Atmos. Meas. Tech. Discuss., 8, C4246–C4251, 2015
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Atmospheric Measurement Techniques Discussions

Interactive comment on "Thermal-optical analysis for the measurement of elemental carbon (EC) and organic carbon (OC) in ambient air a literature review" *by* A. Karanasiou et al.

Anonymous Referee #2

Received and published: 9 December 2015

This paper aims to provide a literature review of the current state of knowledge of thermal-optical methods in the context of a reference method to be defined by CEN to analyze EC and OC in ambient air. This paper provides a quite exhaustive and valuable description of these thermal-optical methods addressing with many details a lot of issues related to charring correction, temperature protocols, optical correction, etc. In that sense, it fulfills its primary objective to gather in one paper all the studies related to this topic but hardly brings really new insights or useful guidance from the synthesis of this large amount of information. The paper is well written (sometimes too much descriptive). However, some sections are closer to a Standard Operating Procedure rather than a real literature review. Several major issues need to be addressed before

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considering it for publication. They are presented below.

Major comments:

- There is a clear need to reconsider the structure of the paper. There is not a clear and well justified scheme in this manuscript. At the end, it appears more like the superposition of several sections having poor interconnections. More specifically several sections are not directly related to the main topic of the paper (Thermal-optical analysis review) and should be either removed or eventually transferred in the supporting information. Namely section 3.1.1 (Laboratory blank filters), 3.1.2. (Field and trip blank filters), 3.2. (Sampling artifacts).

- There is nothing about the different techniques to check/calibrate thermal-optical methods (in terms of μgC) and almost nothing about the accuracy, the uncertainties associated with the few thermal-optical instruments (DRI, Sunset Lab) which cover the big majority of the studies reported here. A section could address this issue.

Specific comments:

- Introduction: Please describe in the introduction section how you have structured your review and justify why you have structured it like that. Please also recall in this section what is "EBC" and justify why thermal-optical analyses are important to determine EBC.

- Page 9652, line 25: "...EC, which does not volatilize in an inert atmosphere at temperature below 700°C" Where you got this number? Not sure that biomass burning EC is resistant at 700°C under inert mode.

- Page 9654, line 9: You should be more specific here. You are missing the step of carbonaceous vapors oxidized into CO2 (and then converted into CH4 with catalyst).

- Page 9654, line 27: Sentence "When PC evolves ... as the charred OC has been removed". As you clearly state later in the manuscript, there is a not a clear understanding of what is removed first under the oxidation step (EC or charred OC). For that reason, you cannot state here that charred OC is removed first.

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- Page 9655, line 10: Sentence “Since EC and PC have different optical properties . . .”. Not clear for me how with the spectral measurement of absorption you can better separate EC and PC. You should provide 1 or 2 sentences to better explain this point.

- Page 9657, line 18: Sentence “Application of a too high maximum temperature . . .”. This sentence is very long. Also I don’t understand the point raised concerning CC. In all cases (low or high Tmax) CC will interfere with OC-EC measurements. So I do not understand why it is only an issue here for very low Tmax.

- Section 2.2.3. Charring and charring correction. You are right to raise the issue of different values of attenuation cross section from PC and EC. But you should also mention that in the real-world we may also have a mixture of different sources of EC (for instance fossil fuel and biomass burning) with different attenuation cross section. This will also contribute to the uncertainties associated with the split point (charring correction) between OC and EC.

- Section 2.2.4. Dependence of OC/EC split on aerosol type. By comparison with wood burning samples, the authors state the traffic sites samples form little PC. One explanation given is the high diesel component (containing non pyrolyzing organic matter). There is a more straightforward reason that can be proposed to explain why fossil fuel samples produce less PC compared to wood burning samples: There is about 5 to 10 times less OC (relatively to EC) in fossil fuel samples compared to wood burning samples. End of this section, you are dealing with interference from other aerosol components (LAC, metal oxides). You should put this part under section 3.3 which is dedicated to this issue (interference).

- Page 9660, line 18: Not sure that the 6 points (i to vi) are the only biases in thermal-optical analysis methods. You have previously reported in the manuscript many other biases (sections 2.1 and 2.2)

- Section 2.2.6. Instrument parameters influencing the analysis. You may focus this title a little more here and change it to something related to “transit time influence on

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OC/EC split".

- Section 3.3.4. Brown carbon. Sentence "BrC is prone to charring . . .". This sentence is not clear for me in particular "the more refractory part of BrC will be wrongly attributed to EC". What do you mean exactly? Do you mean the more refractory part of charred BrC? Or not? Later in this section you state the BrC can generate more PC which, in the end, can lead to an overestimation of EC if charring is not properly accounted for. I don't understand this part. We are talking in this paper about thermal-optical methods which do account for charring. Maybe the authors want to state that the more PC is generated the more uncertainties are associated with EC and OC determination and, since BrC is prone to charring, uncertainties may be higher in atmospheric samples containing significant amount of BrC?

- Page 9675, line 22. Sentence "These differences may be explained . . .". I don't think we can state that rural sites are more influenced by biomass burning than urban environments. Domestic heating should be higher above cities.

- Page 9678, line 26. Sentence "The agreement between laboratories . . .". This is a correct statement for EC and OC; not for TC. The sentence just after "EC concentrations determined . . .". Are you sure that this statement is aligned with the results presented by Schmid et al. (2001) ?

Minor comments:

- In the title ":" could be added before "a literature review"

- Page 9652, line 4: "inorganic carbon (IC), mostly present as carbonate carbon (CC)". Since you state that IC is not exclusively CC, what are the other components of IC?

- Page 9652 line 10: CC is also present in seawater (sea salts).

- Page 9653, line 21: "in accordance to the new Air Quality Directive 2008/50/EC". Not really "new" anymore.

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- Page 9654, line 19: “the Sunset Carbon Aerosol Analysis Field instrument”. This is not the correct name of this instrument. It should be more “semi-continuous OC-EC field analyzer commercialized by Sunset Laboratory Inc.”

- Page 9654, line 23: “. . . while the lab instruments can analyze samples from various sites”. This a bit restrictive. For instance, it can also measure different aerosol sizes

- Page 9655, line 10: “Since EC and PC have different optical properties”. “may” instead of “have”.

- Page 9655, line 17: Please be consistent through the manuscript with some words like “analyzers” (written with z or s in the manuscript).

- Page 9656, line 5: “The main difference from NIOSH-like protocols is the lower temperature in the He phase of the analysis (580°C)”. Do you mean the lower temperature of the last plateau in the He phase of the analysis?

- Page 9659, line 8: “a carbon black sample”. What does it mean exactly?

- Page 9659, line 1: “LAC”. Why, from this point of the manuscript, you decide to speak about LAC whereas this term was not discussed before?

- Page 9672, line 23. “A number of potential SRM candidates for thermal-optical, TOA have been introduced . . .”. I cannot understand this part of the sentence.

- Page 9675, line 4, “. . . adsorbed throughout the filter”. I don’t understand this part which seems to be disconnected for the rest of the sentence.

- Page 9679, line 12. Add “%” after “7”.

- Page 9679, line 15. I had in my mind that Schmid et al. (2001) was not only dealing with thermal-optical methods but also with thermal methods. If so, discussion related to this paper should be removed from the manuscript as we are only dealing here with thermal-optical methods. Please check the other “old” references as well.

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- Page 9680, line 8. Add “%” behind numbers.

- Page 9681, line 1. Sentence “An inter-laboratory . . .”. Again I do not understand why you have decided to discuss on intercomparison studies including thermal methods which methods are not addressed in the paper. If you wish to discuss these results (thermal vs thermal-optical), you may better justify in the manuscript why.

- Page 9684, line 1. Africa is not the only desert to produce dust aerosols.

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 9649, 2015.