



Interactive comment on “Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol” by F. Cavalli et al.

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Interactive comment on “Toward a standardized thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol” by F. Cavalli et al.
Anonymous Referee #1

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General comments The topic of the paper is interesting and the paper aims at defining a new protocol suitable for OC/EC quantification (mainly by networks) at European sites. The main criticisms to the paper are:

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1) even if results/conclusions are often reasonable, they are not always supported by data i.e. very few data are shown although the authors often mention that many samples were collected at different sites (how many in total? Were the samples collected during different seasons? There is no indication in the paper).

As stated in the revised manuscript, our results/conclusions are based on the analyses of 450 samples with various protocols (total run number = 600). We can of course not show 600 thermograms. The ones we chose are examples illustrating best our statements. Further, granting the specific requests of the referee (see below), we have added more examples in the Supplementary Information (SI). The thermal protocol EUSAAR_2 has been developed on the basis of daily samples collected in Ispra (IT) over several years. This site can be impacted by background clean air from the Alps, polluted air from the urban/industrial/farming area of the Po Valley, and intensive domestic wood burning emissions, according to the season and the meteorological conditions. It was validated against samples collected in Birkenes (NO), K-Puszta (HU), and Montseny (ES), i.e. under different pollution and weather climates (Figure A). Feed-backs were provided by people who run the analyses in Birkenes and Montseny, where samples are also collected all the year round. The aim of the present work was to identify the major biases that can affect the determination of OC and EC by thermal-optical analyses and to propose a new protocol, which minimizes these biases. Developing this protocol for a wide European network, it was important to cope with phenomena which can affect a sound determination of OC and EC, from Spain to Finland, and from Crete to Ireland. As very different aerosol constituents can affect the determination of OC and EC (sea salt, desert dust, metal oxides, etc.), we had to go for a protocol which was accepted as the best compromise by our 10 EUSAAR partners from the 4 corners of Europe.

2) Throughout the paper the authors do not mention the possibility of having carbonatic carbon in PM samples. Can the authors exclude CC presence at European background sites? If not, this case should be also investigated before proposing a new protocol for

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Europe.

The contribution of carbonatic carbon (CC) to TC at regional background sites in Europe is generally < 5%, but contributions > 30% can occur. Depending on the chemical nature of the carbonate species – e.g. CaCO₃, CaMg(CO₃)₂, Na₂CO₃ etc.– and on the crystal structure - calcite, aragonite, etc., CC evolves over a broad range of temperatures. Thermal-optical analyses of filters spiked with Na₂CO₃ solution and with CaCO₃ suspension (Fig. B1 and B2) indicate that CC evolves mainly over a range of temperature between 450°C and 650°C. These results are supported by analyses of natural calcite from Spain (grain dimension $\leq 300 \mu\text{m}$) (Fig. B3). Natural calcite evolves in the He-mode with the EUSAAR_2 and the NIOSH protocol, and will be detected as OC, whereas it evolves in the He/O₂-mode with the IMPROVE protocol and will possibly be detected as EC. Neither the NIOSH protocol nor the IMPROVE protocol address definitely this issue of CC. The NIOSH method 5040 recommends fumigation of the aerosol samples with HCl prior to thermal-optical analysis to eliminate any contribution of CC to OC and/or EC signal. However, fumigation with HCl has been shown to cause artificial loss of volatile organic acids (Chow et al., 1993) and to induce intense charring phenomena in ambient aerosol samples (Jankowski et al., 2008). Moreover, the HCl fumigation is time consuming and not applicable to monitoring networks. As alternatives, a method based on a thermal pretreatment of the samples to remove OC and EC (i.e. 460°C for 60 min in an O₂ atmosphere) followed by a total carbon determination (Jankowski et al., 2008), or the direct determination of the amount of CO₂ produced by acidifying the sample, may be envisaged to measure CC. A new paragraph 3.1.4 -Maximum He-mode Temperature and Carbonatic Carbon- has been added in the revised manuscript.

3) the work appears not to be as much systematic as the set-up of a protocol proposed for Europe is expected to be (e.g. no systematic comparison with other protocols widely used also in Europe has been carried out). Nevertheless, this paper could be the starting point for the set up of the "European protocol" but it should be stated more clearly

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in the text (what in the title is "toward" in the text appears as "we got the protocol").

We have developed a new thermal protocol because we observed large differences in the EC measured using the NIOSH-like and IMPROVE protocols, which could be due to: 1) premature light absorbing carbon evolution which occurs if a too high temperature is reached in the He analytical mode and 2) slipping of non-light absorbing carbon into the He/O₂-mode which is enhanced if too low temperature is reached in the He analytical mode. The EUSAAR-2 protocol minimises the frequency and/or amplitude of these phenomena. We completely agree with the referee that the proposed protocol represents the starting point for a potential European standard protocol. We clearly state in the revised manuscript that this protocol (together with others) is currently under evaluation by a dedicated working group of the European Standardisation Committee. The OC and EC results obtained with the 3 most widely used protocols in Europe (NIOSH-like, IMPROVE, EUSAAR) have been extensively compared in the frame of this work and by National Reference Laboratories, and showed expected differences. A systematic comparison between EUSAAR_2 and the protocols used in the past in Europe would make sense only if EUSAAR_2 were adopted as a reference protocol in Europe.

Specific comments Lines 124-126: can the authors explain the 1.7 constant factor?

As shown in Figure C, 1.70 ± 0.01 is the average ratio between reflectance- and transmittance-corrected EC concentrations obtained from two different sampling conditions, i.e. with and without a denuder. The reflectance-corrected EC concentrations are systematically higher than the transmittance-corrected ones. The optical correction by reflectance is known to be sensitive only to the fraction of PC carbon formed on the surface of the filter whereas the optical correction by transmittance accounts also for the PC formed in the inner part of the filter. The PC correction is therefore smaller for the reflectance than for transmittance and consequently the reflectance-corrected EC concentrations are higher than the transmittance-corrected ones.

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Lines 130-131: the authors' hypothesis is that OC particles diffuse inside the filter during sampling or analysis. Can they demonstrate this assumption? Indeed, in standard samplings (especially in background sites where PM concentrations are not so high) the possibility of particles diffusion inside the filter should be quite limited (e.g. about 10-15% as estimated by literature works, e.g. Petzold and Schönlinner, J. Aerosol Science 35, 2004). The diffusion of particles inside the filter during analysis should be proved or referenced too.

Chow et al. (2004) performed visual and microscopic investigations of sample filters at different temperature stages of the thermal analysis. Figure 7 in the Chow et al. paper undoubtedly shows a progressive darkening of the front and back side of the filter and also of inner part as a consequence of charring in the He-mode steps at increasingly higher temperatures. This observation implies the presence of OC throughout the filter that chars as the analysis proceeds. The data shown in Figure C exclude the role of charring from volatile organics absorbed in the filter (as a result of positive sampling artifacts) on the difference between EC_TOR and EC_TOT, since the amount of PC which occurs inside the filter (and not at its surface) is the same for denuded and undenuded samples. The remaining potential sources of OC throughout the fiber filter are therefore i) diffusion of particulate OC into the filter during the sampling (Petzold and Schönlinner, 2004) or ii) diffusion of vaporised OC from the filter surface downward during the analysis as the sample is heated (Chow et al. 2004- this reference has been added in the revised manuscript). Let's assume that OC and EC represent 90% and 10% of TC, respectively and that 10-15% of OC diffuses inside the filter during sampling. Let's further assume that 30% of OC pyrolyses (yearly average of PC fraction from Ispra PM2.5 samples). Neglecting the fraction of PC occurring inside the filter, as TOR does, would already produce an overestimation of 30-40% in the EC determination.

Lines 131-134: the referee agrees, WSOC removal is one of the most efficient way to minimise charring. The authors should compare the results obtained with EUSAAR_2

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protocol with those obtained on the same filters with WSOC removed. It is clear that WSOC removal cannot be proposed in a protocol mainly devoted to networks but it is mandatory to evaluate possible differences before validating a new protocol.

Water extraction of ambient aerosol samples removes both WSOC prone to charring and inorganic catalytic compounds. Thus, the amount of carbon of a water-extracted punch evolving in the He/O₂-mode of a thermal-optical analysis would be much less sensitive to possible biases, and closer to the amount of native EC. Comparing the EC amount observed in the water-extracted and untreated aliquots would allow validating the charring correction by optical transmission in the EUSAAR_2 protocol. As suggested by the referee, five fall samples and six spring samples collected in Ispra were subjected to water extraction; but the extraction procedure, even if gentle, has also affected the EC loading: most water-extracted punches actually appear bleached with respect to the original filter (Fig. D). This prevents from rigorously addressing the referee's requests. However, a comparison of carbon evolution from water extracted aliquots and untreated aliquots of the same filters was performed (Table 1). The removal of WSOC has considerably reduced the charring artefact (Table 1): in the water-extracted punches the PC formation is negligible as the laser transmittance is not attenuated in the He-mode of the analysis. Thus, the carbon evolving in the He/O₂-mode is actually only EC. Comparing the He/O₂-mode carbon evolution from paired water-extracted and the untreated punches one can conclude that PC and EC co-evolve for the analysed samples: in fact, i) the He/O₂-mode carbon remaining after the water extraction (i.e. EC) evolves not just at the end of the He/O₂-mode but throughout the entire mode (Table 1) and, furthermore, ii) He/O₂-mode carbon removed by water extraction (i.e. PC) does not just evolve at the beginning of the He/O₂-mode but throughout the entire mode. This confirms that one of the fundamental assumptions of the thermal-optical methods - considering that PC evolves completely before native EC, i.e. before the OC/EC split point – does not always hold. In particular, i) the fraction of the native EC evolving in the He/O₂-mode before the OC/EC split point in the untreated punch (pre-split point EC in Table 1), was determined as the carbon

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of the extracted punch evolving in He/O₂ before the OC/EC split point defined in the untreated aliquots. For the samples analysed with the EUSAAR_2 protocol (i.e. He-4 at 650°C), 19±12%, on average, of the native EC evolves before the OC/EC split point of the untreated punches. This percentage should be considered as a lower limit since the extraction procedure has partly removed the native EC. Similar experiments were reported by Subramanian et al. (2006). For samples analysed with protocols with He-4 step at 700°C and 870°C (NIOSH-like), 35% and 50%, respectively, of native EC were reported to evolve in the He/O₂-mode before the OC/EC split point of the untreated punches (Subramanian et al., 2006). ii) Further, we have compared the untreated and the water-extracted punch results with respect to the He/O₂ carbon that evolves after the OC/EC split point defined in the untreated sample. For the samples we analysed, the water extraction has removed only 65%, on average, of the He/O₂ carbon after the OC/EC split point of the untreated punches. This percentage should however be considered as an upper limit for the PC evolving after the OC/EC split point in the untreated sample as the extraction procedure has partly removed the native EC and thus has artificially reduced the carbon that evolves after the OC/EC split point in the untreated sample.

Line 141: the authors must specify if they are referring to absorption or extinction/attenuation cross section

We have now specified in the text that we refer to specific attenuation coefficient.

Line 161: why differences in sigma alter EC split point? Please give explanation in the text.

We discuss this question in details in section 3, 3.1.2 and 4 of the manuscript. The light transmission through the filter decreases during the thermal analysis due to the formation of light absorbing carbon (LAC) by pyrolysis. The light transmission through the filter increases again as soon as the rate of LAC evolution is larger than the rate of LAC formation, which generally occurs when shifting to the He/O₂-mode. Assuming

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that EC and PC are the two species responsible for the light attenuation through the filter and that there is no PC at time t = 0, the Lambert-Beer law leads to:

$$\ln(I(t)) - \ln(I(0)) = \sigma_{EC} CEC(t) + \sigma_{PC} CPC(t) - \sigma_{EC} CEC(0);$$

where, for any time t, I(t) and I(0) are the light intensity through the filter at times t and t=0, respectively, and σ and C are the specific attenuation coefficient and the mass per filter area unit, respectively, of EC and PC. The split point t_S is defined as the time when the intensity of the light passing through the filter I(t) is equal to the intensity of the light passing through the filter at the beginning of the analysis I(0), i.e. $\ln(I(t_S)) - \ln(I(0)) = 0$. Therefore:

$$\sigma_{EC} CEC(t_S) + \sigma_{PC} CPC(t_S) = \sigma_{EC} CEC(0).$$

Only if $\sigma_{EC} = \sigma_{PC}$, we can write that the amount of native EC CEC(0) is equal to the amount of LAC (=EC+PC) remaining on the filter at time t_S:

$$CEC(0) = CEC(t_S) + \sigma_{PC} CPC(t_S)$$

As PC and EC generally co-evolve, any deviation from this assumption leads to a bias in the determination of EC, as soon as all PC is not evolved before t = t_S.

Line 173: how many samples? Were they from different sites/seasons or had different composition? Please give details.

The experiments in section 3.1.1 investigate the possibility of minimizing charring formation through the addition of steps at low temperature with a long duration. Figure E shows the contribution of PC to TC (PC has been calculated from the laser transmission and a $\sigma_{PC} = 45 \text{ m}^2/\text{gC}$) for one year of aerosol samples collected in Ispra. PC is more abundant in spring-summer; this is consistent with the fact that it is produced from the pyrolysis of highly oxygenated/oxidised species which are more abundant in spring-summer. Based on this information, the tests were performed on three samples collected in Ispra during spring; PM_{2.5} mass concentrations range from 8 $\mu\text{g m}^{-3}$ to 35 $\mu\text{g m}^{-3}$ and the relative contribution of the major aerosol components is shown in Fig.

C942

F, which shows contrasted PM2.5 chemical compositions.

Line 172/Table 2: How much is the uncertainty on each analysis? The reported values are quite similar when considering, let's say, a 10% uncertainty.

In order to assess the role of low temperature steps and their duration in reducing charring formation, three samples were analysed using the EPA/NIOSH protocol and a modified version of it in which the temperature step at 310°C for 60s has been replaced by two steps at 200°C and 300°C for 180s and 240 s. The experimental uncertainty on each run is 7% at maximum; the OC fractions evolving up to a temperature of 300°C in the modified-NIOSH protocol still remain higher, at 95% confidence level, than those evolving in the EPA/NIOSH protocol. Similarly, the amount of PC formed in the modified-EPA/NIOSH protocol is significantly smaller compared to the EPA-NIOSH protocol at 95% confidence level. The results, in agreement with Yu et al., (2002) and Chow et al. (2004), indicate that low temperature steps with a long duration can reduce charring formation.

Line 191: Again, how many samples? Which type?

In the paragraph 3.1.1, we also investigated the role of the presence of oxygen (2%) at the two steps at low temperature in reducing the charring formation. For this purpose, ten samples collected in Ispra were analysed for each condition, i.e. in presence and absence of oxygen. See also above reply to the referee comment on Line 172/Table2.

Lines 191-198: the authors should take into account that in Cachier et al. (1989) pure oxygen was used while they refer to measurements carried out "in presence of oxygen" or with "oxygen-containing carrier gas": what was the oxygen percentage in the gas used for their tests? It must be specified in the text and it should be demonstrated that the same result is obtained with 100% oxygen or different oxygen percentages. The referee suggests discussing this point further, showing data and giving explanations for different results.

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The EUSAAR_2 protocol was developed to minimize possible drawbacks associated with the use of existing protocols with existing instruments available at European air monitoring network stations. The tens of thermal-optical carbon analyzers available in Europe use a He/O₂-mixture 98:2 as an oxidative carrier gas. We have therefore chosen this helium–oxygen mixture as a carrier gas in the first two analytical temperature steps to assess the effect of the presence of O₂ on PC formation during these steps, as specified in the revised manuscript. The flow rate of O₂ (>100 $\mu\text{mol s}^{-1}$) is thus already much larger than the formation rate of PC (< 1 nmol s⁻¹). The instrument design does not allow for an oxygen mixing ratio larger than 10% in the oxidative mode. We cannot reach 100%, and have therefore removed the sentence referring to Cachier et al. (1989).

Line 202: was it a sample collected in summer or winter?

As specified in the revised manuscript, the sample was collected at Ispra (IT) in May.

Line 206: how many samples in total were investigated? Should the authors show at least one for comparison (possibly with different composition)

In the framework of the EMEP programme for monitoring evaluation of long-range transmissions of air pollutants in Europe, PM2.5 samples are collected daily and weekly at Ispra (IT) and at Birkenes (NO), respectively and analyzed for TC, OC and EC and for the major water soluble inorganic ions. In Montseny (ES), PM2.5 samples are collected two days per week and analysed for their TC, OC and EC content. As from 2008, the EUSAAR_2 protocol is applied. In K-Puszta (HU), eight PM2.5 samples were analysed for OC and EC for purposes of the present work. Premature evolution of LAC species was often observed when using a NIOSH-type thermal protocol (He-4 at 870°C) and even at a lower temperature of about 700°C. Following the referee request we have added in the supplementary information three additional thermograms showing important early combustion of LAC from samples of different composition (EC/TC = (1) 0.16, (b) 0.10, (c) 0.12).

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Line 209: as concerns inorganic oxides, have the authors measured the sample composition? Were there differences between samples? What was the average composition at different sites?

In addition to the carbon content, the samples were analyzed for inorganic water-soluble ions, but no information is available about their mineral oxides content. The potential role of oxygen-containing minerals in the premature loss of LAC in the He-mode is well-documented in literature as from Fung, 1990. We have added references to this phenomenon in the revised manuscript. Investigating the role of chemical composition on the observed biases goes beyond the scope of this work and it might form the topic of a future work. However, to address the referee request, Figure A illustrates the contrasted annual average aerosol composition at different sites, i.e. Birkenes (NO), K-Puzsta (HU), Montseny (ES) and Ispra (IT). Variations in daily chemical compositions are of course even larger. Note that EC is currently not routinely measured in K-Puzsta.

Line 216: the authors must specify if they are referring to absorption or extinction/attenuation cross section because in the latter case it depends on the average composition of the sample.

As specified in the revised manuscript, the authors refer to the attenuation cross section of EC and PC. In literature, a range of values for σ PC and σ PC is indeed reported, depending on various factors including composition and aging of the sample, wavelength, extraction/thermal methods and filter substrate.

Lines 229-240: how many LAC samples were generated and analysed? On how many analyses were the standard deviations calculated? A major concern on these analyses is that using LAC-only samples the authors cannot observe possible effects due to the presence of other compounds (i.e. inorganic oxides) that have an important role as they stated previously in the text.

12 samples per temperature set point, i.e. 650°C, 750°C and 850°C were generated

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and analyzed, and used for computing averages and standard deviations. The LAC-only samples were generated by a thermal treatment (600°C for 60s and 800 °C for 300s in Helium) of ambient aerosol samples. We agree that the thermal treatment has potentially impoverished the filter of mineral oxides. Nevertheless, early loss of LAC in the He-mode was still observable while analysing LAC-only samples (See Fig. 2 in the revised Supplementary Information). Quantifications of the premature evolution of LAC in the He-mode given in the text at various temperatures represent, therefore, lower limits for this phenomenon.

Lines 254-255: the authors should better specify what is this derivative. If it is the time derivative (as time is the variable on the x-axis) the indication is on the rate of formation/release and the peak integration is needed to have the overall quantity formed/released. Otherwise, the independent variable must be specified. The referee supposes that this derivative is the green line called absC in the graph: please write in the caption or in the text what absC*100 (ksigma=45) stands for (remind that not all the Sunset users have the same version of the instrument/software).

The authors discuss the time derivative of the laser signal as time is the variable on the x axis. The overall amount of PC formed/released can be obtained integrating peaks and dividing by appropriate σ . These operations are not done automatically by the instrument software of the Sunset OCEC analyzer but they represent a further elaboration of the traditional output of the Sunset software (T. Bond, personal communication, 2007). A detailed description of the calculation is given by Boparai et al. 2007. We have added this reference to the manuscript and explained in the Figure caption what absC*100 (ksigma=45) stands for.

Lines 268-269: the mentioned 91% was calculated in the He-mode? Probably yes, but please specify for more clarity.

For more clarity we have specified in the revised manuscript that the percentages of OC evolved and/or pyrolysed were calculated in the He-mode.

C946

Line 276/Figure 2d: how the authors explain the large difference between the peaks in green and blue? Could they ascribe this result to differences in σ value?

In the manuscript, we have not discussed the consistency between the FID carbon peak (in blue) and the carbon peak calculated using the laser attenuation and σ 45 m²/gC (in green) during the analysis of pure organic compounds-spiked filters. In case of fulvic acid, the difference between the two signals can be ascribed to differences in the σ value and/or to the presence of a fraction of little volatile non-absorbing OC that still evolves in the He/O₂-mode of the analysis.

Line 277: What exactly the authors mean with the sentence "it is impossible"? Have the authors tried to extend the "residence" time at higher T steps?

We describe an experiment where pure organic compound-spiked filters were analysed. In case of premature evolution of LAC (note that, in this particular case, LAC corresponds to PC) in the He-mode the following events occur simultaneously: i) OC evolves contributing to the FID signal; ii) PC is formed affecting the laser transmittance; but iii) PC also evolves contributing to both FID signal and laser transmittance changes. The available instrumental outputs are the FID signal and laser transmittance: two equations and 3 unknown variables. It is, therefore, mathematically not possible to resolve the system. In particular, it is not possible to discriminate between OC and PC from the FID signal and thus to demonstrate that extending the residence time at high temperature step or increasing the temperature would significantly improve the OC fraction evolved in the He-mode.

Lines 278-282: how many samples were analysed in both cases? What about effects due to differences in composition? Why the "laser derivative approach" this time was not adopted?

In section 3.1.3, we investigate the influence of the highest He maximum temperature on the complete evolution and/or pyrolysis of OC during the He-mode of the analysis. Three replicates were performed for organic compound-spiked filters and thirty am-

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bient aerosol samples were analysed. Independently from ambient aerosol samples origin and chemical composition, 90% of OC evolves and/or chars as the analysis has completed the 650 °C step. At higher temperatures, the premature evolution of LAC can occur. The laser signal derivative approach has been used until it was possible. It served to calculate the amount of PC formed in the He-mode in absence of a premature loss of LAC. In presence of early loss of LAC in the He-mode, at high temperature, i.e. $\geq 750^\circ\text{C}$, the following phenomena occur simultaneously: i) OC evolves contributing to the FID signal, ii) PC and EC co-evolve contributing to both FID signal and laser transmittance. Again FID and laser signals are, therefore, not sufficient to resolve this system with too many unknowns.

Lines 306-308: the conclusion is reasonable but it should be supported by results obtained with tests at different times (please show examples). The range of filter loadings is quite large (about a factor 10): how did the composition change in the analysed filters?

The question is about the influence of the aerosol load and chemical composition on the duration of the temperature plateau. In the EUSAAR_2 protocol, the temperature plateau durations were selected such that the various carbon peaks are separated and further the total analysis time is suitable for routine monitoring applications. In practice, analyses of aerosol filters collected at the four sites with distinct particulate matter compositions (see Fig. A) and with filter loadings ranging from 5 to 62 $\mu\text{gC cm}^{-2}$ were initially performed using a protocol where the EUSAAR_2 temperature steps were prolonged such that the next temperature set-point was not initiated until the slope of the FID response reaches zero. Then, the duration of the temperature steps were shortened to the current final version such that the various carbon peaks were resolved for a vast majority (higher than 80%) of the samples. The authors think that examples for such tests would not be very useful and instructive. An example of the influence of temperature steps duration on the definition of the carbon peaks is already shown in Figures 1 a and b of the manuscript. The two extreme cases with respect to

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the duration of steps, i.e. NIOSH and IMPROVE, are shown: in case of NIOSH peaks are undefined whereas in case of IMPROVE peaks are well defined, but the time at which they evolve is sample-dependent.

Lines 312-317: again, the authors claim for "several" studies but they show only one case. Please show results. How much "frequent" was the occurrence of a split point at maximum carbon peak? How much was it dependent by the aerosol composition or loading?

The first version of the thermo-optical protocol, EUSAAR_1, had only two temperature steps in the He/O₂-mode, at 550°C and 850°C. The protocol has been tested for one year (2007) by nine EUSAAR partners analyzing their local ambient aerosol samples. The partners indicate the occasional occurrence of a split point at maximum carbon peak, independently of aerosol composition and carbon loading. For example, this event was observed in samples collected at Birkenes (NO) and at Ispra (IT) where the annual average concentrations of TC are $1.74 \pm 1.66 \mu\text{g}/\text{m}^3$ and $9.62 \pm 7.98 \mu\text{g}/\text{m}^3$, respectively (Yttri et al., 2007). Thus any aerosol composition and carbon loading contribute to the occurrence of this event. The authors believe that the possible occurrence of this event matters, whatever its frequency could be. It was possible to minimize it simply by adding two steps at 500°C and 750°C in the He/O₂-mode in the EUSAAR_2 protocol.

Lines 320-324: on how many samples were these uncertainties calculated?

In paragraph 3.3 we investigate the role of multiple desorption steps in the He/O₂-mode on the occurrence of a split point at the maximum of a high carbon peak. Eighteen samples analysed using both the EUSAAR_1 (two steps in the He/O₂-mode) and EUSAAR_2 (four steps in the He/O₂-mode) protocol were used to calculate the uncertainties in the EC concentrations.

Lines 377-380: to serve as a tool to understand differences in carbon data reported in the literature a systematic comparison between EC/OC results obtained running

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EUSAAR_2 and other protocols on parallel samples is needed (and it is not present in this work). Moreover, before using this protocol in networks the uncertainties of EC/OC determination on punches from the same filters running the same protocol on different TOT instruments (i.e. in different laboratories) should be carefully evaluated (see for example results given in Schauer et al. 2003).

As already stated in our replies to the general comment (3), OC/EC results obtained running EUSAAR_2 and other protocols have been compared in the frame of 2 intercomparisons among 13-14 EUSAAR partners, and also in the frame of another independent intercomparison exercise among 11 European National Reference laboratories and 5 other institutes, also based on urban aerosol samples. The various protocols lead to different results for OC, and above all for EC, as expected. Differences are systematic when samples of the same kind are compared (e.g. all urban background samples, all collected in September 2009), but not when regional background samples are compared, due the larger variability in aerosol sources at regional background sites. These results are not published yet. We believe it is not useful to go for a more systematic comparison between EUSAAR_2 and the protocols currently used in Europe before the choice for the European standard method for OC/EC measurements is made. However, an action is currently going on to compare EUSAAR_2 with the IMPROVE-A and ENV-Canada protocols, as suggested by the Global Atmosphere Watch Scientific Advisory Group for Aerosols. There is no reason why the uncertainties of EC/OC determination on punches from the same filters running EUSAAR_2 on different TOT instruments should be larger than using other protocols. On the contrary, we believe that EUSAAR_2 is a more robust protocol, i.e. it should lead to smaller uncertainties, because it minimizes biases that can affect a sound determination of OC and EC using other protocols. Again, this aspect will be addressed through specific and independent test performed by the CEN working group 35 on OC and EC in PM.

References

C950

K. E. Yttri, W. Aas, A. Bjerke, J. N. Cape, F. Cavalli, D. Ceburnis, C. Dye, L. Emblico, M. C. Facchini, C. Forster, J. E. Hanssen, H. C. Hansson, S. G. Jennings, W. Maenhaut, J. P. Putaud, and K. Tørseth. Elemental and organic carbon in PM10: a one year measurement campaign within the European Monitoring and Evaluation Programme EMEP. *Atmos. Chem. Phys.*, 7, 5711–5725, 2007.

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

P. Boparai, J. Lee, and T.C. Bond: Revisiting Thermal-Optical Analyses of Carbonaceous Aerosol Using a Physical Model. *Aerosol Science and Technology*, 42:930–948, 2008.

Interactive comment on *Atmos. Meas. Tech. Discuss.*, 2, 2321, 2009.

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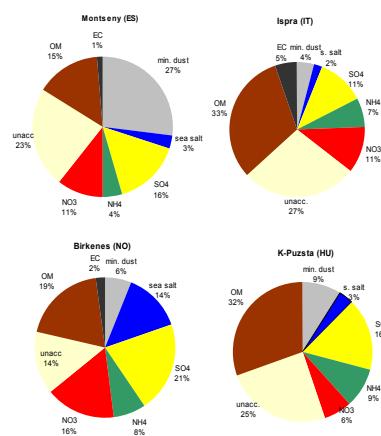


Fig. 1. Figure A

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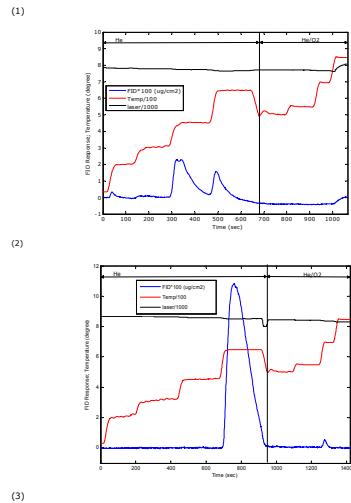


Fig. 2. Figure B: Thermograms from the analysis of a Na₂CO₃ (1), CaCO₃ (2) and natural calcite (3) (1.7 μ g CC) with the protocol EUSAAR-2.

C953

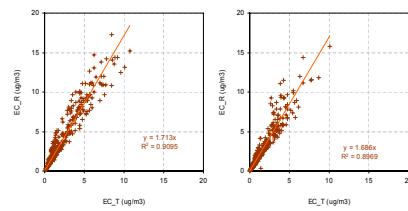


Fig. 3. Figure C

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Fig. 4. Figure D

C955

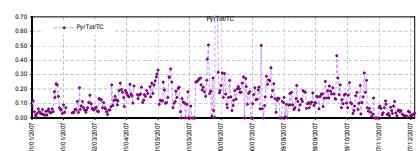


Fig. 5. Figure E

C956

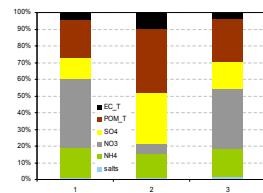


Fig. 6. Figure F

C957

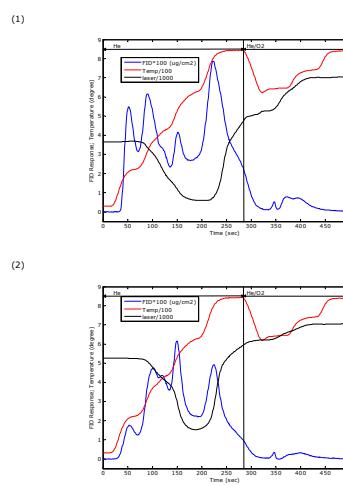


Fig. 7. Figure G: NIOSH-5040 thermogram from PM2.5 collected in (1) K-Puszta, (2) Birkenes and (3) Montseny.

C958

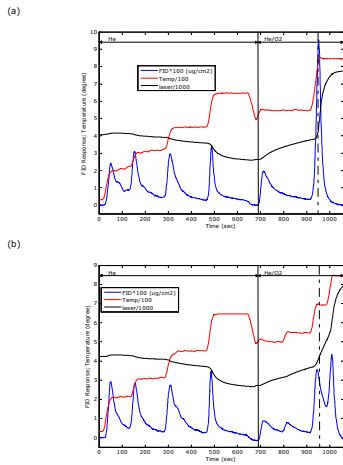


Fig. 8. Figure H1: PM2.5 sample collected on 220308 analysed by EUSAAR_1 (a) and EU-SAAR_2 protocol (b).

C959

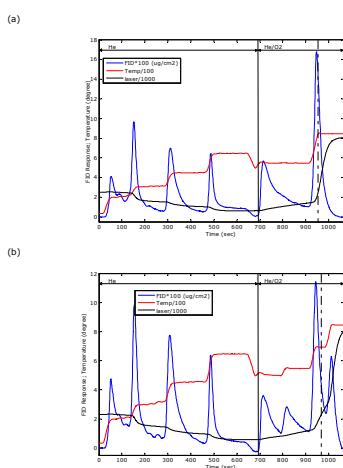


Fig. 9. Figure H2: PM2.5 sample collected on 011008 analysed by EUSAAR_1 (a) and EU-SAAR_2 protocol (b).

C960

Sample name	OC1*	OC2*	OC3*	OC4*	EC1*	EC2*	EC3*	EC4*	PvBC*	Pre-split EC %
030509 untreat.	1.33	1.59	1.59	1.32	0.47	0.70	1.53	0.69	2.16	20
030509 extract.	0.26	0.32	0.50	0.46	d.l.	0.07	0.32	0.14	d.l.	
110509 untreat.	1.19	1.23	1.14	1.18	0.35	0.53	1.32	0.59	1.76	17
110509 extract.	0.22	0.26	0.37	0.32	d.l.	0.05	0.21	0.09	d.l.	
160509 untreat.	0.87	1.40	1.20	1.14	0.31	0.48	1.40	0.71	1.79	19
160509 extract.	0.25	0.32	0.46	0.45	d.l.	0.05	0.26	0.10	d.l.	
210509 untreat.	1.73	2.51	2.09	1.72	0.63	0.75	1.95	0.62	2.46	24
210509 extract.	0.30	0.50	0.87	0.75	d.l.	0.13	0.40	0.11	d.l.	
230509 untreat.	2.63	2.5	2.29	2.02	0.81	1.27	4.29	2.14	5.06	18
230509 extract.	0.36	0.41	0.67	0.71	d.l.	0.18	0.82	0.21	d.l.	
300509 untreat.	1.36	1.38	1.82	1.37	0.57	0.75	0.92	0.31	1.35	9
300509 extract.	0.37	0.41	0.57	0.55	d.l.	0.10	0.40	0.12	d.l.	
031009 untreat.	1.24	1.53	1.97	2.50	0.33	0.80	1.2	0.36	0.54	5
031009 extract.	0.29	0.54	0.98	1.00	0.05	0.26	0.64	0.19	d.l.	
201009 untreat.	3.08	3.99	5.14	6.96	1.58	2.69	3.42	1.64	4.83	16
201009 extract.	0.54	1.56	2.64	2.98	0.26	0.88	2.33	1.00	0.79	
251009 untreat.	2.05	3.14	3.47	4.94	0.67	1.41	2.19	0.89	1.24	5
251009 extract.	0.40	0.69	1.23	1.89	0.14	0.48	1.20	0.38	0.15	
291009 untreat.	3.71	4.70	4.82	7.41	1.35	2.70	4.21	1.21	4.01	28
291009 extract.	0.67	1.38	2.07	3.24	0.39	1.16	2.97	0.59	0.02	

* in $\mu\text{gC cm}^{-2}$

Fig. 10. Table 1

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