

The authors would like to thank Referee #1 for his/her comments and suggestions to improve the manuscript. We address all the comments one by one below.

Anonymous Referee #1

General comments:

To link black carbon from emission sources to climate forcing, the determination of atmospheric black carbon (BC) mass concentration is needed. Thermal-optical / or thermal methods are still widely used for this purpose, measuring BC mass contents in the samples from source regions to rural and to remote areas for both intensive campaigns and long-term observations. Unfortunately, as the nature of carbonaceous aerosols, their changes in optical (e.g., absorption and scattering) and chemical properties (e.g., thermal refractory) are in continuous mode (instead of discrete mode), therefore, the determination of organic carbon (OC) and elemental carbon (EC) is method/protocol dependent. By individual method, a specific part of OC and EC are detected on the continuous spectrum. In this manuscript, the authors have tried to present a comprehensive review for OC and EC analysis (with a focus only on thermal-optical methods), including thermal protocols, critical parameters related to the analysis, the biases/ interferences and references. Although the task is a challenge, the authors did a reasonably good job. However, the contents are not effectively organized, the logic flow is not well presented and some important mechanisms are not discussed. To improve the quality of the manuscript, the authors should address the following concerns and comments for final publication in AMT.

- 1) In general, it seems too much description/assembling information instead of discussions of mechanisms causing the variations, the knowledge gaps and suggestions for future work. It is suggested to condense the manuscript via removing some unnecessary contents (e.g., removing "Sampling artifacts" from the section 3 to focus on the issues of analysis since all the comparison results are not related to the sampling but the analytical protocols using the same filters).

Response: We have changed the structure of the manuscript following the suggestions from both reviewers. Please see our response in general comment 4. The manuscript has been thoroughly revised taking into account all comments. Please see our answers below and Response to reviewer 2

- 2) To my point of view, charring correction /minimization is the most important aspect related to the discrepancies between different thermal-optical methods. To have a consistency in charring correction or to minimize the extent of charring (assuming a constant FID sensitivity in a run), temperature and retention time (i.e., time elapsed at each temperature step), particularly in inert modes, are key factors.

Recent comparison studies show that using the same protocols at different laboratories, the temperature offsets could be significant ranging from -90°C to + 100°C (Panteliadis et al., 2015). It is certain that such large temperature offsets could influence OC and EC determinations. Although it is thought that the higher temperature in an inert mode, the more charring (PC) would be formed, it is also observed that the increase of transmittance signal was observed at the inert mode of T_{max}(>800°C) without evidence of trace oxygen involving (p757 in Yu et al., 2002, Figure 8 in Huang et al., 2006), and that the signatures of transmittance/ or reflectance could return to the initial values at 850°C prior to the addition of oxygen (Chow et al., 2001), cited by the authors in Table 5 of this manuscript. Those observations indicate that not only the temperature but also the residence time at the inert

mode (e.g., the time at each step in IMPROVE protocol could be as long as 580s) is important to affect the amount of charring (PC). As stated in Yu et al., 2002 (p760), the extent of charring formation is dependent on the temperature program parameters and the prolonging the residence time at each temperature step reduces charring formation. It is also known that water soluble OC (WSOC) / or oxygenated OC contributes the most to the charring (Yu et al., 2002; Chan et al., 2010). It is possible to form CO or other trace gases from oxygenated OC through gasification process at such high temperatures ($T_{Max} > 700^{\circ}C$) in the inert mode. This may be one of the possible reasons to explain the long residence time, the less charring formation observed by Yu et al., 2002 (i.e., the possibility of pre-oxidation at $850^{\circ}C$ in the inert mode has been ruled out in these cases). Unfortunately, temperature calibration and the relationship between T_{max} / or the time elapsed at T_{max} and the amount of charring have not been well discussed in the manuscript.

Response: We agree with the reviewer that charring correction is one of the most important aspects in thermal-optical analysis. In the revised paper we better discuss the factors influencing charring. This section has been modified as follows:

“During the inert mode of the analysis a fraction of the OC is charred and converted to PC, a material that absorbs light causing the decrease of both the filter transmittance and reflectance. It is clear that without correction for charring PC can be erroneously identified as EC. Reducing or minimizing the extent of charring would consequently reduce the uncertainty in the determination of the OC/EC split point. Charring depends on the chemical composition of the aerosol, and on the protocol used in thermal-optical analysis with the latter mostly related to the temperature, carrier gas composition and the residence time at each temperature step (Yu et al., 2002). The amount and type of organic compounds and the presence of certain inorganic constituents in the aerosol sample play an important role in charring. It is known that water soluble organic compounds (WSOC) or oxygenated organic compounds are responsible for a large fraction of charring (up to 66%) and that the extent of the charring increases linearly with the WSOC loading up to a certain value (Yu et al., 2002; Huang et al., 2010; Chan et al., 2010). When WSOC is removed from the sample prior to the thermal-optical analysis less PC is formed (Yang and Yu 2002) while the differences in the results between different thermal protocols are reduced (Piazzalunga et al., 2011). Charring is also influenced by the presence of inorganic components such as NH_4HSO_4 . According to Yu et al., (2002), the amount of charring of starch and cellulose was increased in the presence of NH_4HSO_4 while PC formed from levoglucosan was reduced by 15% when NH_4HSO_4 was present in the sample.

Considering the carrier gas and temperature, high temperatures in the He mode tend to generate more PC than less aggressive temperature steps (Yu et al., 2002; Chow et al., 2004; Subramanian et al., 2006; Cavalli et al., 2010). Regarding residence time at a given temperature, short residence times in the He mode can cause incomplete OC evolution at the lower temperature steps and, consequently, may increase PC during the higher temperature steps as more OC will be available for charring (Pavlovic et al., 2014; Yu et al., 2002). Several studies (Cavalli et al., 2010; Zhi et al., 2009; Huang et al., 2006; Yu et al., 2002) point out that prolonging the residence times in the inert mode favours a more complete carbon evolution, which, consequently, reduces charring formation. In fact, a NIOSH-like protocol with residence time 60 to 90s in the inert mode often gives rise to overlapping OC peaks indicating the simultaneous evolution of different carbon fractions. This is not observed in the IMPROVE protocol as the temperature advances to the next step only when a well-defined carbon peak has appeared resulting in much longer residence time (up to 580s) (Chow et al., 2001). Similarly the EUSAAR_2 protocol provides well-separated OC peaks due to longer residence time (120-180s in the inert mode) than the NIOSH protocol. Moreover, long residence times in

the inert mode can cause the removal of PC before the addition of O₂ at high temperatures due to high temperature vaporizations (Huang et al., 2006).

Once PC is formed it is crucial to properly account for it and correct OC, EC concentrations. The principle of the optical correction in TOA is based in two assumptions: (1) PC caused by charring during the inert mode is more easily oxidized than EC; or (2) the specific attenuation cross section, σ of PC is similar to the specific attenuation cross section of the original EC on the filter. If either of these assumptions is correct, then the method will be quantitative for OC and EC. Many researchers have observed an increase of the transmittance or reflectance during the T_{max} step in the inert mode indicating the decomposition of light absorbing compounds PC and/or EC, at high temperatures >750°C (Huang et al., 2006; Chow et al., 2001; Cavalli et al., 2010; Cheng et al., 2010). If this happens it is important to determine what is decomposed during this stage. If it is pure PC or light absorbing OC compounds as suggested by Yu et al. (2002) and Huang et al. (2006) then assumption (1) is correct and the split point of OC and EC is properly determined. However, Chow et al. (2001) attributed the increase of reflectance in the inert mode to the EC premature oxidation caused by the oxygen provided from mineral oxides present in the aerosol sample. Subramanian et al (2006), Cavalli et al. (2010) and Pavlovic et al. (2014) demonstrated that PC and EC co-evolve in the oxidizing mode and even prematurely during the He-mode at high temperatures. Additionally, PC and EC have been shown to have significantly different values of attenuation cross section (e.g: Subramanian et al., 2006; Chow et al., 2004). As a result the true EC concentrations can be either overestimated or underestimated depending on whether the fraction of PC that is burned after the EC/OC split point has a higher or a lower σ value than that of native EC. In the real world we usually have a mixture of different sources of EC (e.g., fossil fuel combustion and biomass burning) with different attenuation cross section. Similarly, the composition of organic compounds varies greatly among aerosols from different sources resulting in various σ values of PC depending on the aerosol sample. Thus, the magnitude of the uncertainty arising from the incorrect EC/OC split is expected to vary from one aerosol sample to another (Yang and Yu 2002). Despite this uncertainty in the optical correction method, the corrected results will be closer to the 'true' EC/OC split than if no correction is applied."

3). Using universally accepted references may be a solution to improve uncertainties in OC & EC analysis via optimizing the protocols to minimize charred PC. However, it is challenging having accepted references due to the definition of EC (which is related to BC definition as discussed in Petzold et al., 2013). It is known that the ambient EC and OC are mixtures from various emission sources with different proportions (e.g., fossil fuel combustions, biomass burning, biogenic emissions and photochemical oxidations in the atmosphere). Although it is impossible to have references representing all kinds of ambient EC and OC aerosols (with a range of mixing ratios from various sources), it is possible having references for representatives of individual OC and EC components. Using those typical OC and EC references, at least, it can be done to optimize /assess the effectiveness of a method for EC and OC determinations.

Response: The authors understand that the reviewer refers to universally accepted reference materials. We agree, it is impossible to produce a reference material of known composition representing all kinds of ambient EC and OC aerosols. At present no reference materials exist for thermal-optical analysis. One requirement for reference materials is that they are representative of the parameter they would be a reference for, and in the case of ambient OC and EC this implies that the EC and the OC/EC ratio of such a material should resemble the EC and the OC/EC ratio of most common types of ambient aerosol (e.g., fossil fuel combustion aerosol). This point has been addressed in the reference material section where the following has been added: "At present no reference materials exist for thermal-optical analysis. One requirement for reference materials is that they are representative of the parameter they are

a reference for, and in the case of ambient OC and EC this implies that the EC and OC of such a material should be representative of most common types of ambient aerosol such as fossil fuel combustion and biomass burning aerosols.”

4). To improve the logical flow, a suggested structure of the manuscript is included below. For a purpose of comparison, the original structure is also assembled here (highlighted in gray).

Response: We agree with the proposed structure. We have additionally moved to the supplement the former section 3.1 OC loading on blank filters as reviewer 2 recommended. The new structure is as follows:

Contents

- 1 Introduction
- 2 Thermal-optical analysis
 - 2.1.1 Thermal-optical analysis protocols
 - 2.1.2 Comparison of TOT and TOR
 - 2.1.3 Comparison of IMPROVE, NIOSH-like and EUSAAR_2 protocols
- 2.2 Inter-laboratory comparison studies
- 3 Critical factors causing uncertainties in thermal-optical analysis
 - 3.1 Temperature calibration
 - 3.2 Maximum temperature in the inert mode
 - 3.3 Charring and charring correction
 - 3.4 Dependence of OC/EC split on aerosol type
 - 3.4.1 Brown carbon
 - 3.6 Dependence of OC/EC split on sample oven soiling
- 4 Biases in thermal-optical analysis
 - 4.1 Interference from other aerosol components
 - 4.1.1 Carbonate carbon (CC)
 - 4.1.2 Metal oxides
 - 4.1.3 Inorganic salts
 - 4.2 Instrument parameters influencing the analysis: transit time
- 5 Reference materials for OC and EC determination by thermal-optical analysis
- 6 Conclusions

Specific comments:

p9651, L15-16: authors said “the difference between reflectance and transmittance correction tends to be larger than the difference between different thermal protocols”. It was also noticed that in Table 5 (p9706) for comparison between TOT and TOR, the slope of TOR to TOT is 1 for NIOSH (850°C), which is not larger than these between IMPROVE and NIOSH (Chow et al., 2001), indicating that the above statement is not valid in this case when the time at Tmax (850°C) is long enough (using the DRI instrument), the signals of either reflectance or transmittance would return to the initial value before the addition of oxygen, the charring was minimized and the slope of TOR to TOT would equal to one.

Response: We agree with the reviewer. In the revised paper we remark this observation. The following has been added in the section Comparison of TOT and TOR: “However in the study of Chow et al., (2001) using the DRI instrument and the NIOSH protocol the signals of both reflectance and transmittance returned to their initial values prior to the addition of oxygen for many of the samples during the 850 °C step of the analysis. As a result the slope of TOR to TOT was equal to one. One explanation could be that using longer residence time (150s in all temperature steps and 160s at Tmax) than in the typical NIOSH protocol (usually 60-120s) can minimize the differences between TOT and TOR.”

P9651, L25-26: it is suggested to include “e.g.,” before the cited references since there are many more references not included.

P9652, L1-2: it is suggested to include “e.g.,” before the cited references since there are many more references not included. You may apply this to other citations too...

Response: Correct, “e.g.,” has been included.

p9652, L21-22: the expression, i.e, “The term EC is used when total carbon is gasified from the sample...” is not clear and please rephrase it.

Response: The text has been changed to: “In contrast, EC refers to chemical properties, i.e. to thermally-refractory carbon, including graphitic structures. EC is then differentiated from OC based on refractiveness properties (in pure thermal methods) or on optical measurements during the course of the thermal analysis (in thermal-optical methods).

P9653, L24: the “chars and pyrolyzes” should be replaced with “is charred and pyrolyzed”.

Response: Corrected.

p9654, L18-23: the main difference between the lab and the field instruments is the detector. The detector of the field instrument is NDIR instead of FID as in the lab one. This should be mentioned here.

Response: The following has been added in the text: “The main difference between the lab and the field instruments is the detector. The detector of the field instrument is a non-dispersive infrared detector NDIR instead of a FID used in the lab analyser.”

P9656, L12: please replace the “accuracy” with “uncertainty” since the accuracy is the difference between the determination and the true value (you don’t know the true value regarding EC and OC contents).

Response: We have replaced “accuracy” with “uncertainty”.

P9657, L1: replace the title with “Critical factors causing uncertainties in Thermal-optical analysis”.

Response: We have changed the title as suggested.

P9658, L10-12: the sentence of “Charring is also influenced by the presence of inorganic constituents such as NH₄HSO₄ that can increase PC formation by a factor of 2 to 3 (Yu et al., 2002).” Is not always correct. According to Yu et al., (2002), although the amount of charring of starch and cellulose was increased in the presence of NH₄HSO₄, the amount of charring from levoglucosan, however, drops by 15% in the presence of NH₄HSO₄ (p760 in Yu et al., 2002).

Response: We have changed the phrase as follows: “Charring is also influenced by the presence of inorganic constituents such as NH₄HSO₄. According to Yu et al., (2002), the amount of charring of starch and cellulose was increased in the presence of NH₄HSO₄ however charring from levoglucosan was reduced by 15% in the presence of NH₄HSO₄.”

P9659, L5-10: the expression is not clear, please rephrase it.

Response: The text has been changed to: “The OC/EC split point for wood smoke source samples and samples dominated by biomass burning emissions is influenced by the temperature protocol since such samples exhibit significant charring (Khan et al., 2012; Schauer et al., 2003; Reisinger et al., 2008; Maenhaut et al., 2009; Soto-Garcia et al., 2011).”

P9659, L18-21: As mentioned before, an increase in transmittance was observed at 850 C in inert mode, regardless of the presence of absence of the trace oxygen (e.g., Yu et al., 2002, Huang et al., 2006), indicating that premature-oxidation of light absorption carbon (LAC) is

not the only reason for the increase of transmittance at T_{max} (> 800C) in inert mode. The possibility of other mechanisms (e.g., gasification of charring (PC) at high temperatures) should be mentioned.

Response: In this part we refer to aerosol samples highly influenced from road dust and soil dust emissions containing high amounts of metal oxides. In this case the premature evolution of LAC is mainly caused by the oxygen released from metal oxides. The other mechanisms: gasification of PC at high temperatures has been added in the section charring and charring correction.

P9660, L1-5: this section should be discussed in relation to laser sensitivity changes due to oven soiling (which is a process). This particularly impacts on trend determinations of long-term measurements.

Response: We have modified the text as follows: "The quartz oven hosting the sample during analysis is gradually soiled by oxidation and inorganic salts originating from filter matrices (when containing binders) and/or loaded samples. This will result in the progressive decrease of the laser transmittance or reflectance intensity. In the work of Chiappini et al., 2014 EC concentrations obtained with a soiled oven were significantly lower (up to a factor of 4) than EC obtained with a clean oven. This phenomenon might be explained by the influence of the oven temperature on the laser signal. Indeed, a slight decrease of the laser signal is generally observed with increasing temperature, even for a blank filter. However, a soiled oven induces an additional decrease of the laser signal, which could generate a bias in the split point determination leading to an underestimation of the EC concentration. This enlightens the necessity to follow the laser signal decrease with time and its impact on measurements.

P9660, L6-16: the factors mentioned in this section (i.e., instrument parameters) belong to the section of "Biases in thermal-optical analysis", as mentioned in General Comments. Agreed with the authors, true OC/EC could be not defined (due to not having proper references).

Response: We agree with the reviewer. This section has been moved to Biases in thermal-optical analysis.

p9660, L17: The "biases" should be defined. To me, they should be deviations between the measured values and the true values. Without knowing true values, it is hard to talk about biases. It may be better to replace "biases" with "systematic uncertainties".

Response: We agree with the reviewer, it is impossible to know the true value. To clarify this point the text has been modified as follows: "The term bias is used to describe the deviations between the measured values and the true, reference values. As in thermal-optical analysis the true value is unknown due to the lack of a reference material, in this section we mostly refer to systematic uncertainties caused by (i) OC loading in blank filters, (ii) catalytic oxidation interactions between OC, EC, and non-carbonaceous material in the sampled particles, and (iii) instrument parameters that influence the analysis. The biases caused by the OC loading in blank filters are discussed in the supplementary material since they are connected to manufacturing, transportation/storage, sampling and analysis procedures and not solely related to thermal-optical analysis.

P9660, L17-22: the "non-uniform particles deposits on the filters" should belong to random events (i.e., outliers which contribute to sampling heterogeneity) instead of systematic uncertainties; categories (ii) and (iii) should be combined into one category as "OC blanks" which could be caused by manufacturing, transportation/storage, sampling and analysis procedures.

Response: Please see our response to the previous comment.

P9664, L20-21: I don't agree on this statement, i.e., "the field blank values should not be subtracted from the sample OC concentrations....". It is suggested to correct the field blank for all measured concentrations using the averages with the same manufacturing lot number (the outliers should be excluded), particularly for the long-term observation.

Response: The EMEP manual <http://www.nilu.no/projects/ccc/manual/>, section 4.22 "Standard Operating Procedures for thermal-optical analysis of atmospheric particulate organic and elemental carbon" states that OC, EC concentrations should not be corrected for field blanks values, which should be reported separately. Moreover, Yttri et al. (2007) states that the adsorbed carbon in the field blanks would partially evaporate, decreasing by as much as a factor of two, when passing a clean air flow through. We have included these two references in the sentence to justify this conclusion as follows: "The field blank values should not be subtracted from the sample OC concentrations as this may lead to overestimation or underestimation of the artifact-free particulate OC (<http://www.nilu.no/projects/ccc/manual/> section 4.22; Yttri et al., 2007)."

P9664, L23: please remove the section as mentioned in General Comments since it beyond the scope of the manuscript (the sampling artifacts do not belong to the factors of thermal-optical analysis).

Response: The section has been moved to the supplement

p9669, L18-21: it could be also important if the sampling sites are close to coast of oceans (due to sea-spray aerosols).

Response: We agree with the reviewer. Coastal sites have been included in the beginning of the section where we mention the areas and aerosols mostly affected by CC. The sentence has been modified as follows: "The non-quantification of existing CC may significantly bias thermal OC and EC determination especially in certain areas (sites affected by construction works or resuspended road dust or at coastal sites), and/or under specific meteorological conditions e.g., during desert dust intrusions."

p9671, L5: It is known (Zhao et al., 2015) that there are some relationship between WSOC/ or oxygenated OC /or pyrolysis OC and brown carbon (BrC). Different terminologies may talk about the same thing, e.g., the former is about chemical properties and the latter is about the optical property of the same thing. It is likely that BrC could be WSOC or oxygenated OC and they could be charred into PC. Part of BrC could also be EC. Therefore, it is a little confusing to consider BrC as interference to OC and EC. BrC should be the optical characteristic of WSOC or oxygenated OC or relatively low temperature EC (e.g., from biomass burning sources). Please re-consider how to accommodate the content of "BrC" in the manuscript

Response: We agree with the reviewer. Brown carbon is part of the carbonaceous aerosol and cannot be considered as interference in thermal-optical analysis. For this reason we have moved this section to Critical factors causing uncertainties in thermal-optical analysis as a subsection to "Dependence of OC/EC split on aerosol type".

p9672, L14-15: what are the ISO or NIST definitions for references material?

Response: The definitions are found in <http://www.nist.gov/srm/definitions.cfm>, and they follow the ISO guidelines (ISO Guide 30:1992/Amd 1:2008). This has now been added to the text as follows: "at present there are no materials that have been shown to meet either these nor the ISO or NIST definitions for reference material (RM) or certified reference material (CRM) (<http://www.nist.gov/srm/definitions.cfm>, ISO Guide 30:1992/Amd 1:2008)."

P9673, L18-20: the expression is not clear. Please rephrase.

Response: The phrase “It should be noted, however, that one requirement for reference materials is that they are representative of the parameter they intend to provide a reference for,” was modified as follows: “It should be noted, however, that one requirement for reference materials is that they should be representative of the parameter they are a reference for,”

p9673, 20-22: I disagree on this statement”... that the EC and the OC/EC ratio of such a material should resemble the EC and the OC/EC ratio of ambient aerosol, as should its refractivity.”. It is known that the EC and OC/EC ratio in ambient aerosols is a range of variations, it is impossible to have references to represent the entire range. However, it should be to have a set of references representing main end members as found in ambient aerosols (e.g., fossil fuel combustions and biomass burning and etc).

Response: We agree with the reviewer’s comment, it would indeed be impossible to have reference materials for as many EC and OC/EC ratios as emission sources and aerosol types that are found in the atmosphere. The text has been rephrased as follows: “in the case of OC and EC, this implies that the EC and the OC/EC ratio of such a material should resemble the EC and the OC/EC ratio (and refractivity) of at least certain frequent types of ambient aerosols, such as those originating from fossil fuel combustion, biomass burning, etc. These tailored materials do not yet meet this requirement because the EC in these materials evolves at a much higher temperature (> 800 °C) than ambient EC. Also the organic coatings tested so far do not resemble ambient aerosols (the coatings were initially selected to show minimum charring).”

p9673, 23-24: According to Bond et al., 2013, black carbon is a distinct type of carbonaceous material. Its properties include strong absorption of visible light and refractory with a vaporization temperature near 4000K (much higher than 800°C). At least, one category of EC (e.g., forming from fossil fuel combustion or flaming) in ambient aerosols should have this kind of refractory if not all EC (e.g. the type of EC from biomass burning). Thus, the materials with EC evolving at high temperature (>800°C) should not be excluded as a candidate of references. This kind of EC should be reasonably detected by all thermal-optical / thermal methods.

Response: The reviewer’s comment is correct, although black carbon (or EC) is rarely (if ever) found as a distinct carbonaceous species in the atmosphere, as it is usually coated to some degree with organics and/or with inorganic species. In this section we were describing the ability of a reference material such as the one proposed by Popovicheva et al. (2011) to represent ambient aerosols, with a material which is an EC core coated with selected organic species. Even if by definition BC vaporizes at 4000k, the behavior of EC from ambient aerosol samples under TOT/thermal analytical methods is very different to that of the here given BC definition (and to that of the EC in the Popoicheva reference material). It is for this reason that we state that this tailored material does not meet the requirements yet. The text has been rephrased as follows:

“These tailored materials do not yet meet this requirement because of their inability so far to represent ambient aerosol behavior under thermal-optical/thermal treatment: the EC in these materials evolves at a much higher temperature (> 800 °C) than ambient EC, and also the organic coatings tested so far do not resemble ambient aerosols (the coatings were initially selected to show minimum charring).”

p9674, L4-7: the expression is not well understood. Please rephrase it.

Response: The phrase “It is important that the method of application, i.e., how the RM is introduced to the measurement system, does not affect the response of the TOA to the SRM and that the method of application is a part of the SRM protocol.” was re-written as follows:

“It is important that the method of application, i.e., how the RM is fed to the analytical instrument, does not affect the response of the TOA, and also that the method of application is considered as part of the SRM protocol and therefore that it is also standardized.”

p9674, L8: what does it mean for the “this parameter”? Do you mean the protocol, including temperature steps and the corresponding residence time ranges?

Response: This was indeed unclear, “parameter” referred to the OC/EC ratio. This has been rephrased as follows: “In addition, if the EC/OC ratio is to be determined, then this ratio must be fully characterized for the selected SRM and remain constant with time.”

p9676, L1-4: According to the description, it sounds that the charring identified by transmittance is better representative of the entire filter than those identified by reflectance (only for the surface charring...). Due to lack of proper references, it is impossible to know the true value.

Response: This is true. The text has been modified to reflect this limitation: “However as no reference material exists, it is impossible to know the true value of the native EC in the sample.”

p9678, L6-7: I agree on this general conclusion, i.e., “that the identification of the “best” method is not possible so far.”, because there no proper references have been used for establishing the true values as benchmarks. Therefore, establishing proper references and carrying out regular inter-comparison exercises (including different networks from different continents) are priorities in the carbonaceous aerosol measurement (i.e., OC/EC) field to maximize the scientific value of the current OC and EC datasets.

Response: We agree with the reviewer. In the conclusions we have added a paragraph regarding future research in the thermal-optical analysis. The following has been added: “At the moment there is no reference material available so the true value of EC, OC is not known. Future research should focus on the development of reference materials that are representative of the EC and OC of at least certain frequent types of ambient aerosols, such as those originating from fossil fuel combustion and biomass burning. In addition carrying out regular inter-comparison exercises (including different networks from different continents) is a priority in the TOA field to maximize the scientific value of the current OC and EC datasets.”

p9678, L26-27: The statement (i.e., “the agreement between laboratories was relatively poor when only thermal methods were used...”) is very ambiguous! In the reported results by Schmid et al., (2001) there are total 17 methods involved in the comparison. The authors only picked up five labs, including only one lab using thermal method without detailed description of the protocol. In fact, the relative standard deviation (RSD) of TC measurements when excluding the lab (using thermal method) is worse than that including the lab. Please clarify the expression.

It is true that Schmid et al. (2001) included more laboratories and results than those reported in the present paper, because the present paper only reports the data from methods using optical correction. In Table 1 from Schmid et al. (2001), it is indicated which laboratories were using methods with optical correction, and those were laboratories #9, #10, #11, #12 and #13. Note that laboratory #11 also used a method without optical correction (#11b) and this has not been included in the present review. Schmid et al. (2001) reported for EC results: “Within-laboratory r.s.d. was up to 18% and somewhat higher than for TC, r.s.d.s between laboratories ranged from 37% for sample Nov 7, 24% for sample Nov 8 to 46% for sample Nov 10”. This is interpreted by the authors of the present manuscript as relatively poor, to avoid reporting the exact numbers. Moreover, the last paragraph of conclusions from Schmid et al. (2001) stated

that the agreement between the amount of EC reported by different laboratories improved when only the methods including correction for charring effect were considered. In order to address the reviewer's concern, the sentence has been modified as follows: "The agreement between EC concentrations reported by different laboratories improved when optical correction was applied with respect to results corresponding to only thermal methods (Birch, 1998; Schmid et al., 2001; EUSAAR, 2011)."

p9680, L11-12, L19-20: It is realized that the RSD of the results in 2007 is 40% is higher than that in 2011 (i.e., 25%). The former is obtained by only using thermal-optical methods, whereas the latter is obtained by both thermal-optical and thermal methods. Please confirm.

Response: The relative standard deviation of EC for the labs using optical correction in EUSAAR (2007) was 40%. Nevertheless, the report also states that "Huge differences are observed in EC determinations, which can be attributed to fundamental differences in analytical techniques" although no exact relative standard deviation is given for this case and hence it cannot be included in the present manuscript, but it is surely higher than the 40% for the optical correction labs. On the other hand, the 25% value for EUSAAR (2011) is the reported random error for 3 laboratories, two of them using optical correction and one of them not using any charring correction.

The text has been modified as follows: "The variation for the EC concentrations was much higher, even up to 40% for laboratories using optical correction (EUSAAR, 2007), and it was protocol-dependent (EUSAAR, 2007 and 2011). The relative standard deviation was 29%..."

p9681, L1-7: The sentences are not clear, please rephrase them. It seems no statistically significant improvement from 13-27% to 9-23% (of total mass of ambient PM or TC?) or from 12-33% to 10-29% for EC/TC.

Response: We do not judge if there is or there is not any statistically significant improvement. We only report what the results are. The paragraph has been modified as follows:

"An inter-laboratory comparison performed within the ACTRIS project with 18 participants applying thermal or thermal-optical methods (NIOSH-like or EUSAAR_2) to ambient PM samples reported reproducibility relative standard deviations for TC concentrations from 13 to 27% (ACTRIS, 2011) and 9 to 23% when only laboratories using the EUSAAR_2 protocol were assessed. For the EC/TC ratio, the reproducibility relative standard deviations ranged from 12 to 33 %, including all the optical correction methods, and 10 to 29% when only laboratories using the EUSAAR_2 protocol were assessed, after excluding one sample with EC/TC ratio below 0.05."

p9681, L9-11: The expression is not very clear to me (should the "between" be replaced with the "within"?). Please re-phrase it.

Response: The sentence has been modified as follows: "Two inter-laboratory comparison exercises were carried out including several European Union National Reference Laboratories for air quality or delegated organizations, organized by JRC-IES European Reference Laboratory for Air Pollution (ERLAP)."

p9681, L24 to p9682, L3: It seems that the RSD results for TC (< 5%), EC (< 20 %) and OC (10%) are within accepted ranges and interesting to see that the RSD results are method-independent.

Response: That is correct.

p9682, L20-23: The expressions are not clear to me. Please re-phrase them.

Response: From the EUSAAR intercomparisons, it is seen that the variations in the EC/TC ratios are often systematic and laboratory-dependent, i.e. for example a given laboratory reports

lower EC/TC ratios than the average for different intercomparison exercises, whereas another laboratory may report higher EC/TC ratios than the average for different intercomparison exercises. So the variation of the EC/TC ratios does not seem to be random but systematic. The results from field instruments used off-line cannot be interpreted in a single direction, since there are different studies providing different assessment for their performance.

The sentence has been re-phrased as follows: "The variations in the EC/TC ratios are often systematic and laboratory-dependent. The results from field instruments used off-line were difficult to assess, given that the performance of this type of instruments is assessed differently by different studies (some works showed a poor agreement between this type of instruments and the remainder of the participants, although some other studies showed a good agreement)."

p9683, L22-23: The results by Chiappini et al. (2014) seems not strongly supporting this point.

Response: This conclusion was drawn from the intercomparison studies in Table 6: Maenhaut et al., 2009; 2012, Khan et al., 2012 where only one instrument type (Sunset Lab.) was used for testing the three different protocols. In Chiappini et al. (2014), results related to the NIOSH and EUSAAR2 protocols were obtained using this same instrument type, whereas results related to the IMPROVE protocol were obtained from a single participant using a different instrument type (DRI).

p9684, L3-5: Brown carbon is a part of charred OC (PC). BrC should not be considered as an interference of OC and EC determination (see comments on p9671).

Response: We have included BrC in the section "Critical factors causing uncertainty"

p9684, L6-12: If "sampling artifacts" is removed from the manuscript as suggested in General Comments, this paragraph should be removed.

Response: It has been removed

p9688, L18-28: Are those five references, i.e. EUSAAR 2007, 2008, 2009, 2010, 2011 publically accessible?

Response: Unfortunately they are not publically accessible.

p9702, Please list the original data sources in Table 2.

Response: Table 2 has been modified. Please also see our responses to major comments by Reviewer 2.

p9704. If "sampling artifacts" is removed from the manuscript as suggested in General Comments, Table 4 should be removed.

Response: The table has been removed

p9706, In the note under the table, it is stated that "the difference between NIOSH EC-TOR and EC-TOT was often zero because reflectance and transmittance returned to their initial values prior to the addition of oxygen for many of the samples during the 850 °C step of the analysis.", indicating that once the residence time is long enough at the high temperatures as used here, the differences between EC-TOR and EC-TOT can be minimized (see point#2 in General Comments).

Response: We agree with the reviewer. The following has been added: "However in the study of Chow et al., (2001) using the DRI instrument and the NIOSH protocol the signals of both reflectance and transmittance returned to their initial values prior to the addition of oxygen for many of the samples during the 850 °C step of the analysis. As a result the slope of TOR to

TOT was equal to one. One explanation could be that using longer residence time (150s in all temperature steps and 160s at Tmax) than in the typical NIOSH protocol (usually 60-120s) can minimize the differences between TOT and TOR.

p9709, in Table 7,

- Is the reference, i.e., Cavalli et al. (2012) publically available?

Response: We have contacted JRC repository department and the report will soon be available online. The updated reference will be included at the time of author proofs.

- Please spell out/ list all the acronym names used (e.g., TLT, and EnvCan) and briefly describe the protocols;

Response: The table footnote includes the description of TLT, TOT and TOR. The protocols are described in other parts of the manuscript (in Table 1: Summary of thermal-optical protocols), so we do not see any need to describe them here. The EnvCan (from Environment Canada) protocol was by mistake included in the table as in this protocol no optical correction was used and the reported results counted in only thermal-optical methods.

- Please provide all the RSD values for EC, OC and TC, if it is any possible (e.g., the cases by Schmid et al 2001; EUSAAR 2008, 2009, 2010, 2011 and the rest of the table). As long as there are OC and EC or EC/TC measurements, the corresponding RSD values should be available.

Response: Unfortunately the different reports include different information, are not always reporting the RSD values, and not always reporting the raw data (so that we could make the calculations as wished). The table was built based on the available information, trying to homogenize as much as possible and making additional calculations not done in the original works when the raw data was provided and sufficient information was available.

- What is the difference in definition between the superscripts “b (random error)” and “c (reproducibility)” for EUSAAR (2011)? It seems that EC, OC and TC have been measured for all samples.

Response: In that report, the reproducibility was calculated as the average percentage deviation (or the slope of the linear regression) between TC determinations from 2 laboratories whereas the random error is the R² of the linear regression between TC determinations from 2 laboratories.

p9711, in Table A1, please add “TLT” and “EnvCan” in the table.

Response: The table has been updated.