in step 2, it is claimed that one can derive BC fraction, as well as BC and OC refractive index. If more unknowns are obtained than variables measured, something is wrong-it is mathematically impossible.

Response: Of course only two independent parameters have been derived in step 2, namely the real part of the OC refractive index and the imaginary part of the BC refractive index. This requires the assumption that 1) the imaginary part of the refractive index of OC is zero, i.e. OC is non-absorbing, 2) the real part of the refractive index for BC is 1.75 and 3) the apparent elemental carbon mass fraction determined with the thermographic method is used as a proxy for the BC volume fraction. We removed the sentence saying that the refractive index of BC and OC were derived, since this implies the real and imaginary part of both components. As suggested in Comment 14 of this review we've shortened this paragraph and hope that the modelling description is clearer now. The new text version is given in Comment 14.

Comment 5: Spherical particle assumption for fresh particles could be a problem. Authors claim these are compact. One must hope there is no BC. SMPS will also respond incorrectly to fractal particles. Also authors' statements about integrated scattering of nonspherical particles (p 12669 last paragraph) are incorrect when applied to the mass scattering efficiency of aggregates. There is classic literature on this topic; see e.g. Dobbins, R.A., and C.M. Megaridis (1991), Absorption and scattering of light by polydisperse aggregates, Applied Optics, 30 (33), 4747-4754.

Although we can not rule out that there are some fractal-like BC agglomerates, the good alignment of SMPS and APS size distributions indicates that agglomerates are not dominating our measurements, since the aerodynamic diameter of fractal-like particles is substantially smaller than (and not equal to) their respective mobility diameter (see e.g. DeCarlo et al., Aerosol Sci. Technol., 38, 1185-1205, 2004), which would result in a shift of the APS size distribution (relative to the SMPS data) to smaller sizes (Schmid, O., Karg, E., Hagen, D. E., Whitefield, P. D., and Ferron, G. (2007). On the

effective density of non-spherical particles as derived from combined measurements of aerodynamic and mobility equivalent size. Journal of Aerosol Science 38, 431-443). During the EFEU experiments substantial amounts of fractal-like agglomerates were only observed for one type of fuel (beech sticks) (Schneider et al., 2006), while all other fuels showed SMPS-APS shifts similar to the oak burns, for which Schneider et al. (2006) found dynamic shape factors of <1.2, which indicates compact particle shape.

Comment 6: Claim of good agreement between measured and modeled (p12671 line 5, for example) is completely unwarranted. So many parameters were 'tweaked' that lack of agreement would be more surprising! Any agreement is not a success of the study but merely demonstration that real refractive index does not vary much.

Response: Indeed, the average agreement between the measured and optical properties is not surprising, because the refractive index was changed until the mean calculated optical properties best matched the measured ones. However, as indicated under comment 2, the good agreement between model and measurements for most of the 2 min data points indicates, that most of the observed changes in scattering and absorption are due to changes in particle size not chemistry. Thus good agreement in the temporal evolution of the optical properties is not trivial and deserves being discussed.

To clarify this, Section 4.2.1 was rewritten in the manuscript.

Comment 7: There is much discussion about the high mass scattering efficiency. Authors honestly acknowledge the possibility of experimental errors. But the (real) refractive index is similar to the one from field measurements. The size distribution is different than field measurements because there are large particles. Is this the reason for the high scattering? Something is not consistent. With the same refractive index as in the field, and size distribution that is almost the same, there ought to be similar scattering unless the large particle mode is contributing. Explanation on (p12670 line 19) is not reasonable. If condensation occurred it would enhance the mass in addition

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to the scattering.

Response: To investigate the influence of the size distribution, we've performed Mie calculations for the size distribution from the Otavi fire (remark: we replaced the size distribution from the SMOCC campaign by Rissler et al. (2006) through a size distribution obtained in Africa during SAFARI2000 as suggested by the anonymous referee #3 (Comment 4)) and the SAVA20a experiment assuming the same refractive refractive index (1.60-0.01i). We found that the higher concentration of large accumulation mode particles during EFEU account for a factor of 1.7 higher mass scattering efficiencies. Hence, it can be concluded that the size distribution is one important reason for the high scattering efficiency. To include this finding we have substantially revised the corresponding section in the manuscript (Section 4.1).

Comment 8: There is a lot of discussion about whether the material is fully graphitized or partly graphitized (Section 4.2.2). The facts from this study seem to be: (1) thermal method gives a relatively high fraction of apparent EC (6-10%); (2) this is inconsistent with the low imaginary refractive index of the average aerosol; (3) high-MW substances were present. I think the authors have a good point: something is inconsistent. Either the thermal method responds to high-MW substances (or something else), or there is apparent EC that is not completely graphitized and thus has a lower imaginary refractive index. But this is not is not clearly stated. I think the message ought to be that we do not have closure between optics and chemical composition+size distribution-End of story.

Response: We did not intend to raise the impression that closure between optics and chemistry-size distribution was accomplished. We have rephrased the paragraph according to Tami Bond's rationale. Now we explicitly mention the inconsistency between the high ECa fraction obtained from the thermographic method and the low imaginary refractive index. As explanation we mention the response of the thermal method to high molecular weight organic substances. The graphitisation argument was removed in the updated text version.

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Comment 9: Authors undoubtedly recognize that their refractive indices are only derived, and they are only part of an exploration in seeking how chemical composition and optical properties are linked. However, modelers searching for optical properties don't know that. If authors are not careful, I would not be surprised to see these optical properties appear in a future modeling paper.

Response: We have discussed the possible shortcomings of the data presented here throughout the manuscript. However, in order to avoid that the 'quick reader' overinterprets our results we have added a cautionary note not only in the conclusions (as we had done already), but in the abstract.

Comment 10: Statement in conclusions: 'This suggests that the aerosol produced under the controlled laboratory conditions consisted of more highly scattering material than typically reported for biomass burning aerosol.' 'Highly scattering' is technically correct but could be read as misleading. The material itself doesn't appear to have a higher refractive index; thus, probably the size distribution is different, and this suggests that some processes in the laboratory are not representative of those in the field. Authors appear well aware of this, but need to communicate this to the readers as well.

Response: Mie calculations with the measures size distributions indicate that at least part of the higher scattering values can be attributed to the larger size of the particles. We have added this information to Section 4.1.

Specific comments

Comment 11: page 12660 - line6 - It doesn't seem that authors were successful in deriving apparent refractive index for light absorbing fraction. This is not really their fault, because the analytical techniques are not good at detecting the light absorbing fraction. However, it should not be stated as a main focus of the paper.

Response: We've changed the revised version of the manuscript as indicated below.

old: The main focus of this paper is the calculation of the refractive index using Mie

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theory and the derivation of the apparent refractive index for the light absorbing fraction and the organic matter component.

new: The measured optical properties are compared to results from previous field and lab experiments and possible reasons for the differences are discussed in combination with model calculations using Mie theory.

Comment 12: page 12660 - last paragraph - Authors need not devote so much text to describing tests when these results do not appear in the paper.

Response: This section was shortened.

Comment 13: page 12663 - entire last paragraph - This description is quite verbose. Clarity would be increased if word count were reduced by about 30%.

Response: The paragraph was shortened and rewritten.

revised version: The measured particle size distribution and the measured scattering and absorption coefficients were used to derive an effective refractive index from Mie theory. This was accomplished by iteratively adjusting the effective complex refractive index until the calculated scattering and absorption coefficients best matched the measured ones. In a second step, we assume that the model particles are composed of non-absorbing organic carbon (with an imaginary part of the refractive index equal to zero) and strongly absorbing black carbon only (having 1.75 as real part of the refractive index) (Lenoble, 1991; Penner et al., 1998; Reid and Hobbs, 1998; Haywood et al., 2003). This allows us to derive the real part of the OC refractive index as well as the imaginary part of the BC using the ECa mass fraction (thermo-graphic method) as proxy for the BC volume fraction. Thereby .....

Comment 14: page 12665 - paragraph beginning on line 19 - This paragraph is much too long- simply say that the particles here are much larger, as indicated by Angstrom exponent, and give some ranges.

Response: As suggested, this paragraph was shortened.

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old: To overcome the lack of information on coarse mode particles, the scattering Angstrom exponent was derived from the nephelometer measurements. The mean scattering Angstrom exponents were 1.2 (SAVA20a) and 1.1 (MUSA23a) in the spectral range from lambda=0.45 um to lambda=0.55 um, or 1.8 (SAVA20a) and 2.1 (MUSA23a) from lambda=0.55 um to lambda=0.70 um (Table 1). Angstrom exponents determined in a similar way during the Smoke, Clouds and Radiation-Brazil (SCAR-B) campaign were between 2.1 and 2.3 (0.45-0.55 um) and between 2.4 and 2.6 (0.55-0.70 um) (Reid et al., 98a). Hence, the smaller Angstrom exponents for the EFEU experiments confirm the higher fraction of large particles.

new: The smaller scattering Angstrom exponents for the EFEU experiments (1.2 (SAVA20a) and 1.1 (MUSA23a)) in the spectral range between 0.45 and 0.55 um compared to typical values for fresh smoke (2.0-2.5, Reid et al., 2005b) confirm the higher fraction of large particles.

Comment 15: page 12666 - line 3 - give a reference for this boundary between smoldering and flaming combustion (11% CO)

Response: The review article by Reid et al. (2005) (Part II) was added as a reference. For an explanation, please refer to the answer to Referee #1, Comment 10.

Comment 16: page 12666 - line 19 - Parmar is not in the reference list

Response: This is due to the fact that this article is still in preparation. We have now eliminated this reference and inserted a more detailed description of the experimental setup (including a figure of the setup; see Figure 1) instead of referring to Parmar et al.

Comment 17: page 12669 -line 4 - IPCC is not a primary reference. I suggest that authors read and cite the original papers since this is their area of research.

Response: The range of the mass scattering efficiencies and the cited mean of 3.6 m2 g-1 are all given in the review paper by Reid et al. (2005a). Since all important field and laboratory studies on biomass burning aerosol are included in this review, we do not

see the need to cite all of the original articles here as well. The reference to the IPCC Third Assessment Report (IPCC-TAR) was included to provide additional support for the mass scattering efficiency of 3.6 m2 g-1 using another highly cited meta-analysis. Since this is not absolutely necessary, and in the interest of brevity, we removed the IPCC reference from the manuscript.

Comment 18: page 12669 - line 25 - this sentence should be in the method section

Response: The sentence is moved to the method section accordingly.

Comment 19: page 12673-line 28 - statement 'Subsequently, these pyrolysis products. . . ' implies that this further thermal processing always occurs. Should be rewritten.

Response: Due to changes regarding Comment 9 of this review, we removed the graphitization argument (including line 28ff) in the text. Hence, changes are not necessary any more.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 12657, 2007.