

We re-evaluated our whole data set, checked all numbers and performed t-tests to obtain a quantitative measure for the assignment of the samples to the Raman categories. The introduction was shortened somewhat without detracting from the main message, new references were added, the text was edited and revised to address the Reviewers' comments, the order of the sections was changed (section about washed samples was shifted towards the front) and new figures (Fig. 6, additions to Fig. 3, 4 and 5) were added to better demonstrate our findings and to give better graphical overviews. The former figures 4 and 5 were shifted to the supplementary material. In former section 2.2 (sample selection) the part about air mass back trajectories was removed because we did not use this information in the MS. A new section "sample selection and preparation" was inserted (2.3) which contains now parts of former section 2.2, section 2.1 and section 3.1. The t-tests refined the sample assignment to the Raman categories, which led to a re-assignment of two samples (30.06.2015, 03.01.2015). One sample (13.06.2015) was categorized as "non-defined" since the Raman spectra for one heated sample was measured with another exciting laser wavelength than the others in the EUSAAR2 heating series of the respective filter sample. We checked again whether only samples analyzed with the same laser for the Raman analysis were compared to each other, which resulted in the removal of 6 samples analyzed with the NIOSH870 protocol from the discussion. This reduction of samples, however, did not change our findings. The specific comments of the reviewers are addressed below.

## **Anonymous Reviewer #2**

Received and published: 5 December 2020

This study investigated the structural changes of aerosol while heating of atmospheric aerosol samples during thermal-optical measurements. Two different thermal-optical measurement protocols (EUSAAR2, NIOSH870) were investigated. Charring of organic carbon is an important issue to investigate and can impact the thermal-optical measurements. The authors used Raman spectroscopy to track structural changes upon heating the atmospheric aerosol samples. They also used ion chromatography and integrating sphere measurements to derive ionic compositions and light absorbing fraction of carbonaceous material. They used different peak ratios derived from Raman spectra as an indicator to probe structural changes. The authors observed that D/G peak ratios of the Raman spectra was higher for sample heated via NIOSH870, suggesting higher degree of structural ordering. Samples heated via EUSAAR2 protocol exhibited complex behavior of structural changes. Investigation of washed sample with low water-soluble organic carbon and inorganic salts showed no structural ordering and darkening of sample. Overall, the authors suggested that structural ordering of sample may not be responsible for darkening of sample.

I think the research topic is relevant and important for the community. However, the overall presentation of the manuscript bit convoluted and it can be structured better way so that it will easier for readers to follow. For example, discussion of structural changes for unwashed (original) and washed sample should be discussed together. Perhaps a comparison of Fig 2 and Fig. 10, maybe just compare for one temperature would be useful for readers.

We replaced figure 10 with a figure comparing the Raman spectra obtained for the same filter where one part was washed and the other unwashed. Washed samples and their unwashed counterparts, were analyzed only for the EUSAAR2 protocol, because one half of each filter was used for washing so no material was left for additional analysis with NIOSH870. A direct comparison between Fig. 2 and Fig. 10 is not feasible, because Fig. 2 shows a comparison between spectra obtained for samples heated according to the NIOSH870 and EUSAAR2 protocols.

Some of discussions need to elaborate. When you state about some observation and I suggest elaborating what does that mean. After revision of the manuscript, I think it will be suitable for publication.

55 Specific comments:

In the abstract the authors highlighted that structural ordering may not be responsible for darkening of sample, I suggest the authors to put the hypothesis here, what might be the possible cause for this.

60 *We added our hypothesis at the end of the abstract: "Possible transformations at lower temperatures could include the formation of non-graphitic light absorbing intermediate organic carbon, the release of C-H groups or the decrease of carbonyl groups."*

I was wondering if the pre-edge of the spectra was considered or normalized while comparing the spectra?

70 *The spectra were normalized to the maximum of the G-Peak after subtracting the background, which differed for different samples because of the various amounts of light absorbing species. The normalization to the G-peak accounts for these variations and was therefore preferred over a pre- or near-edge normalization.*

It was not clear to me how the different "Raman categories" were assigned? I suggest the authors to provide quantitative peak ratios to define more robust categories.

75 *We performed t-tests to substantiate the assignment of the samples to the categories and added diagrams showing the change of the peak ratios with increasing temperature.*

80 It was not clear to me how the authors relate the structural changes with the changes in the transmission laser signal. Having a quantified variable structural change (may be using the peak ratios) and compare with the transmission laser signal will be useful.

85 *Diagrams were added showing the change of the D/G ratio compared to the change of the laser signal for each sample. (Fig. 6)*

I see the Fig 7 discussed the BrC/LAC ratios with qualitative structural changes. A quantified comparison would be useful here too.

90 *We quantified the categorization of the changes of the Raman spectra by performing a t-test. So BrC/LAC ratios are now compared with mathematically more stable categories of structural changes.*

95 Comparison of washed and unwashed samples are interesting. Just wondering if authors investigated any standard water-soluble organic carbon to investigate the laser signal.

100 *An earlier analysis with sucrose showed that transmission and reflection laser signals decreased during TO measurements and that the pyrolyzed material showed the two typical soot peaks as well. The investigation of charring of sucrose, however, is outside the scope of this study, which is focused on atmospheric samples.*

Observation of higher initial laser signal of washed samples compared to unwashed samples need to be discussed in detail.

105 *Since the washed samples were mechanically shaken, also part of BC was removed from the filter. Integrating sphere measurements showed that absolute BC loadings were lower after washing. We added a sentence in line 255 to state this more precisely.*

110 I was wondering about the sensitivities of the Raman peaks here. How confident authors are regarding the graphitization of carbon. Some of the previous studies showed changes in graphitic structure upon heating black carbon particles using high resolution TEM imaging.

115 *We are confident that the sensitivity of the Raman peaks is acceptable for the purpose of this study. In our recent study (Haller et al., 2019) we used TEM imaging and electron scattering additional to Raman spectroscopy for the investigation of structural changes of miniCAST-soot (i.e. propane combustion aerosol; sootgenerator.com). The Raman spectra as well as the electron diffraction patterns did not change for a sample with a large amount of BC.*  
120 *The advantage of Raman spectroscopy was that we could get averaged information about the whole illuminated area and that the quartz fiber filter did not influence the measurements. Our experiences with TEM showed that the electron beam interfered with the quartz fibers, which made the sample preparation and the measurement very complicated.*

125 Why the early and fast category of Raman categories are noisier compared to others?

*The signal to noise ratios as well as the signal to fluorescence background differed for different samples. The first occurred because of differing absorbance depending e.g. on the amount of BC on the filter and hence a generally lower Raman signal. The latter might be caused by the presence of fluorescent species (An analysis of these species was beyond the scope of the present study.)*

130

The increase of laser signal above 650 degree C maybe due to the decomposition of the dark intermediate OC products without graphitic structures. Please elaborate the discussion about the decomposition of the dark intermediate OC products.

135

*We changed the whole paragraph to clarify our argument about building of non-graphitic structures – which is the main message of it – and deleted the sentence about decomposition of dark intermediate OC products. After the changes this additional information is no more relevant at this place.*

140

The authors stated that EUSAAR2 produced less pyrolyzed carbon. Please add some discussion here.

*This statement was made by Cavalli et al. (2010) who found from the analysis of the transmission laser signal that more PC was built during a NIOSH protocol compared to EUSAAR protocol. We added the reference a second time in the introduction (line 54) for clarification.*

145