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

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Anonymous Referee#2:

Reviewers' comments: The paper presents an approach to generate model soot particles for instrument calibration or laboratory studies. While the method proposed may be of interest, the lack of rigorous quality assurance data regarding the generated particles makes the the reliability and consistency of the proposed mechanism difficult to evaluate.

First of all, we would like to express the authors' gratitude for this review. The authors are in complete agreement 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.

The authors stress the flexibility of the proposed method – by varying the purging gas flow rate or laser power, different number concentartioons and particle sizes can be generated. However, this flexibility is only of value if it is robustly repeatable. A series of controlled duplicate measurements would credence to the ability of the proposed technique to be used as a calibration method or to generate particles of known size.

Authors' response: We really agree with the Reviewer that although the goal of this study was not to introduce a new soot generating instrument but only to demonstrate the novel methodology and its flexibility for carbonaceous particulate generation, the reproductivity study of the proposed methodology is necessary to be described even in this context as well. Therefore, according to this *suggestion the revised MS is extended with a new paragraph focusing the robustness of the proposed methodology. Moreover, we also indicate the technical limitation of the presented experimental set-up in the revised MS which is to be solved in the future in order to make it become a real alternative of the presently available real-time soot generators.*

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/cm^2 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 (±5%) presently limit the reproducibility"

Further, while mass and particle size data are presented, no information on the chemical composition is provided making it difficult to assess if the particles would be truly valuable as a balck carbon surrogate. Simple thermal-optical characterization on the generated particles should be performed.

Authors' response: We really agree with the Reviewer that although the microphysical characterization of the generated plume are described in details, the chemical aspect of the laser ablated particles is missing in the original MS. Moreover, the terminology "black carbon" which is frequently used in the MS might also mislead the reader, since this terminology which is an operational definition based on the spectral responses of the carbonaceous particulate matter. So if we used this terminology, it would need to be confirmed with optical measurements. Therefore, *we changed this terminology to carbonaceous particulate or soot throughout the revised MS and also extended it with new results focusing the chemical characterization of the generated particles which is also missing in the original MS.*

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/cm^2 fluence in nitrogen purging gas. Figures 7b and 7c demonstrate more complex soot structures corresponding to 0.9 J/cm^2 and 2.5 J/cm^2 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/cm^2 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/cm^2 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].“

Finally, the above mentioned shortcomings are significant and without being properly addressed, the value of the proposed method compared to the existing approaches is difficult to access. If the authors can address the above mentioned concern, they should also more strongly assert why the proposed method is of value over other apporoaches to generate calibration or model carbon soot particles.

Authors' response: We really agree with the Reviewer that the relative advantages over the presently available approaches for soot generation is need to be described in more details in the revised MS. Therefore, according to this suggestion, all the above mentioned concerns and also this specific issues are implemented into the revised MS.

We added the following on page 14 line 300:

- “Particles with various complexity and microstructure can be generated (Figure 7).”

And also from page 15 line 326 to 16 line 345:

- „Special advantages of the method are that the target material can also be changed from any real solid phase target sample so, the real combustion processes such as biomass or coal burning can be modelled accuratelly in this set-up as well (Ajtai et al., 2011)
- Finally, besides its flexibility, one of the major advantages of the proposed method is that all the parameters of the generated aerosol plume can be tuned can be tuned independently from each other.

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 an alternative surrogate for modelling the real atmospheric soot aerosol further technical development is nedded including i.e. more robust and simplified excitation sources, more sophisticated physical and chemical characterisation of 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."

*And on: page 16 line 357-363_*

"The measured micro-physical properties confirm that the generated particles have properties which are very close to those of real atmospheric carbonaceous particulate (Fig. 7 and 8). A special advantage of the proposed method is its flexibility in the use of various gases and gas mixtures as local gas ambient during the formation of carbon particles. This opens up the possibility of quantitative investigation of the gas ambient effect on the particle formations (Fig. 6). As a target material not only graphite but e.g. coal samples can be used, as it was already demonstrated before (Ajtai et al., 2010). This gives further flexibility for the generation method. "