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 #1

Received and published: 9 December 2020

The manuscript by Haller et al. studies atmospheric light-absorbing carbon (LAC) in particulate matter (PM) by measuring quartz filter samples with thermal-optical analysis (TOA) and Raman spectroscopy. Filter punches were removed from the TOA instrument at various temperature steps and measured with Raman spectroscopy. Filters were also "washed" by stirring in water and measured again. The filters were categorized according to "brown carbon" content as BrC/LAC and the authors discuss the interpretation of the NIOSH870 and EUSAAR2 protocols in light of their results. The experiments provide very useful data for the interpretation of LAC measurements and warrant publication in AMT. However, the writing, analysis, interpretation, and literature discussion could all be improved.

MAJOR COMMENTS

The filter samples were categorized conceptually in Section 3.2.2 according to features shown in Figure 3. These categories are fundamentally an attempt to position the samples on the plane of D/G ratio (first axis) and TOA temperature (second axis).
The authors can very simply produce a plot of D/G vs T to demonstrate their interpretation. This would address an overall lack of higher-level analysis in this manuscript.

Diagrams for each category showing D/G vs T were added.

I appreciate that the authors have shown extensive amounts of raw data, but summary plots are needed.

We changed three plots to give better graphical overviews:
A new Figure 6 was inserted instead of former Fig 4 and 5: Instead of showing the laser signals over the whole heating process we plotted only their values at the end of each temperature level (for the first five temperature-levels) and for comparison the D/G ratios for the same samples. This was done for each Raman category separately.
In former figure 10 (now Fig. 3), which showed the Raman spectra of a washed filter, Raman spectra of the unwashed filter were added for a better visual comparison.
In the plots showing examples of Raman spectra for each category (former Fig. 3) diagrams with the progress of D/G over temperature were added (now Fig. 5).

On line 430, the authors note that the Raman spectra of washed samples do not change noticeably during TOA, even when the unwashed counterparts did change. This is the key result of this entire manuscript and should be introduced first. This experiment shows that all observed changes in Raman spectra can be attributed to PC formation (carbonization of organic compounds to form EC during heating).

We shifted this chapter towards the front (now chapter 3.2) and introduced the changes of the washed and unwashed samples directly after the description of the original samples to highlight this key result.

It is not clear to me that the authors' criticisms of earlier work on PC are valid. On lines 450-460 the authors summarize that earlier work argued that more PC is formed during NIOSH870. The current work shows that the PC which forms during NIOSH870 has a higher degree of structural order. I agree with the conclusion but I don't agree that the two are in contradiction. "PC" is measured optically. LAC with a higher degree of graphitization will absorb more. So, it will be correctly described as "more PC". Please rephrase the conclusion here.

We removed this argument and rephrased the whole paragraph, which now reads:
"These differences could be caused by a stronger graphitization during the NIOSH870 protocol than during EUSAAR2 at least in three cases out of six. This would mean that PC developed during the heating with different protocols might also have different optical properties which would influence the decrease of the transmission / reflection laser signal during the thermal-optical measurement procedure. This would be in good agreement with Yu et al. (2002), who found that light absorption coefficients of PC formed during a thermal-optical heating procedure are not identical over the whole heating procedure. It is plausible that this might be true also for two protocols with different maximum temperatures in He. The higher D/G ratio for a higher heating temperature is also in accordance with Le et al. (2019) who found increasing D/G ratios between 600°C and 800°C for their OC rich samples heated in N2.
As suggested by Chow et al. (2001) part of EC could leave the filter already during the 870°C temperature level in helium because of oxygenation or catalysis caused by mineral or other oxides at temperatures >700°C. This premature evolution of relatively structured material could also affect the D/G ratio during the highest inert temperature step in NIOSH870.
Therefore we assume that the higher D/G ratio of NI870 for some samples could be a combination of stronger graphitization caused by the higher temperature and premature oxidation of EC during the 870°C level in NIOSH870."

This comment also applies at line 477 (and 489 and 281) where the authors claim that "processes other than graphitization lead to a darkening ... for instance the separation of oxygen and hydrogen [...] not necessarily graphitization". Yes – these processes are carbonization of organics, especially WSOC. Carbonization is, by definition, the process being described.

We changed the term "graphitization" to "increase of structural ordering" in this section and in the conclusion (Lines 434, 438).

In general, uncertainty calculations were not described. Please refine this, and replace statements like "outside of the error bars" with "significantly different according to a t-test".

T-tests were performed to show which changes in the Raman spectra were significant and which were not. The t-tests confirmed the assignments to the Raman categories for all samples except for two: One sample (03.01.2015) was assigned to the category "late and fast" instead of "non-defined" after the t-test. For the second sample (30.06.2015) which we had assigned to the category "early and fast" the p value of the t-test was just above the significance level. Therefore we shifted this sample to the category "non-defined". The respective graphics were changed.

Section 3.1, the argument about diesel cars is invalid. It is likely that residential wood burning produces a similar ratio of BC/PM to diesel cars, so the fraction of BC in PM 2.5 need not change.

We refined this argument and included data about domestic space heating and fuel use in Vienna. Biomass burning is used by less than 1% of the households in Vienna and also the use of oil or coal is negligible. Most households use district heating or natural gas (about 45% each). The diesel source, however, is present and strong throughout the year. About 57% of all passenger cars and 100% of heavy duty vehicles in Vienna had diesel engines in 2015. 80% of total fuel sales in Austria was Diesel.

At the end of Section 3.2.1 the authors should discuss possible hypotheses to explain their results. They may find inspiration from the literature, for example the similar study by Kim Cuong Le et al. 2019 https://doi.org/10.1016/j.combustflame.2019.07.037. Possibilities include the formation of PC from organics with a range of degrees of order (carbonization) and catalysis by sulfate or metals which varies between samples.

We broadened the discussion in section 3.2.1 (now section 3.3.1) and referred also to the paper by Le et al. (2019) who found increasing D/G ratios also between 600°C and 800°C and give therefore evidence that the structural ordering at the end of the inert phase of the NIOSH870 protocol could indeed be higher than at the end of EUSAAR2. We also point to the possibility of premature oxidation of PC or EC during the highest temperature level in NIOSH870 as suggested by Chow et al. (2004). The reference to Le et al. (2019) was also inserted in section 3.3.3 for a discussion of the decreasing laser signal without increasing structural ordering which could be caused by a removal of C-H "out-of-plane" bonds around 350-400°C, a decomposition of surface carbonyl (C-O, C=O) groups or a decrease of cross-linkages between polyaromatic units and carbon chains (Le et al., 2019).

MINOR COMMENTS

The authors should probably follow Petzold et al. (2013)'s recommendation and call their Raman signals EC, not BC or LAC. (They are certainly not LAC: see comment on washing above.)

We do not call our Raman signals BC or LAC. The Raman spectra are coded only with the date of the sampling day, as well as the heating temperature and measurement protocol. The samples were then categorized according to changes in the Raman spectra and these categories were compared to several features of the original samples, among others also BrC/LAC. EC values are not derived from the Raman spectra in our work.
In our nomenclature, we followed Petzold et al. (2013) already in the first version of the MS: We call results obtained by thermal-optical analysis EC, OC or TC, and results obtained by integrating sphere measurements BrC, BC or LAC.

The discussion of Yu et al. (2002) on line 370 should be introduced in the introduction.

We revised the discussion about processes occurring during heating that lead to a darkening of the sample but not to an increase of structural ordering. Our main reference for this is now the paper by Le et al. (2019) who give more detailed suggestions on the processes happening at lower temperatures in the absence of oxygen. Both references, Yu et al (2002) as well as Le et al. (2019), are discussed in the new introduction.

Generally, "WSOC", not "WSOCs" (applies also to the figures)

done

The introduction could be more structured as it moves back and forth between topics.

We changed the structure of the introduction and eliminated some repetitions.

Line 13, "have been" not "was" found.

done

Line 167, please explain why the detection limit is higher for OC than EC.

Actually, OC and EC have the same detection limit of 0.1µgC/cm². We corrected this in the MS.

Table 1, instead of grey shading add a column for Raman measurements.

A new column was inserted showing whether Raman measurements were performed for the respective temperature level and the shading was removed.

Line 197, please comment on wavelength dependence of Raman measurements here.

A short description of the wavelength dependence of D/G ratio was added in line 171. Since we use the same excitation laser for all measurements done on a single sample and compare only the relative changes among them, the wavelength dependence does not interfere in our analyses.

Line 203, why was lower laser power used? Please explain.

An explanation was added in line 151: "Generally laser power was lowered for highly absorbing samples to prevent thermal destruction of the material, and for samples containing fluorescent material to reduce the interfering fluorescence background."

Line 205-215 please mention that 5+ Raman peaks are often fitted.

We now mention that several authors fit 5+ Raman peaks to their soot spectra and added the following references: Le et al. (2019), Sadezky et al. (2005), Zickler et al. (2006).

Line 224 please cite the calculation of mean crystallite size.

For the calculation of the mean crystallite sizes the Scherrer equation was used. The reference (Fultz, B. and Howe, J. M.: Transmission electron microscopy and diffractometry of materials, Physics and astronomy online library, Springer, Berlin, 2001.) was added.

Line 246 please cite.

These data were obtained in our study.

Figure 1 and others: define error bars in caption.

done

Please don’t abbreviate the words transmittance and reflectance to trans and refl. Simply write out the words.

done