

We would like to thank the reviewer for the helpful and constructive comments. The answers addressing the reviewer's comments are given below (referee comments first, followed by our response in italics).

**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 CaCO<sub>3</sub>, 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 in thermal-optical analysis. However, the manuscript has serious shortcomings. As indicated below, it is on several occasions unclear.

1. 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.

*Response:*

*We agree with the reviewer, fumigation with HCl might change the OC and /or EC content regardless of the thermal protocol used. This is clearly stated in the article, quoted from the manuscript: "Acid fumigation procedure seems effective in relation to CC removal but may lead to a significant overestimation of EC and under- or over-estimation of OC (Jankowski et al., 2008; Chow et al., 1993). Furthermore, it might cause damage to the combustion oven of the OCEC analyzer (JRC Report, 2009)."*

*For this reason the suggestion of using acid fumigation has been removed and the text has changed as: page 5390, line 24 "The results suggest that during dust episodes, common for the Southern Europe, the analytical laboratories could use the NIOSH-840 protocol (regardless of the thermal protocol used in a routine basis) as a suitable and rapid method for the carbonate determination and manually integrate the sharp peak that appears in the maximum temperature step in the inert mode. In this way any overestimation of OC and/or EC due to the CC presence is avoided".*

2. 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.

*Response:*

*The effect of fumigation of the measured OC and EC concentrations is still an open issue. Nevertheless the present paper examines this procedure with the main objective to confirm that the peak that is quantified as CC indeed corresponds to carbonate carbon. The results were positive regarding the presence of CC. Nevertheless they also supported the observations of other researchers who state that acid fumigation procedure may interfere with EC and OC content as well. An example of one treated and untreated sample is given in Figure 7 in the manuscript. It is stated in the manuscript that the fumigation method also affected the OC peaks and the split point. Page 5384, line 25: "However, the fumigation procedure did not affect only CC but the other two carbonaceous constituents as well, by decreasing the OC and increasing the EC content. The examination of the thermograms revealed that, in reality, the fumigated samples presented both EC and OC peaks with larger areas in relation to the untreated samples. In addition, fumigation shifted the split point towards earlier steps in the He/O<sub>2</sub>-mode, thus attributing to EC part of the peaks corresponding to OC in the untreated samples."*

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.

*Response:*

*Indeed there are many issues regarding EC and OC determination (temperature protocol, TOT or TOR). This work does not aim to state which temperature protocol provides a better estimation of OC and EC, but instead looks at how the different protocols deal with carbonate carbon contents. The conclusion about the thermal protocol used for the OC and EC determination has been changed, please see answer 1.*

*The contribution of this work is limited to the TOT technique since the SUNSET instruments available to us are designed for this approach. Further work on this issue should be pursued by workers with TOR instruments.*

3. 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.

*Response:*

*It is not suggested that LAC should be counted as EC, only that it could also include EC but the term is mainly used by other workers in order to describe light absorbing material other than EC. This section refers mainly to the evidence presented by Cavalli et al. (2010) in order to consolidate the necessity for introducing new protocols.*

*Quoting from text: “It has been reported that the chemical nature of carbon evolving in the He mode at temperature around 850°C is actually EC. Chow et al. (2001) suggested that EC is partly oxidised from the oxygen provided by the mineral oxides present in the sample. Their supporting evidence is that during this temperature step in the He mode the reflectance/transmittance increases. Cavalli et al. (2010) also report that using high temperatures during the He mode (>750°C) might lead to a premature evolution of light absorbing carbon (LAC) possibly containing EC. In that study, more than 20% of LAC prematurely evolved when the maximum He-mode temperature is 850°C as in a NIOSH-type protocol. For these reasons in the EUSAAR-2 protocol the maximum temperature in the He mode is set at 650°C, to prevent LAC pre-combustion and to accurately determine carbon sub-fractions.”.*

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".

*Response:*

*We agree with the reviewer the term will be changed to CC*

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 O<sub>2</sub>/He) the carbon evolves, but on the setting of the split point, which is made by the optical correction (TOT in the current study).

*Response:*

*These lines described certain aspects of uncertainty arising from the complex nature of the EC and OC fractions and the possible improvements introduced by the different thermal protocols. Indeed part of the LAC may be “brown carbon”, that is light-absorbing organic matter. Nevertheless the distinction between OC and EC based on the setting of the split point by optical correction also presents certain limitations (Yu et al., 2002).*

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.

*Response:*

*The OC/EC split points will be added on Figures 4, 5 and 6. The text will be also modified as follows: Page 5383, line 20 “The NIOSH-700 thermograms presented a quite different pattern (Fig. 5). Again there was a clear peak corresponding to the CC content at the maximum temperature step of the He-mode (at 150–195 s). Nevertheless, the peak was not as sharp as in the case of the NIOSH-840 protocol. Moreover, for filters with high CC loadings, the thermograms presented a very wide peak at around 150–195 s, quantified as CC, and a sharper one at 360–370 s, in the He/O<sub>2</sub>-mode, quantified as OC or EC, according to the position of the split point. The same pattern was observed when the EUSAAR-2 protocol was applied, (Fig. 6) the thermogram presented a wide peak in the inert mode and a sharp one in the He-Ox mode. In*

the case of the low loaded filter the split point was set in the He mode while for the higher concentration of CC the split point was set at the beginning of the He-Ox mode.”  
 The updated figures 4, 5 and 6 have been included in the manuscript:

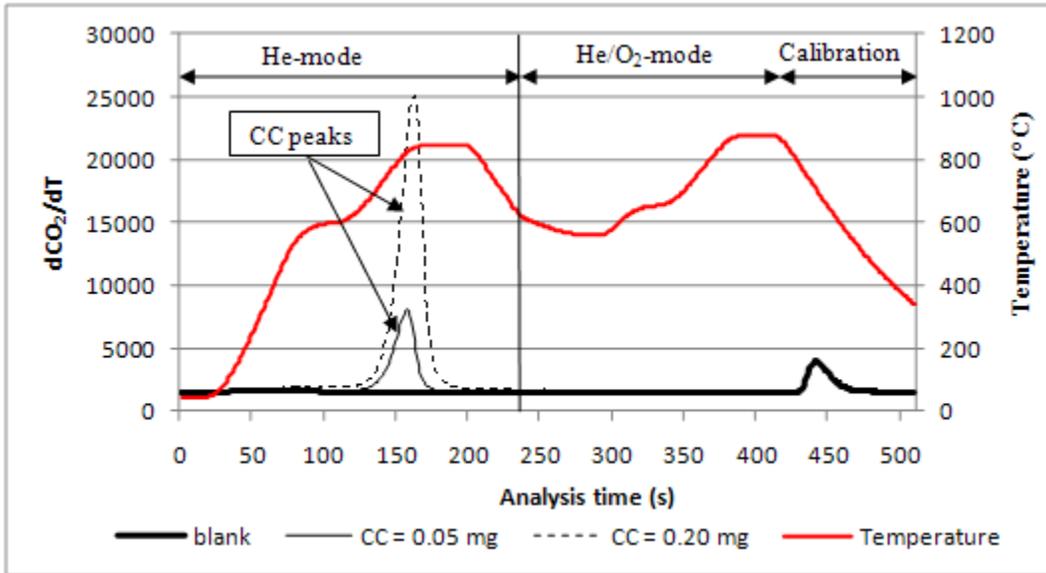


Figure 4. NIOSH-840 thermogram for a blank and two CC-loaded filters (He-mode: 1 – 230 s, He/O<sub>2</sub>-mode: 231-410 s and Calibration-mode: 410 – 510 s). Split point at 235 s for both samples.

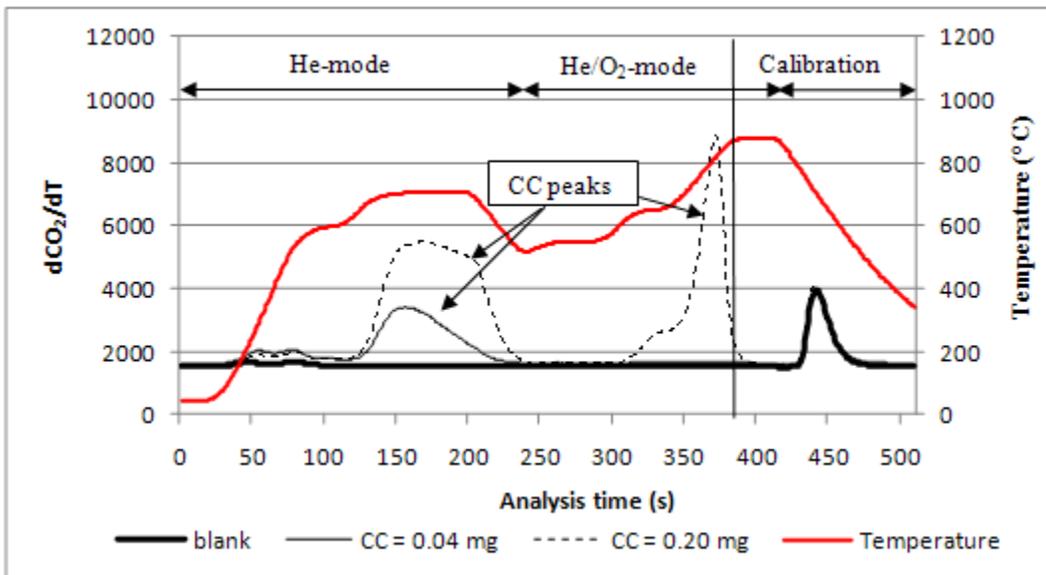


Figure 5. NIOSH-700 thermogram for a blank and two CC-loaded filters (He-mode: 1 – 230 s, He/O<sub>2</sub>-mode: 231-410 s and Calibration-mode: 410 – 510 s). Split point at 385 s for both samples.

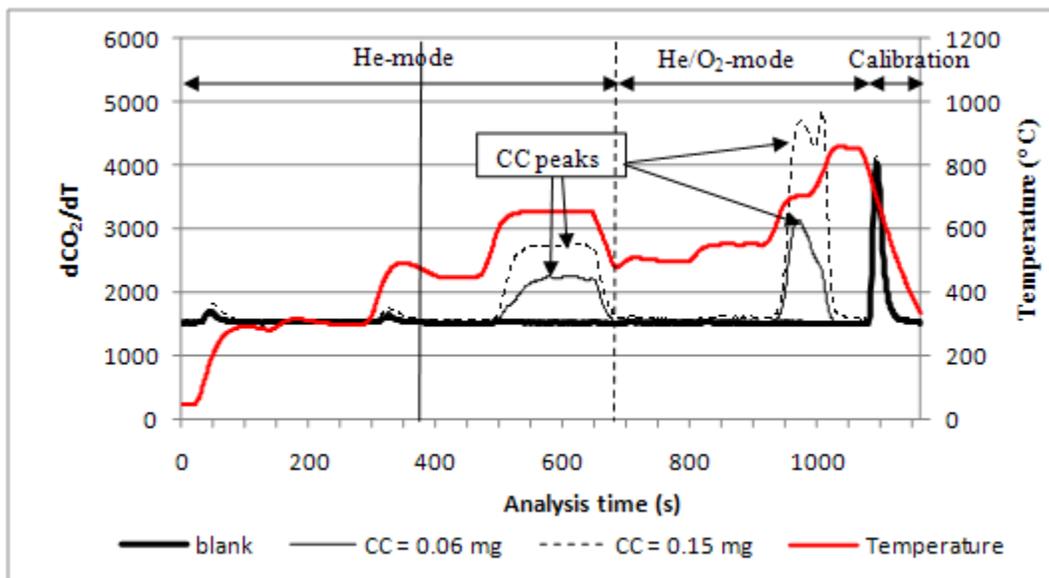


Figure 6. EUSAAR-2 thermogram for a blank and two CC-loaded filters (He-mode: 1 – 673 s, He/O<sub>2</sub>-mode: 674-1063 s and Calibration-mode: 1064 – 1163 s). Split point at 371 s and 678 s for low and high CC loaded samples, respectively.

4. Pages 5385-5386, section 3.3: Both the laboratory OCEC analyzer and the semicontinuous 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?

*Response:*

*The following text will be added in the manuscript, page 5385, line 17: "Both the laboratory OCEC analyzer based in Idae, Barcelona and the semicontinuous OCEC field instrument installed in GAW-DEM station in Athens were used for this comparison.*

*With the term "the same instrument" we mean 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.

*Response:*

*This error has been corrected. The phrase will be changed as follows:*

*Page 5386, line 7-8: "As it was shown in Fig. 6 when CaCO<sub>3</sub> was present in the filter the thermogram of EUSAAR-2 protocol presented a very wide peak in the He mode, and also a sharper one in the He/O<sub>2</sub>-mode, quantified as EC or OC, depending on the split point. Since this second peak appeared at the end of the analysis, it is most probable that it was quantified as EC. Indeed, for all standard samples but one, the split point was set much earlier in the analysis, usually in the He-mode."*

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).

*Response:*

*Please see answer #2.*

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

*Response:*

*Please see answer #2.*

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

*Response:*

*The text now at page 5386, line 24 changed to : "A total of 25 ambient PM high volume samples collected in the Barcelona urban site were analysed using two different protocols, NIOSH-840 and EUSAAR-2 by means of the laboratory and the semi-continuous OCEC analyzers."*

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

*Response:*

*In the study of Aurela et al., (2011) the OC and EC determined by the online Sunset analyzer with a time resolution of 2h or 3h are averaged to 24h concentrations and then compared to OC and EC determined by 24h filters by the Lab analyser. The average mean concentration (and the standard deviation) of OC and EC is compared. In contrast, we provide the correlation (as scatter plots) between the measurements obtained by the two instruments when punches of the same filter (24h sampling) are used. However, now in the manuscript we compare the results from the two analyzers in the same way, the average values and the standard deviation of OC, EC concentrations determined by the two analyzers for the same data set. The following table has been added. We have also combined section 3.4 with section 3.5 where we provide measurements of real atmospheric samples (reviewer 1 also suggested this merge).*

*Table 2. Average concentrations and standard deviation of 25 ambient filters (PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub>) measured by the semi-continuous and the lab analyzer using NIOSH-840 and EUSAAR-2 thermal protocols.*

	Semi-continuous analyzer		Lab analyzer	
	<b>NIOSH-840</b>		<b>NIOSH-840</b>	
$\mu\text{gm}^{-3}$	Mean	SD	Mean	SD
<b>EC</b>	1.28	0.70	1.31	0.59
<b>OC</b>	3.54	1.23	2.82	0.70
	<b>EUSAAR-2</b>		<b>EUSAAR-2</b>	
$\mu\text{gm}^{-3}$	Mean	SD	Mean	SD
<b>EC</b>	1.63	0.81	1.70	0.68
<b>OC</b>	3.06	0.82	2.43	0.61

*Furthermore as the purpose of this comparison was to quantify the differences between these two protocols with regards to the EC and OC content, with the possible occurrence of CC we decided not to exclude the CC content (when detected). As the thermal protocols used are the same we assumed that some technical differences between the two analyzers might cause this discrepancy (mainly of the OC content) in the comparison. The works of Phuah et al., 2009 and Bauer et al., 2009 provide evidence for these different characteristics.*

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.

*Response:*

*Looking at Figure 8b), Figure 9b), Figure 10a) and Figure 10b) the correlation coefficient  $R^2$  was higher than 0.90 in all graphs and the calculated slopes were in the range 1.07-1.18. We think that this can be characterized as "a rather good agreement" taking into account that the uncertainty of EC measurements is around 2-7% (Cavalli et al., 2010, EUSAAR-2 protocol) or higher.*

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.

*Response:*

*Corrections in the reference list were made accordingly.*

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.

*Response:*

*The text will be modified as follows: Page 5387, line 21-23: "Finally, CC was determined in two sets of ambient samples representative of Mediterranean urban aerosols, collected in Barcelona and Athens during different periods. The NIOSH-840 protocol was used for the analysis of all samples."*

*CC is not included in the OC and/or EC data given in Table 2, since it is presented separately in the same table.*

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".

*Response:*

*Corrections were made accordingly.*

## References

- 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.*, 45( 7), 1394-1401, 2011.
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- Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., and Putaud, J.-P.: Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, *Atmos. Meas. Tech.*, 3, 79–89, doi:10.5194/amt-3-79-2010, 2010.
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- Jankowski, N., Schmidl, C., Marr, I. L., Bauer, H., and Puxbaum, H.: Comparison of Methods for the Quantification of Carbonate Carbon in Atmospheric PM10 Aerosol Samples, *Atmos. Environ.*, 42, 8055–8064, 2008.
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