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Atmospheric Measurement Techniques Discussions
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Interactive comment on "Micro-physical properties of carbonaceous aerosol particles generated by laser ablation of a graphite target" *by* T. Ajtai et al.

T. Ajtai et al.

ajtai@titan.physx.u-szeged.hu

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Title: Micro-Physical properties of carbonaceous aerosol perticles generated by laser ablation of a graphite target

Authors: T. Ajtai, N. Utry, M. Pintér, G. Kiss-Albert, R. Puskás, Cs. Tápai, G. Kecskeméti, T. Smausz, B. Hopp, Z. Bozóki, Z. Kónya, G. Szabó

Anonymous Referee#1:

Reviewers' comments: This paper proposes a new method of formulating a new surrogate for atmospheric black carbon. This is an important issue that has confounded atmospheric chemistry and air quality for a while.

First of all, we would like to express the authors' thanks for this review. The authors are at the common platform regarding that all the implementing comments and suggestions in the revised MS have really improved its scientific level and also its impact on the field. However, my main concerns with this paper are as follows:

- Table 1 suggest that there is no monotonic relationship between CMD and laser fluence, and little differeces are seen in the size distribution under various conditions. That tells me some of these features that the authors discuss are just due to method variability. This needs to be discussed under a discussion of the method reproductibility, which is not presented here. This is a critical issue for suggesting a new BC surrogate. Authors' response: We really agree with the Reviewer that despite the FWHM values which show monotonic relation with laser fluences, the CMD values do not shows such correlations, therefore, a possible explanation of that (which is missing in the original MS) is necessary to be described in the revised MS. Moreover, although the main scientific goal of this study was not to introduce a new surrogate, but only to demonstrate a novel methodology and its variability for carbonaceous particle generation where the experimental set-up is needed to be further improved to become a real alternative, we really agree with the reviewer, that the reproducibility is also an important issue even in this context, therefore in the revised MS an additional paragraph is implemented characterizing the reproductivity of the proposed methodology.

We added the following paragraph on page 12, line 236 to page 12 line 247:

"The reproducibility of the generated carbonaceous aerosol plume was determined from 60 spectra gathered from two hours continuous measurement period which was repeated three times at three different days at 2 J/cm2 laser fluence. The uncertainty of the CMD, FWHM and the total particle number concentration were found to be below 10% in all cases which is very typical in real-time soot generators [Spanner et al., 1994; Horvath and Gangl, 2003]. Therefore, the slight and not monoton changes in CMD val-

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ues observed by varying the fluence of excitations (Table 1) can be definitely explained by the instrument uncertainty in the whole range of the applied laser fluences, while the changes in FWHM value can only partly by interpreted by that even in the subsequent fluences depicted in Table 1. However, in the presented methodology, the main critical sources of errors are the optical alignment and the long term instability of the applied laser source. These and the uncertainty of gas flow rates of the purging gas mixtures ($\pm$5%) presently limit the reproducibility"

- A 4-wavelength PAS (photoacoustic spectrometer?) is shown in Figure 1, but no data presented. While the size and the shape of some of the particles may be similar to that of atmospheric BC, we need to know the particle optical properties. - Do the authors assueme the generated particles are pure carbon? They should at least present some results from basic thermal-optical OC/EC analysis if not more sophisticated instruments like the single particle soot photometer (SP2). Does the use of synthetic are as carrier gas result in oxidized carbon, so the mass is no longer "pure BC" if it was so with nitrogen? - Authors' response: The 4-wavelength PAS instrument was not used in this study therefore, we modified this figure according to this (thanks for calling our attention this fault). We really agree with the reviewer that the usage of the terminology "Black Carbon" is not adequate in this study and could mislead the readers that the generated carbonaceous particulate is really black carbon which is not confirmed in this work i.e. by using instrumentation suggested by the reviewer. Therefore, in the revised MS except of this terminology we used carbonaceous particulate or soot consequently throughout the text. Moreover, we extended the revised MS with new results in which we made a complete micro-chemical characterization of the generated particles and confirmed that the generated soot well modeled a realistic ambient carbonaceous particulate originating from i.e. diesel exhaust. Also according to the reviewer's suggestion the effect of purging gases on particle formation including the cited nitrogen effect is more emphasized in the revised MS.

We added the following sentence in page 6 line 145-146:

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“The TEM and HRTEM pictures taken of various generated particles are shown in Fig 7. Finally, The Raman spectra of the laser generated aerosol plume are depicted in Figure 8.”

Furthermore we added the following text from page 13 from line 248 to page 14 line 289:

“Finally, the morphology, the microstructure and the Raman spectra of the generated aerosol plume were investigated. In Figure 7 three different, representative soot structures can be seen. These experimentally demonstrated that the morphology of the laser generated soot aerosol well models the real carbonaceous atmospheric particulate originating from i.e. diesel exhaust or a kerosene flame [Park et al., 2004; Fruhstorfer and Niessner, 1994; Randall and Vander, 2010;]. Figure 7a represents primary particles with the average diameter of 7±0.8nm which was collected at 0.7 J/cm2 fluence in nitrogen purging gas. Figures 7b and 7c demonstrate more complex soot structures corresponding to 0.9 J/cm2 and 2.5 J/cm2 excitations, respectively. The mean particle diameter, calculated from about 200 primary particles, was found to be in between 8.5nm and 13.7nm respectively with the average diameter of 9.9nm with standard deviation of 2.3 in case of fractals aggregates (Fig. 7b and c). Fractal dimension of the generated carbonaceous aggregates was determined by using a simple relation between the number and mean diameter of primary particles as well as their radius of giration with the aid of an image analysis software (Digital Micrograph 3, Gatan Inc.) [Park et al., 2004]. The fractal dimensions calculated from well separated aggregates on the grid associated with 0.9 and 2.5 J/cm2 fluences ranged from 1.65 to 2.1 with the mean value of 1.88±1.4. Therefore, the morphology and the characteristic dimensions of the fractals experimentally demonstrated that the laser generated carbonaceous aerosol particulate shows high similarity with real soot or soot containing ambient aerosol such as diesel or biodiesel soot [Tumolva et al., 2010; Song et al., 2004] The structural properties of the primary particles obtained in the high resolution TEM mode at 2 J/cm2 fluence are shown in Fig. 7d-f. Besides some amorphous

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and disordered arrangements, the laser generated soot typically forms in a shell-core (graphitic) structure where graphene layers are oriented parallel to the external outer surface (Fig. 7d), in a locally and concentrically structured graphene layers but with random orientation respect to each other (Fig7e), and graphene layers structured parallel to each other but without concentric orientation (Fig 7f). The typical distance between the layers are about 0.34 nm (Fig. 7d). These types of microstructures are also in good agreement with a more realistic ambient or other artificially generated soot originating from i.e. diesel exhaust or spark discharged of a carbon rood [Sadecky et al. 2005; Sze et al., 2001; Jawhari et al., 1995; Mertes et al., 2004]. The Raman spectra of the laser generated soot aerosol exhibit two broad and strongly overlapping peaks with the maximum intensity at around 1350 cm-1 and at around 1585 cm-1 (first-order) and one individual peak with relatively lower intensity laying between 2700cm-1 and 3500 cm-1 (second -order) (Fig. 8). The latter one has not showed in Fig. 8. The feature around 1585 cm-1 designated to G (graphite) peak indicates the fundamental mode of a graphite crystal, while the peak around 1350 cm-1 denotes the D (disordered) lines mostly associated with amorphous or randomly oriented (turbostratic) graphene layer structures. The detailed analyses of the first-order spectra where the originally measured Raman data is further structured by a multi-peak fitting algorithm including all first-order Raman bands of soot or soot containing materials (G and D1-D4) are also shown in Fig. 8 [Sadezky et al., 2005]. The obeyed Raman spectra are in accordance with the results of the HRTEM images and further confirmed that the laser generated aerosol plume well modelled the realistic soot or soot containing ambient particulates [Tumolva et al., 2010; Song et al., 2004].“

And also from page 15 line 318 to page 15 line 325:

“However, this study is only serve to demonstrate the variability if the presented methodology regardless of the detailed investigation of the gas to particle interaction during the particle formation i.e. contamination of the generated particles by the composition of purging gases, therefore further studies are needed to investigate the pos-

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sibilities and advantages of using other types of purging gases. Further studies are needed to investigate the possibilities and advantages of using other types of purging gases i.e. using argon to avoid the nitrogen contamination of the generated primary particles [Voevodin et al., 2002; Ritikos et al., 2011; Yang et al, 2007].”

Other issues the authors may want to consider are: - How will the generated material be stored and transported? Or does everyone need one of these laser ablation set-up in their labs? (This is why fullerene soot and aquadag are used widely, even though Kirchstetter's flame set-up produces more realistic BC.) - We really agree with the reviewer that the main advantages of the real-time soot generators over soot modeling materials stored in powdered form is that the former ones produce more realistic soot, however, for the re-dispersion procedure of the latter one, additional laboratory instrumentation is also required. Therefore, although the goal of this study was only to demonstrate the flexibility of this novel methodology, we also mentioned some technical limitation of the experimental set-up, which needs to be solved in the future to become a real alternative of the presently existing instrumentations.

We also added the following from page 15 line 332 to page 16 line 345:

“As a result of the advantages listed above, the laser ablation method has a high flexibility and consequently, it offers a novel possibility of generating carbonaceous particulates with atmospherically relevant parameters as far as mass concentration, aerosol modes, size distribution, morphology and microstructure and Raman spectra are concerned. Although the major scientific goal of this study was to demonstrate and to investigate the variability of the presented methodology we also demonstrated some preliminary results about the reproducibility and the robustness of the method as well as the complete micro-chemical characterisation of the generated carbonaceous particulate matter as well. However, it is noteworthy, that in order to introduce this methodology as a real alternative surrogate for modelling the real atmospheric soot aerosol further technical development is needed including i.e. more robust and simplified excitation sources, more sophisticated physical and chemical characterisation of

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the generated aerosol plume including measurement of i.e. optical and thermo-optical parameters and detailed intercomparison study with the alternatives. These works are in progress and the related results are planned to be demonstrated in other studies."

- How many TEM images have the authors taken? How reproducible are the fractal shapes at larger sizes? - More than 100 TEM images were analyzed which were taken at three different laser fluences, purging gases and flow rates. However, it is noteworthy, that statistically relevant conclusion cannot be made from these images due to the limited number of the captured fractals and primary particles at a given parameter set since the sample collection was carried out at atmospheric pressure in the experimental set-up depicted in the revised MS (Fig.1). Therefore, the presented TEM pictures in the original MS and the HRTEM images implemented into a revised MS serve only demonstration purposes in this study to show and characterize some representative fractals which were found to be typical in the associated parameter set. âĂČ

Page 9 line 170-175:

Figure 7. TEM and HRTEM images of various laser generated carbonaceous aerosol particles.7.a: primary particles obeyed at 0.7 J/cm2 laser fluence at nitrogen purging gas, 7b and c: more complicated fractal aggregates gathered at 0.9 J/cm2 and 2.5 J/cm2 laser fluences in nitrogen purging gas respectively. In 7d-f typical microstructure of the generated particles are shown (see text in details).

I cannot stress this enough – reproducibility of the generated particles is a critical issue for BC surrogates. This and other issues raised above need to be addressed before the manuscript can be considered for publication.

The author's agree with the reviewer that although the major goal of this MS is to demonstrate a novel methodology, the reproductivity and the robustness are very important issues even in this context and should be addressed in the revised MS. âĂČ

We added the following paragraph from page 12, line 236 to page 13 line 247:

“The reproducibility of the generated carbonaceous aerosol plume was determined from 60 spectra gathered from two hours continuous measurement period which was repeated three times at three different days at 2 J/cm2 laser fluence. The uncertainty of the CMD, FWHM and the total particle number concentration were found to be below 10% in all cases which is very typical in real-time soot generators [Spanner et al., 1994; Horvath and Gangl, 2003]. Therefore, the slight and not monoton changes in CMD values observed by varying the fluence of excitations (Table 1) can be definitely explained by the instrument uncertainty in the whole range of the applied laser fluences, while the changes in FWHM value can only partly by interpreted by that even in the subsequent fluences depicted in Table 1. However, in the presented methodology, the main critical sources of errors are the optical alignment and the long term instability of the applied laser source. These and the uncertainty of gas flow rates of the purging gas mixtures ($\pm$5%) presently limit the reproducibility. ”

Two papers discussing the generation of BC and the characterization of BC surrogates that may have serve as a model to the authors are:

Kirchstetter, T.W.; Novakov, T. (2007) Controlled generation of black carbon particles from acombustion flame and applications in evaluating black carbon measurement methods. Atmos. Environ., 41, 1874-1888, doi:10.1016/j.atmosenv.2006.10.067. Gysel et al. (2011) Effective density of aquadag and fullerene soot black carbon reference materials used for SP2 calibration. Atmos. Meas. Tech., 4, 2851-2858, www.atmos-meas-tech.net/4/2581/2011/

The author’s give a thanks to the reviewer this suggestion and used these papers to modify the MS. We have also cited these papers in the revised MS.

Page 2 line 48: “[Baumgarden et al., 2012; Gysel et al., 2011]”

Page 2 line 56: “Kirchstetter and Novakov, 2007.]”

Specific comments: Line 20: “strong but featureless” optical absorption properties? Please explain what featureless means in this context.

The author’s agree with the reviewer that the cited terminology is misleading and need to be explain in more detailed in the revised MS.

We added the following on page 2 line 37-38:

“. . .(the optical absorption shows inverse relation with wavelength). . .”

Table 1: no monotonic correlation between laser fluence and CMD of primary particles, the particle concentration increases with fluence. The author’s agree with the reviewer that the recognized undefined correlation can be explicitly explained in the revised MS especially in the context of the reproductivity. .

We added the following paragraph from page 12, line 236 to page 13 line 247:

“The reproducibility of the generated carbonaceous aerosol plume was determined from 60 spectra gathered from two hours continuous measurement period which was repeated three times at three different days at 2 J/cm2 laser fluence. The uncertainty of the CMD, FWHM and the total particle number concentration were found to be below 10% in all cases which is very typical in real-time soot generators [Spanner et al., 1994; Horvath and Gangl, 2003]. Therefore, the slight and not monoton changes in CMD values observed by varying the fluence of excitations (Table 1) can be definitely explained by the instrument uncertainty in the whole range of the applied laser fluences, while the changes in FWHM value can only partly by interpreted by that even in the subsequent fluences depicted in Table 1. However, in the presented methodology, the main critical sources of errors are the optical alignment and the long term instability of the applied laser source. These and the uncertainty of gas flow rates of the purging gas mixtures ($\pm$5%) presently limit the reproducibility.”

Figure 2 and 4: what do the error bars represents? Variability over time? Or standard deviation over several runs?

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The author's agree with the reviewer that meaning of the depicted error bars in these figures are misleading and should be clarified in the revised MS. We added on page 6 lines 149-150: "The error bar represents the standard deviation of the measured data including concentration and instrument instability." And on page 7 lines 157-159: "The error bar represents the standard deviation of the measured data including concentration and instrument instability."

Figure 7 needs more descriptive caption

The author's agree with the reviewer that Figure 7 needs a more descriptive caption and according to this suggestion we modified the related caption and also made some modifications in the text in the revised MS. âĂČ

Page 9 line 170-175:

Figure 7. TEM and HRTEM images of various laser generated carbonaceous aerosol particles.7.a: primary particles obeyed at 0.7 J/cm2 laser fluence at nitrogen purging gas, 7b and c: more complicated fractal aggregates gathered at 0.9 J/cm2 and 2.5 J/cm2 laser fluences in nitrogen purging gas respectively. In 7d-f typical microstructure of the generated particles are shown (see text in details).

Furthermore we added the following text from page 13 from line 248 to page 14 line 289:

"Finally, the morphology, the microstructure and the Raman spectra of the generated aerosol plume were investigated. In Figure 7 three different, representative soot structures can be seen. These experimentally demonstrated that the morphology of the laser generated soot aerosol well models the real carbonaceous atmospheric particulate originating from i.e. diesel exhaust or a kerosene flame [Park et al., 2004; Fruhstorfer and Niessner, 1994; Randall and Vander, 2010;]. Figure 7a represents primary particles with the average diameter of 7$\pm$0.8nm which was collected at 0.7 J/cm2 fluence in nitrogen purging gas. Figures 7b and 7c demonstrate more complex

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soot structures corresponding to 0.9 J/cm2 and 2.5 J/cm2 excitations, respectively. The mean particle diameter, calculated from about 200 primary particles, was found to be in between 8.5nm and 13.7nm respectively with the average diameter of 9.9nm with standard deviation of 2.3 in case of fractals aggregates (Fig. 7b and c). Fractal dimension of the generated carbonaceous aggregates was determined by using a simple relation between the number and mean diameter of primary particles as well as their radius of giration with the aid of an image analysis software (Digital Micrograph 3, Gatan Inc.) [Park et al., 2004]. The fractal dimensions calculated from well separated aggregates on the grid associated with 0.9 and 2.5 J/cm2 fluences ranged from 1.65 to 2.1 with the mean value of 1.88$\pm$1.4. Therefore, the morphology and the characteristic dimensions of the fractals experimentally demonstrated that the laser generated carbonaceous aerosol particulate shows high similarity with real soot or soot containing ambient aerosol such as diesel or biodiesel soot [Tumolva et al., 2010; Song et al., 2004] The structural properties of the primary particles obtained in the high resolution TEM mode at 2 J/cm2 fluence are shown in Fig. 7d-f. Besides some amorphous and disordered arrangements, the laser generated soot typically forms in a shell-core (graphitic) structure where graphene layers are oriented parallel to the external outer surface (Fig. 7d), in a locally and concentrically structured graphene layers but with random orientation respect to each other (Fig7e), and graphene layers structured parallel to each other but without concentric orientation (Fig 7f). The typical distance between the layers are about 0.34 nm (Fig. 7d). These types of microstructures are also in good agreement with a more realistic ambient or other artificially generated soot originating from i.e. diesel exhaust or spark discharged of a carbon rood [Sadecky et al. 2005; Sze et al., 2001; Jawhari et al., 1995; Mertes et al., 2004]. The Raman spectra of the laser generated soot aerosol exhibit two broad and strongly overlapping peaks with the maximum intensity at around 1350 cm-1 and at around 1585 cm-1 (first-order) and one individual peak with relatively lower intensity laying between 2700cm-1 and 3500 cm-1 (second -order) (Fig. 8). The latter one has not showed in Fig. 8. The feature around 1585 cm-1 designated to G (graphite) peak indicates the fundamental mode of a graphite crystal, while the peak around 1350 cm-1 denotes the D (disordered) lines mostly associated with amorphous or randomly oriented (turbostratic) graphene layer structures. The detailed analyses of the first-order spectra where the originally measured Raman data is further structured by a multi-peak fitting algorithm including all first-order Raman bands of soot or soot containing materials (G and D1-D4) are also shown in Fig. 8 [Sadezky et al., 2005]. The obeyed Raman spectra are in accordance with the results of the HRTEM images and further confirmed that the laser generated aerosol plume well modelled the realistic soot or soot containing ambient particulates [Tumolva et al., 2010; Song et al., 2004]."

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/7/C4611/2015/amtd-7-C4611-2015-supplement.pdf

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Interactive comment on Atmos. Meas. Tech. Discuss., 7, 10159, 2014.

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Interactive Comment

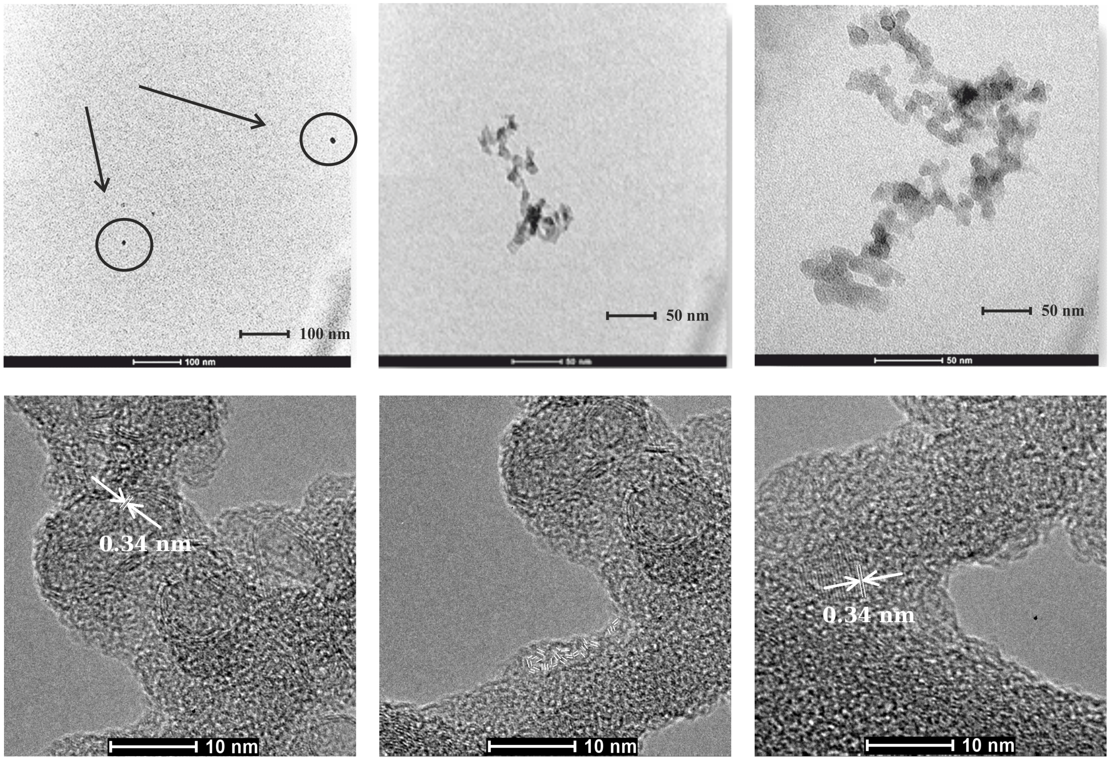

Fig. 1.