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Atmospheric Measurement Techniques Discussions

Interactive comment on "On the quantification of atmospheric carbonate carbon by thermal/optical analysis protocols" *by* A. Karanasiou et al.

Anonymous Referee #2

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This manuscript addresses the issue of the possible interference from carbonate carbon (CC) in the measurement of organic and/or elemental carbon (OC and/or EC) by thermal-optical analysis. It addresses the possibilities of quantifying CC (when applying the NIOSH-840 thermal protocol) and of removing CC from the filter sample by fumigation with HCl prior to the thermal analysis. Three different temperature protocols (i.e., NIOSH-840, NIOSH-700, and EUSAAR-2) were applied to filter punches, which were spiked with known amounts of CaCO3, and to atmospheric aerosol filter samples, which were collected in Barcelona and Athens. Both untreated filters and filters treated with HCl fumigation were analyzed, and the results from these two treatments and from the three temperature protocols were compared with each other. These were valuable experiments to perform and the results provide further insights in the behaviour of CC

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in thermal-optical analysis. However, the manuscript has serious shortcomings. As indicated below, it is on several occasions unclear. More important, the conclusion that one needs to apply the EUSAAR-2 protocol to samples subjected to the fumigation method for obtaining precise (do the authors mean "accurate"?) OC and EC data is not warranted at all. Firstly, the fumigation method, as described in the manuscript, has serious drawbacks. Some are mentioned in the manuscript, but there are potential problems, which are not addressed. What does the fumigation do to the organic aerosol? Is there no loss of OC from the filter? This could have been examined by subjecting treated and untreated filter samples with very low CC content to thermal-optical analysis. Secondly, and even more important, concluding that the EUSAAR-2 protocol is needed for proper differentiation between OC and EC is not justified. It is well-known that the EC/OC ratio (for samples with negligible CC content) depends upon the temperature protocol used and that the IMPROVE protocol gives a larger ratio than the EUSAAR-2 protocol and that the latter gives a larger ratio than the NIOSH-840 protocol. It is unclear which of these three protocols (or of any other protocol) gives the "correct" or "true" EC/OC ratio. Furthermore, all measurements in this study were done with thermal-optical transmission (TOT); there is also thermal-optical reflectance (TOR) and the latter gives normally larger EC/OC ratios than TOT. Which one of the two approaches (TOT or TOR) gives data that are closest to the truth is also far from clear. After all, OC and EC in thermal-optical analysis are essentially operationally defined. The manuscript also suggests that light absorbing carbon (LAC) should be counted as EC. Also this is very far from sure. Where are the arguments for this? The authors should definitely downplay their suggestion that LAC is EC.

Specific comments:

1. Page 5376, line 4, and page 5377, line 26: The impression is given here that inorganic carbon and CC are the same. Not all inorganic carbon is necessarily CC. I suggest to leave "or inorganic carbon," out and to replace "inorganic carbonate" on page 5381, lines 26-27, by "CC".

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2. Page 5381, lines 16-22: It does not really matter that some LAC already evolves in the He-mode. Most of the LAC is presumably "brown carbon" (see: Andreae and Gelencsér, 2006) and thus not really EC, but rather OC from large-molecular weight organic compounds. After all, the distinction between OC and EC is not based on in which mode (He or O2/He) the carbon evolves, but on the setting of the split point, which is made by the optical correction (TOT in the current study).

3. Page 5383, line 25: It is unclear why the sharper peak is quantified as EC. The OC/EC split points are not shown in Fig. 5. They should.

4. Pages 5385-5386, section 3.3: Both the laboratory OCEC analyzer and the semi-continuous OCEC field instrument were used for the comparisons in this section. This should be clearly indicated in the first paragraph of this section. It is also not fully clear what the authors mean by "the same instrument" in line 16 of page 5385. Does this imply one single instrument?

5. Page 5386, lines 7-8: It is unclear why the sharper peak is quantified as EC. The OC/EC split points are not shown in Fig. 5. They should.

6. Page 5386, lines 13-14: Like was the case for LAC (see above), it does not really matter that some EC already evolves in the He-mode. After all, the distinction between OC and EC is not based on in which mode (He or O2/He) the carbon evolves, but on the setting of the split point, which is made by the optical correction (TOT in the current study).

7. Page 5386, lines 18-19: As indicated above, there is no problem with LAC already evolving in the He mode.

8. Page 5386, line 24: It is unclear where the "before" is to which reference is made in "As mentioned before".

9. Page 5387, lines 14-19: The explanation given here is not plausible and at least questionable. In other studies (e.g., Aurela et al., in press) good agreement was found

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between OC data from the laboratory OCEC analyzer and the semi-continuous OCEC field instrument.

10. Page 5390, lines 11-12: The authors written here "while a rather good agreement was established for the elemental carbon content". Do they mean a good agreement between the EC data from the two temperature protocols? If so, this is clearly not the case.

11. Pages 5393-5394: There are 3 references here (Pey et al, 2009; Putaud et al., 2004; Van Dingenen et al., 2004) to which no reference is made within the manuscript.

12. Page 5396, Table 2: It should be indicated with which temperature protocol the EC and OC data were obtained. It is also unclear whether CC is implicitly included in the OC and/or EC data given here.

13. Grammatical and other technical corrections:

p. 5377, l. 19: replace "Park et a.l," by "Park et al.,".

p. 5378, l. 26: replace "dessert dust" by "desert dust".

p. 5383, l. 26: replace "low-loading" by "low-loaded".

p. 5389, l. 21: replace "quantify" by "quantified".

References

Andreae, M. O. and Gelencsér, A., Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, Atmos. Chem. Phys., 6, 3131-3148, 2006.

Aurela, M., Saarikoski, S., Timonen, H., Aalto, P., Keronen, P., Saarnio, K., Teinilä, K., Kulmala, M, and Hillamo, R: Carbonaceous aerosol at a forested and an urban background sites in Southern Finland, Atmos. Environ., doi:10.1016/j.atmosenv.2010.12.039, in press.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 5375, 2010.