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Discussions

Clues for a standardised thermal-optical protocol for the assessment of organic and elemental carbon within ambient air particulate matter

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Abstract

Along with some research networking programs, the European Directive 2008/50/CE requires chemical speciation of fine aerosol ($PM_{2.5}$), including elemental (EC) and organic carbon (OC), at a few rural sites in European countries. Meanwhile, the thermal-optical technique is considered by the European and US networking agencies and normalization bodies as a reference method to quantify EC–OC collected on filters. Although commonly used for many years, this technique is still suffering from a lack of information on the comparability of the different analytical protocols (temperature protocols, type of optical correction) currently applied in the laboratories. To better evaluate the EC–OC data set quality and related uncertainties, the French National Reference Laboratory for Ambient Air Quality Monitoring (LCSQA) has organized an EC–OC comparison exercise for French laboratories using different thermal-optical methods. While there is good agreement on total carbon (TC) measurements among all participants, some discrepancies can be observed on the EC / TC ratio, even among laboratories using the same thermal protocol. These results led to further tests on the influence of the optical correction: results obtained from different European Laboratories, confirming that there are higher differences between OC_{TOT} and OC_{TOR} measured with NIOSH 5040 in comparison to EUSAAR-2. Also, striking differences between EC_{TOT} / EC_{TOR} ratios can be observed when comparing rural and urban results whatever the thermal protocol EC_{TOT} being 50 % lower than EC_{TOR} at rural sites whereas it is only 20 % lower at urban sites. The PM chemical composition could explain these differences but the way it influences the EC–OC measurement is not clear and needs further investigations. Meanwhile, some additional tests seem to indicate an influence of the oven soiling on the EC–OC measurement data quality. This enlightens the necessity to follow the laser signal decrease with time and its impact on measurements. Nevertheless, this should be confirmed by further experiments, involving more samples and various instruments, to enable statistical processing. All these results provide insights

to determine the quality of EC–OC analytical methods and may contribute to the work toward establishing method standardisation.

1 Introduction

The European Directive 2008/50/EC on ambient air quality and cleaner air for Europe requires measurements of elemental carbon (EC) and organic carbon (OC) in fine aerosols ($PM_{2.5}$, i.e. particles having aerodynamic diameter below 2.5 µm) at rural background sites. This is in line with several recommendations arising from the scientific community stressing the need to monitor these components in Europe (e.g. Kahnert et al., 2004). However, there is still no universal standard procedure to quantify these carbonaceous fractions in PM and important discrepancies have been observed worldwide between different instruments and analytical protocols. These differences can bring large uncertainties when comparing datasets, estimating combustion sources or modelling the impact of carbonaceous aerosol on climate (Vignati et al., 2010).

In this context, the European Committee for Standardisation is currently working on a common standardised methodology (CEN/TC 264 TR 16243). As recommended by the scientific community and implemented in the United States, this methodology will be based on thermal-optical techniques. Based on the differentiation between EC and OC according to their thermal and optical properties, such methods primarily consist of two progressive heating steps and one internal calibration. The desorption of carbonaceous matter from the filter sample begins under an inert gas (He) and continues in a second step under an oxidising atmosphere (He/O_2). The carbon volatilised from the filter is catalytically oxidised into CO_2 which can be measured directly with a non-dispersive infrared detector (Chow et al., 1993) or indirectly by a flame ionization detector (FID) after quantitative reduction to CH_4 (Birch and Cary, 1996). Ideally, the whole OC content should be desorbed during the first step while EC should be burned off under the oxidizing atmosphere at the higher temperature. This is, however, not the case as a fraction of the OC is pyrolytically converted to EC (Hutzincker et al., 1982). This OC fraction usually referred to as pyrolysed organic carbon (POC) evolves off the filter under the oxidative atmosphere, concomitantly to the genuine EC, resulting in a bias when discriminating EC and OC. To overcome this artefact, a continuous monitoring of the filter transmittance (TOT) and/or reflectance (TOR) is highly recommended (Dod et al., 1978; Johnson and Huntzicker, 1979).

Three different thermal protocols are nowadays commonly used: the IMPROVE (Interagency Monitoring of Protected Visual Environments) and NIOSH 5040 (US National Institute for Occupational Safety and Health) protocols have been implemented within networking activities in the US and worldwide since the 1990s, while the EUSAAR-2 protocol has been optimized more recently in the framework of the European project EUSAAR (European Supersites for Atmospheric Aerosol Research, (Cavalli et al., 2010). These protocols (Table 1), developed mainly for background sites (IMPROVE and EUSAAR-2) and urban sites (NIOSH), differ in their highest temperature set points in an inert atmosphere, higher for NIOSH 5040 (up to 850 °C under the He atmosphere step) than for IMPROVE and EUSAAR-2 (up to about 580 and 650 °C, respectively), in the durations of the temperature step, longer for IMROVE and EUSAAR-2, and in the optical correction type: reflectance for IMPROVE, transmittance for NIOSH and EUSAAR-2. Differences up to a factor of two have been observed by Chow et al. (2001) when comparing the IMPROVE and NIOSH protocols. Chow et al. (2004) demonstrated that EC measured with TOT correction is 30 % lower than EC measured with TOR correction when employing the same thermal protocol, whereas it is 70 to 80 % lower when comparing a low temperature protocol (IMPROVE) and a high temperature protocol (NIOSH). Schauer et al. (2003) also evidenced that the EC–OC split is highly sensitive to the temperature program used.

Moreover, the optical correction for charring is not the only source of discrepancies: the temperature and residence time at each thermogram plateau, as well as the catalysts used, are among the many parameters that can influence EC–OC measurements (Schauer et al., 2003; Schmid et al., 2001; Chow et al., 2004).

As strongly recommended by the European Commission and to better understand the quality of EC–OC data provided by thermal-optical analyses, the French Reference Laboratory for Ambient Air Quality Monitoring (LCSQA) organized an EC–OC comparison exercise in 2010 for the 5 laboratories using thermal-optical methods for EC–OC measurement in France at that time. To investigate the discrepancies observed between these laboratories, further comparisons were performed on results obtained from the analysis of samples from different European sites with the optical reflectance (TOR) and transmittance (TOT) charring corrections. The influence of the EC filter loading and the laser signal on the EC–OC split were also addressed.

2 Interlaboratory exercise organisation

2.1 Methodology

2.1.1 Participating laboratories and instruments used

All five French laboratories performing routine off-line EC–OC thermal-optical analyses, participated in the intercomparison exercise which was conducted in spring 2010 on PM_{10} ambient air filters that were collected in October 2009. A code number was assigned to each laboratory to preserve anonymity. Since the aim of this exercise was to evaluate the uncertainties related to EC–OC measurements in the present state of the art (i.e. no unique standard protocol is available), each laboratory was asked to analyze the samples (test materials) with its routine procedure. Table 1 lists the different methodologies and instruments used by the participants. Three different thermal protocols were employed: EUSAAR-2, NIOSH 5040 and IMPROVE. For the sake of clarity, a color was assigned to each protocol: 4th column for EUSAAR-2, 2nd column for NIOSH 5040 and 3rd column for IMPROVE.

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2.1.2 Test materials

Real ambient air PM_{10} samples collected on pre-baked (at 500 °C during 2 h) Whatman QM-A quartz fiber filters of 150 mm diameter were chosen as test material. The samples were collected with high-volume samplers (DA80, Digitel) during 24 h with an operating flow rate of $30\,m^3\,h^{-1}$ at two urban sites within the CARA program (PM chemical characterization (Chiappini et al., 2010; Colette et al., 2010). Three filter samples displaying different PM_{10} concentration levels denoted N1, N2 and N3 and corresponding to 19, 68 and 32 $\mu g\,cm^{-2}$ of total carbon (TC) respectively (10, 45 and 70 $\mu g\,m^{-3}$), as measured by INERIS with the EUSAAR2 method, were chosen from the sets available. Each laboratory received three 1.5 cm^2 punches of each filter and three punches from a blank filter also pre-baked (i.e. total of 12 punches per laboratory).

Prior to the comparison exercise, the homogeneity of the sample deposits collected with the DA80 sampler was checked at INERIS by comparing TC, EC and OC concentrations on central and surrounding punches. A total number of 18 punches were taken from each of three sampled filters, denoted N'1, N'2, N'3, chosen so that they were similar to the test samples N1, N2 and N3 (same sampler, same sampling site, same period, same PM_{10} concentration levels). The overall relative standard deviation (RSD) was below 5 % for TC and ranged between 2 and 6 % for OC and between 3 and 4 % for EC. The higher RSD obtained for N'1 could be explained by its lowest PM_{10} filter loading. All results concerning homogeneity tests are given in Table 2. The calculated RSD will be taken into account to interpret the results obtained for each laboratory.

The filters were stored in a freezer before sample punching. The punches were sent to the participants in closed Petri slides under refrigerated conditions (below 4 °C). The planning of this interlaboratory comparison exercise is given in the Supplement.

2.1.3 Statistical results processing

Within the process of interlaboratory exercises, *Z* scores are usually calculated to evaluate the capability of a laboratory to comply with the data quality objective (DQO) of the measurements, as reported in the International Standard (ISO 5725-2, 1994). However, the number of participants in this particular exercise was not sufficient to implement such a procedure. To deal with the results provided by the five laboratories, only repeatability standard deviation (S_{rj}) for a laboratory j, the interlaboratory standard deviation (S_{Lj}) for a laboratory j the reproducibility standard deviation for the laboratory j, summing both S_{rj} and S_{Lj} and the overall uncertainty (corresponding to twice the reproducibility) were calculated. The formulae used for these calculations are provided in the Supplement.

Throughout the manuscript, the thermal-optical method is referred to "EC–OC" and the ratio between EC and TC is written as EC / TC. The latter parameter is used to investigate discrepancies related to various optical corrections.

2.2 Results

2.2.1 TC, EC, OC and EC / TC individual results

Figure 1 shows the statistical distribution (general Mean and standard deviation SD) for the TC and EC / TC datasets obtained by the five laboratories while Table 3 gives the mean concentration, the standard deviation, the repeatability relative standard deviation calculated for OC, EC, TC, and EC / TC for each laboratory and each filter test material. For laboratory 3, results are given for both reflectance and transmittance within Table 3.

For sample N1, laboratories 1 and 5 obtained a satisfactory repeatability for TC of about 1 %, whereas for the other laboratories the repeatability of the TC measurement was between 5 and 7 %, which remains very satisfactory considering the low TC loading ($\sim 19\,\mu g\,cm^{-2}$) and possible related sample inhomogeneity. As to the EC / TC, laboratory 1 found substantially higher values but a lower dispersion compared to laboratories 2, 3, and 4, whereas laboratory 5 was in between, suggesting that the differences cannot be clearly attributed neither to the analyzer nor to the thermal-optical protocol.

For sample N2, the TC and OC measurement repeatability values remain low (< 10 %), but the repeatability of the EC and EC / TC data reaches values as high as 17 %. This dispersion may be related to the high EC filter loading ($\sim 18.6\,\mu g\,cm^{-2}$), as will be discussed below in section 5. For this specific sample N2, laboratory 2, which applies a high temperature protocol and short durations of the temperature plateaus (NIOSH), obtained the lowest EC value of all laboratories. This is similar to results from Chow et al. (2004) who have analyzed the same samples with NIOSH 5040 and IMPROVE protocols, the latter one using longest temperature plateaus.

Considering sample N3, the results are similar to those for sample N1 in terms of repeatability and reproducibility.

For all filters, laboratory 3 obtained slightly higher TC values compared to the other laboratories (about 8 % on average), which could be due to an erroneous concentration of the standard solution used for external calibration or erroneous volumes injected for this calibration.

2.2.2 Correlation between laboratory results (for EC and OC)

Figure 2 shows the results of a one-way ANOVA test aiming at comparing laboratories by pair in order to determine if some are statistically different from the others. Two figures are provided. One corresponds to the results of laboratory 3 given in transmittance while the other is for results given in reflectance. When all the results are given in transmittance, no laboratory distinguishes itself from the others. However, when the reflectance results are used for laboratory 3, much higher EC and lower OC concentrations are obtained compared to the other laboratories. Such discrepancies between optical corrections have already been observed within previous studies (Chen et al., 2004; Cheng et al., 2011; Chow et al., 2001, 2004; Schauer et al., 2003; Schmid et al., 2001). The different optical configurations of the DRI and Sunset instruments used here could be partly responsible for these discrepancies. Indeed, illumination of the sample filter or detection of scattered light from different angles may alter measurements (Chen et al., 2004). More insights into TOT and TOR differences will be given in Sect. 3 of the present manuscript. Since laboratory 3 provided both TOT and TOR results, EC and OC concentrations obtained using TOT charring correction will be considered in the following discussion for comparison with the other four laboratories.

2.2.3 Overall reproducibility and repeatability

Table 4 presents the overall results obtained for each filter (N1, N2 and N3), comprising the mean concentration of all laboratories (µg cm^{-2}), the standard deviation (µg cm^{-2}), the interlaboratory reproducibility (corresponding to the ratio between the standard deviation for all laboratories and the general arithmetic mean for all laboratories) and the intralaboratory repeatability % (corresponding to the mean of each laboratory repeatability), and the overall uncertainty corresponding to twice the interlaboratory reproducibility % as stated in the NF EN ISO/CEI 17025 standard for TC, EC, OC and EC / TC. Despite the instrument and protocol heterogeneity, the reproducibility and repeatability for TC analysis are respectively below 7 and 4 %, which is similar to what has been commonly reported in the literature (Schmid et al., 2001; Park et al., 2005; ten Brink et al., 2004). The highest values of reproducibility and repeatability were obtained for filter N1 and may be explained by its lowest TC filter loading (19.3 µg cm^{-2}). The repeatability and reproducibility values are higher for EC (from 6.8 to 19.7 % and from 2.2 to 8.7 %, respectively) and OC (from 4.1 to 9.6 % and from 1.5 to 5.2 %, respectively) and consequently for the EC / TC ratio too. The least satisfactory results regarding reproducibility and repeatability standard deviations are obtained for EC in sample N2. This could be related to the high EC filter loading (~ 19 µg cm^{-2}), as discussed further on.

Finally, for a given thermal protocol, the discrepancies observed between the laboratories have to be primarily attributed to the lack of temperature offset calibration by the time of the analyses, as a deviation of the front oven temperature may lead to a shift of EC / TC. Indeed, temperatures higher than expected during the inert phase may lead to premature EC degradation, while temperatures lowest than expected during the same phase may reduce the efficiency of OC volatilization. In this respect, Sunset Inc.

nowadays proposes a toolkit dedicated to the correction of the lack of fit of the front oven temperature probe, which was not available when the intercomparison presented above was conducted. This toolkit was distributed in July 2012 to some European laboratories, including the ones that used the EUSAAR2 protocol within the present intercomparison exercise. These three laboratories could then investigate the temperature offsets for their instrument. As presented in Table 5, the more important this temperature offset for the last step under He, the higher the EC / TC that was obtained. This might be explained by a lack of volatilization of the most refractory OC species under the He phase when the temperature of the front oven is significantly lower than expected. However, in the particular case of filter N2 (exhibiting the highest EC and OC loadings), laboratory 5 obtained a lower EC / TC than laboratory 4, while the latter one presented a less pronounced temperature offset. It appears thus that another parameter may contribute to the discrepancies observed for EC / TC. This additional parameter might be the apparent laser signal intensity, which also seems to correlate with EC / TC in particular for filter N2 (Table 5).

2.2.4 Conclusions on the inter-laboratory comparison exercise

Several conclusions can be drawn from this first French interlaboratory comparison study:

- Whatever the analytical protocol (NIOSH 5040, IMPROVE, or EUSAAR2), the repeatability for each laboratory is satisfactory, with a corresponding standard deviation for TC, OC, and EC being mostly below 10 % for the three test filters.
- As previously reported in the literature (Chen et al., 2004, 2011; 2011; Chow et al., 2001, 2004; Schauer et al., 2003; Schmid et al., 2001), the differences between results obtained with a charring correction based on transmittance or reflectance for the same thermal protocol (the IMPROVE protocol in our case) is significant, OC_{TOT} being about 30 % higher than OC_{TOR} and EC_{TOT} being about 50 % lower than EC_{TOR}.

- When considering TOT results only, the overall uncertainty of the mean TC, OC and EC concentrations among the 5 laboratories ranges from 6 to 39 %, with the mean uncertainties being 10, 16 and 29 %, respectively.
- The carbon filter loading seems to have an impact on the data quality: higher loadings lead to poorer results for the reproducibility of the EC measurement among the laboratories. Also a low TC loading may lead to less satisfactory repeatability results. It is worth mentioning that for this inter-laboratory comparison, the oven temperature probes were not calibrated. Since then, a calibration procedure has been implemented and another comparison should be organized. To go deeper into the issues of charring correction (TOT or TOR), an additional study based on the comparison of reflectance and the transmittance results for OC and EC measured on about 700 filters sampled at rural, urban, and suburban sites, in France, Belgium, and Italy was performed and is presented below.

3 Charring optical correction: reflectance and transmittance comparison for filter samples from different types of sites

3.1 Methodology

To systematically study the differences in EC and OC measurements as a function of the optical technique implemented to correct for charring, three batches of filter samples were considered. The first one was provided by the CARA program, and therefore sampled in the same conditions as described previously for the test filters of the French interlaboratory comparison study. The 245 PM_{10} filters studied here were sampled in 2008 and 2009 in urban sites in northern France and analyzed with the EUSAAR-2 protocol.

The second one was provided by the Flemish Environmental Agency (VMM) and analyzed by the Ghent University (UGent) with the NIOSH 5040 protocol. PM_{10} and $PM_{2.5}$ were simultaneously sampled on 47-mm diameter Pallflex Tissuquartz 2500 QAT-UP (pre-fired in the factory) at a urban background site with extensive traffic influence and at a rural background site, for 24 h with a low-volume sampler (Leckel SEQ47/50) running at 2.3 $m^3 h^{-1}$ flow rate. A total of 128 filters are considered in this study.

The third batch of filter samples was obtained by the EC-JRC-IES-Climate Change Unit and consisted of $PM_{2.5}$ samples taken in 2007 at the Ispra EMEP station (IT04). The samplings lasted 24 h and were performed with low volume samplers at 1 m63 h^{-1} on 47-mm diameter Pallflex 2500 QAT-UP. A total of 329 filters were taken and analyzed with the EUSAAR-2 protocol.

The EC–OC analytical results were provided by each laboratory with both transmittance and reflectance optical correction of charring.

3.2 Results

3.2.1 Comparison of OC measured with transmittance (OC_{TOT}) and reflectance (OC_{TOR})

Whatever the temperature protocol or the site, the correlation between the TOR and TOT data was good with squared correlation coefficients (R^2) ranging from 0.904 to 0.997. However, as shown in Fig. 3, the transmittance optical correction led to higher OC values than TOR. Chow et al. (2004) have explained this pattern by the charring occurring within the filter and not only at the surface. Since transmittance correction is influenced by char present within the filter and light reflected may be absorbed or scattered by particulate matter at the filter surface, higher OC data may be expected with the TOT correction.

Compared to EUSAAR-2, the NIOSH protocol showed a larger difference between TOT and TOR. The main differences between the two protocols lie in the highest temperature step during the He mode and the shortest durations of the temperature plateaus for NIOSH 5040 (see Table 1). These two points appear to be key parameters that define the split point between EC and OC (Subramanian et al., 2006; Cavalli et al., 2010). In particular, when the last temperature step in He mode is too low, OC is not likely to evolve completely, resulting in OC underestimation. However, for filters containing metal oxides and/or sea salts, EC may already evolve during the inert phase under high temperature (Sciare et al., 2003). Therefore, depending on the filter loading of non-carbonaceous particles, the NIOSH protocol may systematically overestimate OC compared to EUSAAR-2. In addition, as stated above, the different optical configurations could be partly responsible for these discrepancies. Interactions with the light pipe walls as well as possible drift of the laser diode could also affect measurements. Finally, the influence of these phenomena on measurements may also depend on the temperature prevailing when the split point occurs (see Sect. 4.2).

In our case, there did not seem to have much difference between the results of rural and urban areas, with OC TOT versus TOR ratios being only slightly higher for the rural sites in the case where the NIOSH protocol was applied. Still, for both types of sites, OC_{TOT} remained higher than OC_{TOR}, which is consistent with the results reported by Cheng et al., (2011).

3.2.2 Comparison of EC measured with transmittance (EC_{TOT}) and reflectance (EC_{TOR})

Although rather good, the correlation between reflectance and transmittance results was less satisfactory for EC than for OC, with squared correlation coefficients (R^2) ranging here from 0.851 to 0.861. As shown in Fig. 4, measurements obtained with the transmittance optical correction led to lower EC than reflectance, as already observed by Zhi et al. (2011) and Cheng et al. (2011) comparing NIOSH and IMPROVE. Also Chow et al. (2004) observed differences while varying the temperature protocol (EC data determined by simultaneous TOT correction were 30 % lower than TOR data for the same temperature protocol and 70–80 % lower for a protocol with higher heating temperatures and shorter residence times) (see Table 1).

In addition to these phenomena, these differences could be explained by the distribution of the carbonaceous material on the filter and more precisely of the light absorbing carbon which lies mainly at the surface whereas the pyrolytic carbon is mainly present inside the filter. The reflectance signal consequently returns to its original value earlier than the transmittance one Chow et al. (2004) leading to higher EC values. In Fig. 4, the largest differences between the TOT to TOR ratios were observed when comparing rural results for NIOSH5040 and EUSAAR-2, on the one hand, and urban results for NIOSH5040 and EUSAAR-2, on the other hand. The rural results displayed the lowest TOT to TOR ratio of about 0.5 in agreement with previously reported results (e.g. Cheng et al., 2011). These differences may be explained by the aerosol chemical composition or its mixing state, which can be rather different between urban and rural sites. For example, the latter could be much more influenced by light absorbing organic material at the Sunset laser wavelength (660 nm), such as brown carbon and/or humic like substances (Lukacs et al., 2007). It can also arise from biomass combustion processes leading to the formation of what is called “tar balls” (Chakrabarty et al., 2010). Indeed, when comparing different techniques for black and elemental carbon, Sciare et al. (2003) and Reisinger et al. (2008) showed that a high influence of biomass burning sources led to the largest differences between the different techniques, while no differences could be observed for traffic samples (Hitzenberger et al., 2006). Furthermore, Schauer et al. (2003) indicated that the EC data of NIOSH-like and IMPROVE-like protocols (both with transmittance optical correction) exhibited larger differences for biomass burning particles than for urban ambient $PM_{2.5}$ particles. Cheng et al. (2011) also compared the NIOSH and IMPROVE protocols and observed significant discrepancies between both protocols. These discrepancies, displaying clear seasonal and spatial variations, were found to be higher at sites where abundant SOA was present. This supports the evidence that SOA contributes to higher discrepancies between both protocols in summer.

However, the way brown carbon and more generally the particle chemical composition can influence the TOT and TOR correction is still not clear and would need further investigations.

4 Laser signal intensity

4.1 Methodology

The apparent laser signal intensity decreases generally with the number of analyses due to the soiling of the front oven. A decrease of the laser intensity may also be enforced by adjusting the laser potentiometer setting. However, in the latter experiment, the increase of the light scattering due to clusters deposited or formed at the inner surface of the oven is not taken into account. In order to distinguish between the latter effect and the one due to a pure laser signal decrease, we set up an experiment in which measurements were conducted just before and just after the replacement of a soiled oven. In this experiment, 20 samples from various locations in France (mainly PM_{10} samples collected at urban background sites, as detailed in the supporting material) were analyzed in the following three conditions:

1. With a soiled oven (oven 1) and for a laser transmission signal intensity for blank filters of 3000. It should be emphasized that this oven exhibited a very significant soling, due to previous analyses of samples containing large amounts of sea salt, samples containing large amounts of Saharan dust, as well as samples collected in the plume of woodstoves. The soiling was observed in the form of a white circle at the place where the laser signal enters the oven. This experiment can therefore be seen as an “extreme case”.
2. With a brand new and clean oven (oven 2) for the same laser transmission signal intensity for blank filters of 3000.
3. With the same new oven, but for a laser transmission signal intensity for blank filters of 12 000.

Moreover, 7 of the 20 tested samples had already been analyzed with oven 1 just after its setting up (i.e. when it was quite clean).

4.2 Results

The results of the present experiment are shown in Fig. 5, allowing for the comparison of TC and EC data obtained for (i) two different laser signal intensities when using a clean oven and (ii) soiled versus clean ovens. The very good agreement obtained for TC in both comparisons enforces the consistency of the EC data.

It appears that only decreasing the laser intensity from 12 000 to 3000 does not have any significant impact on the EC concentration. In contrast, EC concentrations obtained with the soiled oven are significantly lower (up to a factor of 4) than the ones obtained with the clean ovens. This phenomenon might be explained by the influence of the front oven temperature on the laser signal. Indeed, a slight decrease of transmission is generally observed with increasing temperature, which could be observed for instance for an instrumental blank (using a blank filter resulting from a previous analysis). The additional light scattering due to the oven soiling may enhance this phenomenon (Fig. 6), which would generate a bias in the split point determination as detailed in the supporting material.

As shown in Fig. 7a, highest discrepancies were obtained for samples containing the highest EC loadings and presenting the highest contents of OC pyrolysed during analysis. These samples were actually collected during wintertime and probably contained high amounts of brown carbon emitted from biomass burning. Similar results were obtained for a second dataset corresponding to 16 samples collected at Belgian traffic sites and analyzed using the NIOSH protocol and two different ovens: a dirty oven with an apparent laser transmission signal intensity of approximately 4000 and a clean new oven (Fig. 7b).

It thus appears that the use of soiled ovens may lead to an underestimation of EC concentrations, especially for samples containing high loadings of EC and brown carbon. However, the limited number of data available for the present study, as well as the lack of systematic temperature offsets calibration before each batch of analyses, prevent making any definitive conclusions and could only call for more investigations.

A same statement may be made for the influence of the decrease of the laser light transmission intensity when only caused by adjusting the laser power. Indeed, the results presented above are only based on the comparison between two laser signal intensities and one may wonder whether a lower intensity (e.g. around or below 1000) would also have no impact on the measurements. In particular, the analysis of highly loaded samples using a weak laser power will lead to a very low initial laser transmission signal intensity, which may generate a bias in the split point determination. This phenomenon is still to be extensively investigated too.

5 Influence of the EC loading

To investigate further the influence of the filter loading on the data quality (i.e. lower quality for large loading), the potential influence of the EC concentration on the EC–OC measurement quality was examined with two different experiments designed to load quartz fiber filters with increasing EC amounts. The first experiment involved the use of a propane burner (LNI Schmidlin SA) in order to load filters with different amounts of "pure" EC. Since it is not simple to generate a known and controlled amount of particles with such a burner, different EC filter loadings were obtained varying the sampling time and using simultaneously two low volume $PM_{2.5}$ samplers (Partisol 2025, Thermo Scientific): a single filter was collected using one sampler while the second sampler was used to collect soot on several consecutive filters. For the latter sampler, the number of samples depended on the total sampling time performed with the first sampler (typically one filter every 10 min). Seven different sampling times were tested this way. The surface EC content (in $\mu g\,cm^{-2}$) measured on the filters collected using the first sampler was systematically compared to the sum of the surface EC contents measured on the filters collected using the second sampler. Very low contents of OC ($EC/OC > 0.9$) were obtained on these filters. Then, in a second step, ten microliters of a $2\,gC\,L^{-1}$ glucose solution (corresponding to $20\ \mu g\,cm^{-2}$ of OC deposited on the filter) was spiked on the filter punches in order to reproduce as much as possible a real carbonaceous PM content. Seven EC levels, ranging from 4 to 38 µg cm^{-2}, were tested. As presented in Fig. 8a, a very good agreement was obtained when directly comparing EC concentrations obtained from the two sampling devices. The addition of glucose a posteriori on long-time duration samples led to a less satisfactory correlation (Fig. 8b), suggesting an increase of the uncertainty due to the enhanced influence of charring. However, despite this uncertainty increase, no significant systematic influence of EC loading could be observed.

The second experiment was performed on real ambient particles (collected during late summer at a peri-urban background site) and involved the use of two high-volume samplers (Digitel DA80) to simultaneously sample PM$_{2.5}$ with various sampling times. Using one of these samplers, four sampling durations were tested: (i) three filters sampled for 24 h, (ii) one filter sampled for 48 h, (iii) two filters sampled for 72 h and (iv) one filter sampled for 120 h. For each set of sampling time, the other high-volume sampler covered the same period with filters collected every 24 h. Therefore, 24-h filter samples were compared to 24-h filter samples, 48-h filter samples were compared to two 24-h filter samples, and 120-h samples sere compared to five 24-h samples. As presented in Fig. 9, both EC and OC measurements actually displayed the same tendency: the differences between the sum of 24-h samples and the long-time samples (48, 72 and 120 h) depend on the sampling duration, with higher differences for both EC and OC for longer experiments. This cannot be attributed to between-sampler biases, as no significant differences were obtained for each one of the three 24-h sampling time tests (when samplings corresponded to only one filter per sampler). Alternatively, for OC, the highest concentrations derived from the sum of 24-h samples are consistent with the increasing positive organic adsorption artifact with decreasing sampling time and the increasing negative artifact with increasing sampling time, as shown by Kirchstetter et al. (2001). Similar results obtained for EC seem to indicate that semi-volatile organics involved in positive/negative sampling artifacts could influence the determination of the EC concentration. It might also be hypothesized that higher loadings of refractory scattering material (e.g. ammonium sulfate) on filters of longer sampling duration have a similar effect than the soiling of the oven, i.e. a possible decrease of the EC / TC ratio (see Sect. 4).

6 Conclusions

Different analytical protocols have been widely used for many years to determine EC and OC in aerosols. The thermal-optical method is nowadays considered by the US and European normalization works as a reference methodology to quantify EC–OC. However, the comparison between various thermal-optical methods still results in significant discrepancies. This work aimed at providing information on some parameters influencing these discrepancies. The two major conclusions are presented here:

1. There are higher discrepancies between $\mathrm{OC_{TOT}}$ and $\mathrm{OC_{TOR}}$ measured with NIOSH in comparison to EUSAAR-2. Significant differences between $\mathrm{EC_{TOT}}$ / $\mathrm{EC_{TOR}}$ ratios can also be observed when comparing rural and urban results whatever the thermal protocol, NIOSH or EUSAAR-2. At rural sites, $\mathrm{EC_{TOT}}$ is 50 % lower than $\mathrm{EC_{TOR}}$ whereas it is 20 % lower at urban sites. The PM chemical composition could explain these differences, but the way it influences the EC–OC measurement is not clear and needs further investigations.

2. The EC / TC ratio seems to decrease when a soiled oven is used. At this point, no threshold value may be definitely proposed for the laser signal intensity, and the present study can only call for more investigations. However it could be strongly recommended to use a large test filter to track long-term change in charring correction in the course of day to day analyses.

These results provide insights to determine the accuracy of EC–OC analytical methods and certainly contribute to the work which has to be done to establish method standardisation.

Supplementary material related to this article is available online at http://www.atmos-meas-tech-discuss.net/6/10231/2013/amtd-6-10231-2013-supplement.pdf.

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So sadly, Laura Chiappini passed away a couple of weeks after the initial submission of the present manuscript. All other co-authors spare friendly thoughts for her and her familly. They also warmly acknowledge her for the intensive efforts she put in the present study, for which she has been the main responsible.

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Table 1. Analytical protocols, type of charring correction and instrument used by each laboratory. In fourth column laboratories using EUSAAR 2, in third column IMPROVE, in second column, NIOSH protocol.

	NIOSH 5040	IMPROVE	EUSAAR_2
Laboratory code	2	3	1, 4, 5
Step	T (°C), duration (s)		
He1	250, 60	120, 150–580	200, 120
He2	500, 60	250, 150–580	300, 150
He3	650, 60	450, 150–580	450, 180
He4	850, 90	550, 150–580	650, 180
He/O_2 1	650, 30	550, 150–580	500, 120
He/O_2 2	750, 30	700, 150–580	550, 120
He/O_2 3	850, 30	800, 150–880	700, 70
He/O_2 4	940, 120		850, 80
Charring correction	Transmittance	Reflectance	Transmittance
Laboratory and instrument type	Lab. 2, Sunset Lab. Inst.	Lab. 3, DRI Model	Lab. 1 Sunset Lab. Inst. Lab. 4 Sunset Lab. Inst. Lab. 5 Sunset Lab. Inst.

Table 2. Mean, standard deviation (SD), relative standard deviation (RSD) obtained for the 18 punches made on filters N'1, N'2 and N'3 to evaluate the filter sample homogeneity.

Filter N'1			
Mean (µg cm^{-2})	10.0	3.6	13.6
Standard deviation (µg cm^{-2})	0.6	0.1	0.7
Relative standard deviation (%)	6.1	3.3	4.8
Filter N'2			
Mean (mug cm^{-2})	21.4	8.0	29.5
Standard deviation (µg cm^{-2})	0.5	0.3	0.5
Relative standard deviation (%)	2.2	3.5	1.9
Filter N'3			
Mean (µg cm^{-2})	27.5	8.3	35.8
Standard deviation (µg cm^{-2})	0.6	0.2	0.7
Relative standard deviation (%)	2.3	2.7	1.9

Table 3. Mean, Standard deviation (SD), repeatability relative standard deviation calculated for OC, EC, TC and EC / TC ratio for each laboratory and each filter (N1, N2 and 3 N3).

		OC			EC			TC			EC / TC		
	Lab code	Mean µg cm^{-2}	SD µg cm^{-2}	CVr	Mean µg cm^{-2}	SD µg cm^{-2}	CVr	Mean µg cm^{-2}	SD µg cm^{-2}	CVr	Mean µg cm^{-2}	SD µg cm^{-2}	CVr
	1	*11.98*	*0.03*	*0 %*	*5.44*	*0.08*	*1 %*	*17.41*	*0.11*	*1 %*	*0.312*	*0.0029*	*0.9 %*
	4	*14.84*	*1.23*	*8 %*	*4.97*	*0.22*	*4 %*	*19.81*	*1.31*	*7 %*	*0.254*	*0.0210*	*8.3 %*
N1	**3**[*]	**15.59/13.61**	**1.26/1.18**	**8 %/9 %**	**5.34/7.32**	**0.35/0.29**	**6 %/4 %**	**20.93**	**1.08**	**5 %**	**0.256/0.350**	**0.024/0.0243**	**9.5 %/6.9 %**
	2	13.92	1.21	9 %	4.73	0.15	3 %	18.65	1.09	6 %	0.251	0.0146	5.8 %
	5	*14.03*	*0.09*	*1 %*	*5.59*	*0.24*	*4 %*	*19.62*	*0.27*	*1 %*	*0.285*	*0.0087*	*3.0 %*
	1	*41.58*	*0.87*	*2 %*	*23.02*	*0.78*	*3 %*	*64.60*	*0.90*	*1 %*	*0.356*	*0.0107*	*3.0 %*
	4	*48.90*	*2.22*	*5 %*	*19.18*	*1.60*	*8 %*	*68.08*	*1.49*	*2 %*	*0.208*	*0.0270*	*13.0 %*
N2	**3**[*]	**51.39/36.70**	**3.84/2.53**	**8 %/8 %**	**20.65/35.34**	**3.45/3.12**	**17 %/9 %**	**72.04**	**0.59**	**1 %**	**0.287/0.49**	**0.0492/0.039**	**17.2 %/8**
	2	51.47	1.75	3 %	13.49	1.81	13 %	64.96	0.87	1 %	0.282	0.0243	8.6 %
	5	*52.67*	*0.85*	*2 %*	*16.75*	*0.25*	*1 %*	*69.42*	*0.72*	*1 %*	*0.241*	*0.0051*	*2.1 %*
	1	*22.31*	*0.08*	*0 %*	*8.30*	*0.12*	*1 %*	*30.61*	*0.19*	*1 %*	*0.271*	*0.0021*	*0.8 %*
	4	*24.59*	*0.86*	*3 %*	*6.91*	*0.36*	*5 %*	*31.51*	*0.58*	*2 %*	*0.218*	*0.0026*	*1.2 %*
N3	**3**[*]	**25.27/18.41**	**0.39/1**	**2 %/5 %**	**8.10/14.96**	**0.21/0.6**	**3 %/4 %**	**33.37**	**0.59**	**2 %**	**0.243/0.448**	**0.0021/0.231**	**0.9 %/5.1**
	2	24.67	0.17	1 %	6.86	0.07	1 %	31.54	0.13	0 %	0.220	0.0145	6.6 %
	5	*23.66*	*0.32*	*1 %*	*8.44*	*0.08*	*1 %*	*32.10*	*0.25*	*1 %*	*0.263*	*0.0044*	*1.7 %*

[*] For laboratory 3, results are given in transmittance and reflectance, respectively. In italic laboratories using EUSAAR 2, in bold IMPROVE, in underline, NIOSH protocol.

Table 4. Overall laboratory mean concentration (µg cm^{-2}), standard deviation (µg cm^{-2}), reproducibility and repeatability % standard deviations (%) for TC, EC, OC and the EC / TC ratio in samples N1, N2 and N3.

		Mean concentration (µg cm^{-2})	Standard deviation (µg cm^{-2})	Reproducibility s.d. (%)	Repeatability s.d. (%)	Overall uncertainty (%)
N1	TC	19.28	1.32	6.9	3.9	14
	EC	5.21	0.35	6.8	3.9	14
	OC	14.07	1.35	9.6	5.2	19
	EC / TC	0.27	0.03	9.7	5.5	19
N2	TC	67.82	3.12	4.6	1.4	9
	EC	18.62	3.66	19.7	8.7	39
	OC	49.2	4.48	9.1	3.8	18
	EC / TC	0.27	0.06	20.3	8.8	40
N3	TC	31.82	1.02	3.2	1.1	6
	EC	7.72	0.77	10	2.2	20
	OC	24.1	1.15	4.8	1.5	10
	EC / TC	0.24	0.02	10.1	2.2	20

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Table 5. Dependence of EC / TC on the temperature offset of the front oven and/or on the laser intensity for laboratories using the same thermal protocol (EUSAAR 2).

	Temperature offset for the last step under He	Laser transmission intensity for a blank filter	EC / TC for N1 (mean EC loading of 5.2 $\mu g\,cm^{-2}$)	EC / TC for N2 (mean EC loading of 18.6 $\mu g\,cm^{-2}$)	EC / TC for N3 (mean EC loading of 7.7 $\mu g\,cm^{-2}$)
Lab. 1	−80	15 000	0.31	0.36	0.27
Lab. 5	−55	1600	0.28	0.24	0.26
Lab. 4	+30	4400	0.25	0.28	0.22

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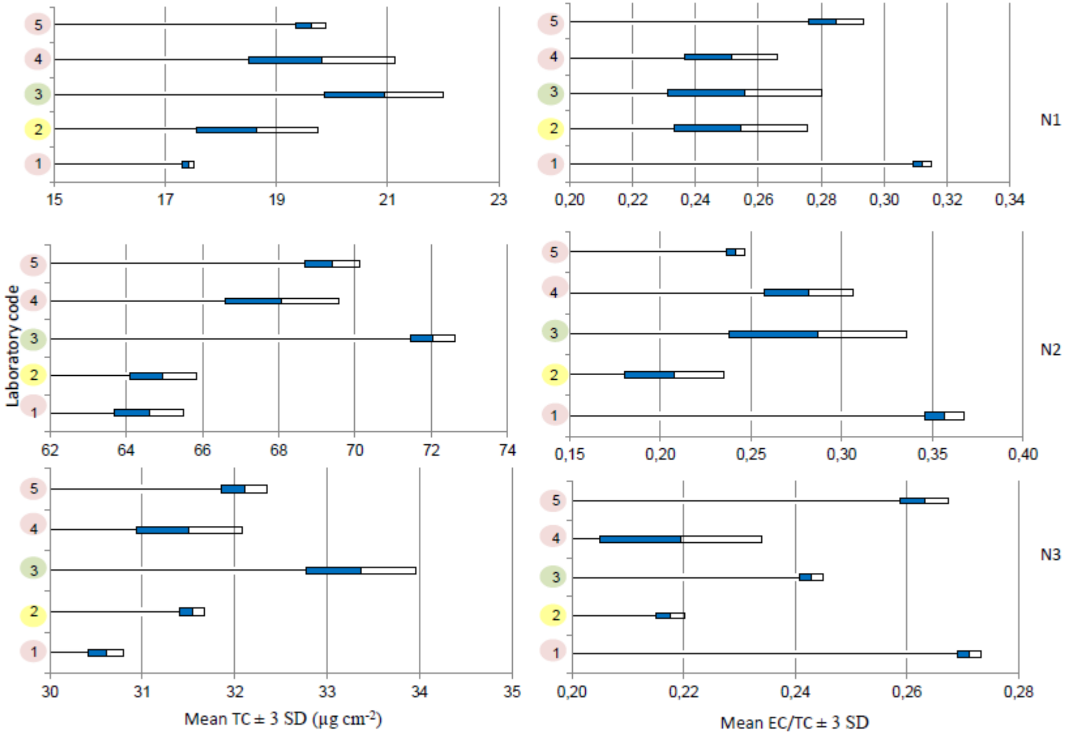

Fig. 1. Statistical distribution (general Mean and standard deviation SD) for TC (left panels) and the EC / TC ratio (right panels). In red laboratories using EUSAAR 2, in green IMPROVE, in yellow NIOSH protocol.

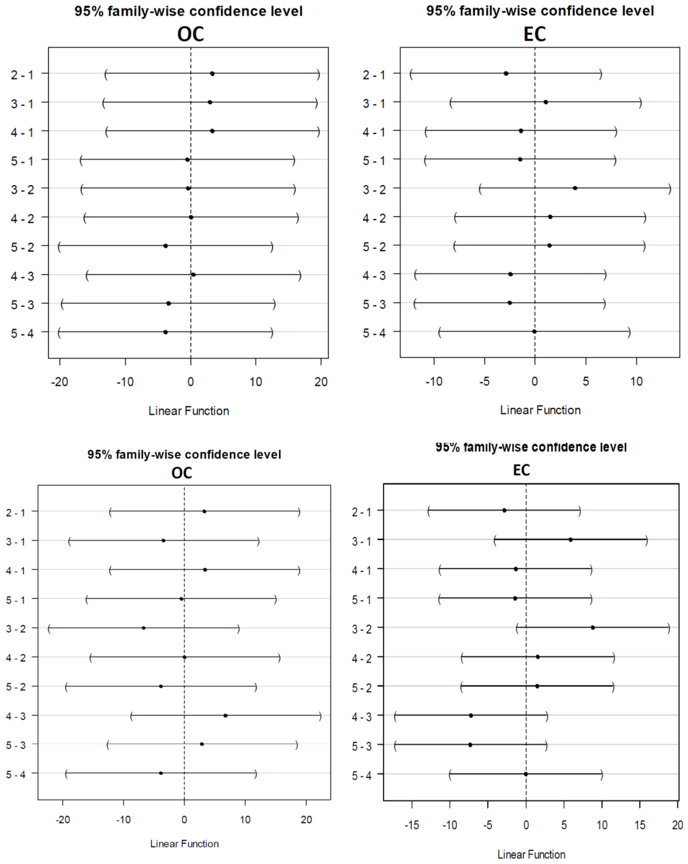

Fig. 2. One way ANOVA test to compare laboratory pairs for OC and EC measurement. Top panels contain results from laboratory 3 in transmittance. Bottom panels contain results from laboratory 3 in reflectance.

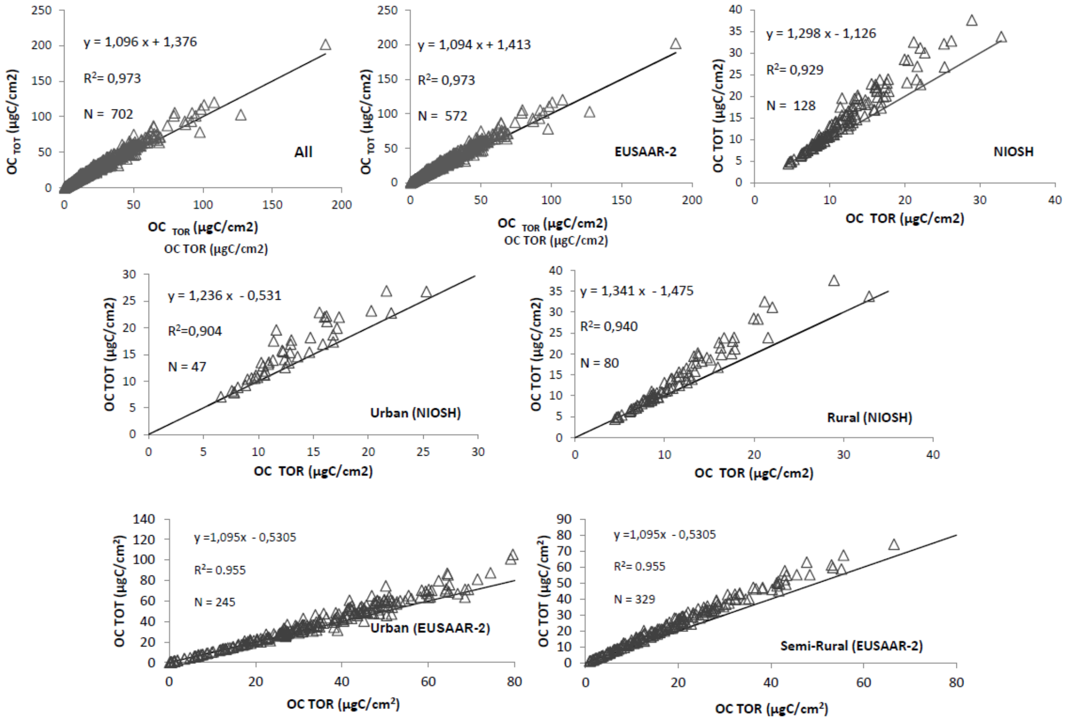

Fig. 3. Comparison between reflectance and transmittance for OC for all samples. EUSAAR-2 analyzed samples. NIOSH analyzed samples. urban and rural samples. Slope coefficients ($y = ax + b$). correlation coefficients (R^2) and the number of samples (N) are given.

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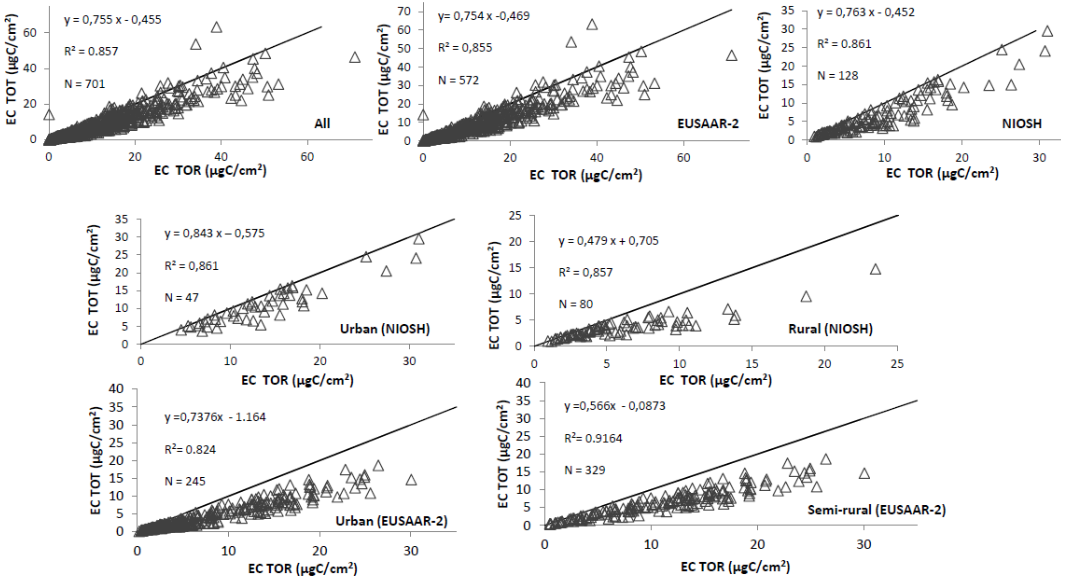

Fig. 4. Comparison between reflectance and transmittance for EC for all samples. EUSAAR-2 analyzed samples. NIOSH analyzed samples. urban and rural samples. Slope coefficients ($y = ax + b$). correlation coefficients (R^2) and the number of samples (N) are given.

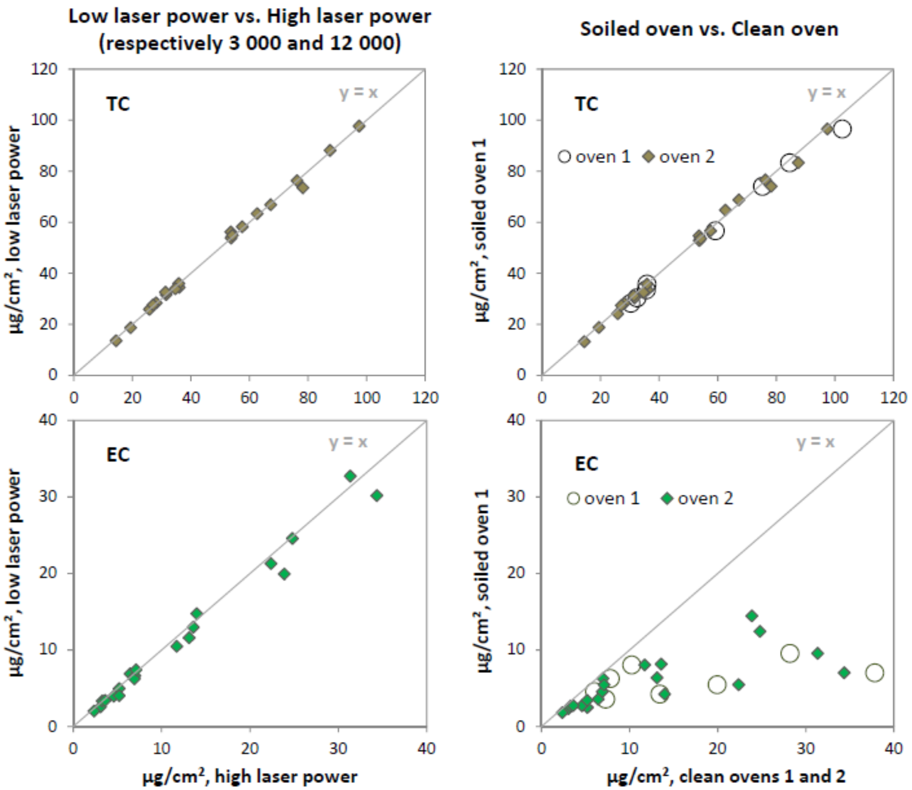

Fig. 5. Influence of the laser power (for a clean oven, right panels) and of the oven soiling (extreme case, left panels) on EC measurements.

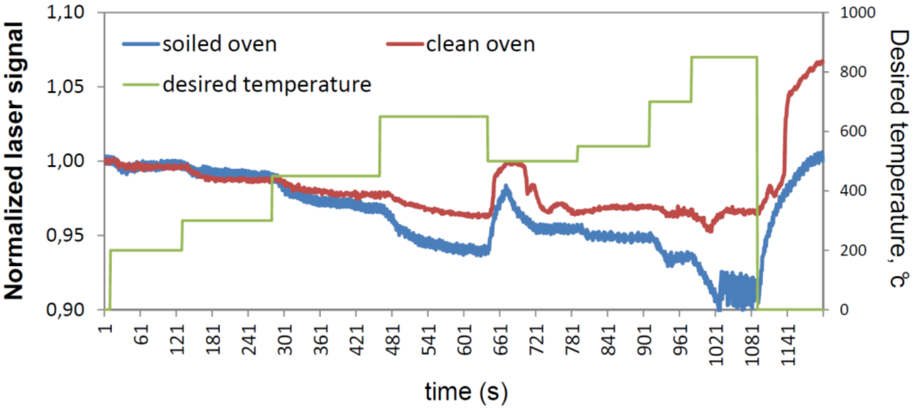

Fig. 6. Time evolution of the laser transmission signal intensity during instrumental blank analysis with a clean and a soiled oven. For comparison purpose, the laser signals have been normalized to their initial value.

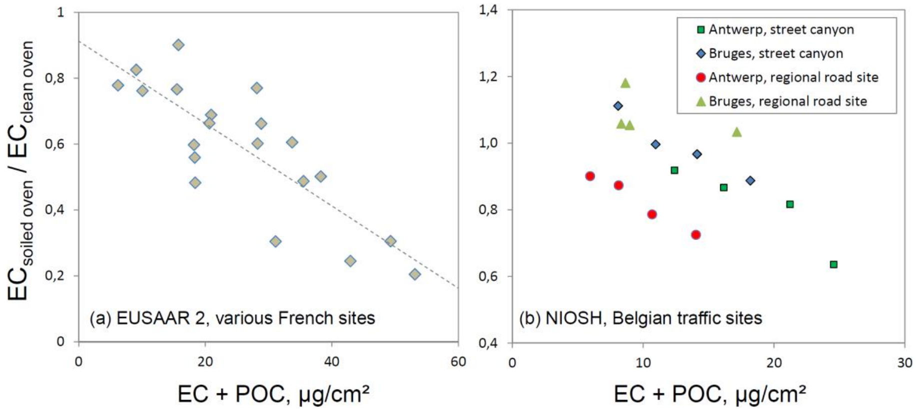

Fig. 7. Ratios of EC concentrations obtained when using a clean and a soiled (extreme case) ovens as a function of the EC + POC filter loading. Using the EUSAAR 2 (right panel) and NIOSH (left panel) thermal protocols.

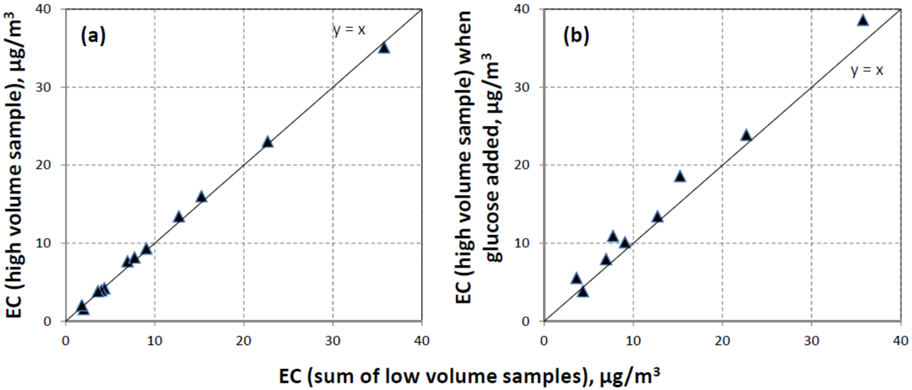

Fig. 8. Comparison between EC measured on high volume samples and EC calculated as the sum of low volume samples. **(a)** EC only. **(b)** EC plus glucose spiked on the filters.

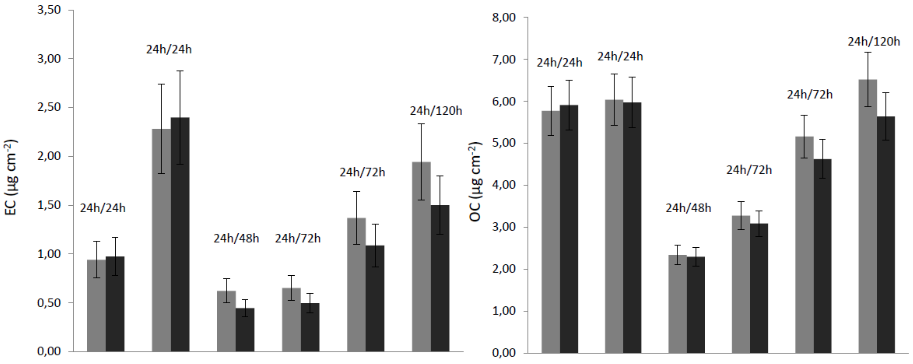

Fig. 9. Comparison of EC and OC concentrations for different lengths of sampling time. Error bars correspond to 20 and 10 % uncertainty for EC and OC, respectively.