

Interactive comment on “Investigation of structural changes of atmospheric aerosol samples during two thermal-optical measurement procedures (EUSAAR2, NIOSH870)” by Theresa Haller et al.

Anonymous Referee #1

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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

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

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).

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. 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.

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".

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.

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.

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.)

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

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

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

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

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

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

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

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

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

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Line 224 please cite the calculation of mean crystallite size.

Line 246 please cite.

Figure 1 and others: define error bars in caption.

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

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