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Results of the 2nd comparison exercise for EU National Air Quality Reference Laboratories (AQUILA) for TC, OC and EC measurements (2011)

Fabrizia Cavalli, Kevin Douglas and Annette Borowiak

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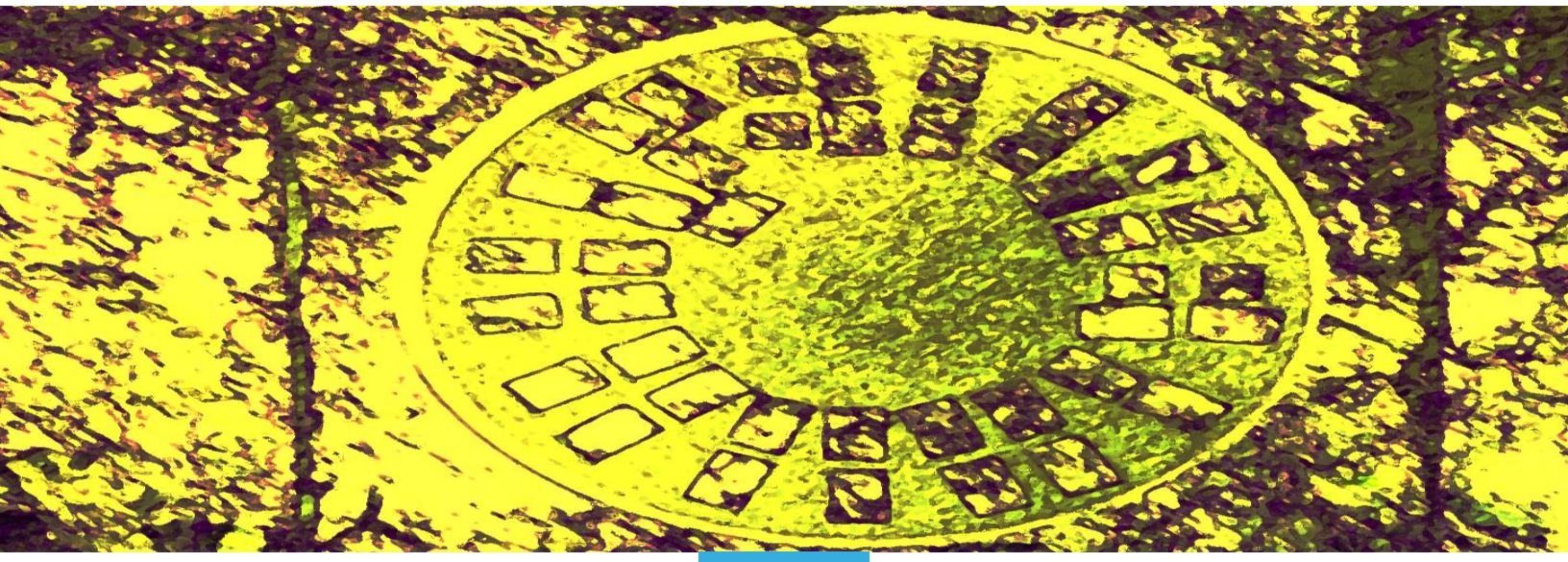

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Results of the second comparison exercise for EU National Air Quality Reference Laboratories (AQUILA) for TC, OC and EC measurement (2011)

Summary

The EC-JRC European Reference Laboratory for Air Pollution (ERLAP) has organized an inter-laboratory comparison for the measurement of total carbon (TC), elemental carbon (EC) and organic carbon (OC) in particulate matter collected on filters.
To this comparison seventeen European Union National Reference Laboratories for air quality or delegated organizations participated, all using thermal-optical analysis with the same analyzer (Sunset Lab off-line carbon analyzer).

The aim of this comparison was to evaluate the performances of participants but also to study the effects of applying different thermal protocols, i.e. NIOSH and EUSAAR_2 protocols, currently in use in Europe for such analysis.

In absence of a general consensus by the scientific community on the definition of a reference material for EC and, thus, of a standard analytical method, method performances [ISO5725-2] and laboratory performances [ISO 13528:2005(E)] were evaluated for TC and EC/TC ratio in the present comparison exercise.

For TC, repeatability and reproducibility relative standard deviations ranged from 2% to 6% (s_r = 0.017 × m + 0.227) and from 5% to 11% (s_R = 0.038 × m + 0.389), respectively.
For EC/TC ratio, repeatability and reproducibility relative standard deviations ranged from 2% to 10% and from 8% to 35%, respectively for the NIOSH-like protocol, and from 2% to 14% and from 4% to 19%, respectively for the EUSAAR protocol. (No satisfactory dependence was found upon EC/TC ratio).

Furthermore, based on z-scores, three outliers were identified in the TC database when applying as *standard deviation for proficiency assessment,* σ*, that one calculated *from data obtained in a round of a proficiency testing scheme.* These outliers would also not comply with the DQO (i.e. expanded uncertainty, with a coverage factor of 2) of 25%, as in the EU Directive 2008/50/EC for PM at its limit value of 50 μg m^{-3}.

Laboratory performances were evaluated for EC/TC ratio, separately on the two data subsets from the NIOSH and EUSAAR_2 protocols using as σ* a common level of performance (i.e. 15%) that the inter-laboratory comparison coordinator would wish participants to achieve. Under this condition, four outliers were identified in the subset of data from the NIOSH-like protocol and one outlier in the subset of data from the EUSAAR_2 protocol.

1 Introduction

Total Carbon (TC), including Organic Carbon (OC) and Elemental Carbon (EC), is a relevant constituent of the fine fraction of particulate matter (PM), both from the perspective of health risks due to inhalation and indication of sources of air pollution. The latter has been the reason for including requirements for measuring EC and OC in $PM_{2.5}$ at rural background locations in Air Quality Directive 2008/50/EC. The directive does not contain further clarification on the definition of EC and OC, or on measurement methods to be used.

In the Technical Specification (TS) by the CEN/TC265 WG35, thermal-optical analysis has been indicated as the most suitable method for the determination of EC and OC collected on filters. However, in absence of a general consensus within the scientific community on the definition of EC, and standard reference material of it, all three available thermal protocols, i.e. NIOSH (and variations of it), IMPROVE and EUSAAR_2, can be currently applied (with a transmittance or reflectance optical correction for pyrolysis).

The JRC European Reference Laboratory for Air Pollution (ERLAP) organized the second inter-laboratory comparison among European Union National Reference Laboratories (NRL) for air quality or delegated organizations in 2011, with the aim of evaluating the performances of participants but also to study the effects of using different thermal protocols for determining OC and EC.

2 Samples, sub-samples and homogeneity

High-volume samplers (Digitel DHA80, face velocity of 54.1 cm s^{-1}) were used to collect two PM_{10} samples on 150 mm diameter quartz-fiber filters (Whatman QMA/ Pallflex Tissuequartz) at each of the following locations:

- Zagreb, urban (traffic-dominated) location, HR;
- Vienna, urban background location, AT;
- Duebendorf, suburban location, CH;
- Ayia Marina, rural background location, CY;
- Verneuil-en-Halatte, semi-rural location, FR.

A total of 10 samples were collected over a period of 24 hours during the month of September 2011 in order to obtain: i) carbon concentrations in the range of those expected in rural background sites (according to EU Directive 2008/50/EC); ii) no influence from biomass burning emissions (biomass burning aerosols comprise high molecular weight refractive carbonaceous compounds which would add an additional level of complexity to this comparison exercise. The effect of specific sources on different thermal-optical protocols will be addressed in future exercises) and iii) a higher stability of OC due to a limited absorption of volatile OC species (positive artifacts).
Upon receipt at ERLAP, filters were stored in a freezer.
From each sample, two rectangle punches of 1x1.5 cm^2 were prepared and mailed to the participants. To help interpreting the consistency of results (i.e. between-laboratory and within laboratory consistencies), a progressive number was assigned to the participants and punches taken in circle following a prescribed scheme (Figure 1). Sub-sample punches were dispatched to participants in closed petri dishes.

The homogeneity of all samples was investigated by the ERLAP laboratory. Four filter punches, in total, were taken along two perpendicular radii at fixed positions. The homogeneity was assessed as the relative standard deviation (%rsd) of TC determinations and resulted in: 2% for HR-1; 2%, HR-2; 1%, AT-1; 1%, AT-2; 4%, CH-1; 3%, CH-2; 4%, CY-1; 7%, CY-2; 2%, FR-1; and 2%, FR-2. These values represent, however, only an upper limit of the between-sample standard deviation (i.e. filter homogeneity). In fact, the procedure used here for homogeneity checks did not allow determining the within-samples standard deviation (accounting for the ERLAP laboratory repeatability) which should be subtracted from the standard deviation of the sample average to derive the between-sample standard deviation (according to ISO 13528:2005 EC, Annex B).

Figure 1: Subsamples and homogeneity.

2.1 Participants

The list of the 17 participants is reported in Table 1. The Environmental Protection Agency of Lithuania and the Estonian Environmental Research Centre did not participate in the comparison due to technical problems with their analyzers.

Table 1: List of participants and contact persons. Most laboratories are designated National Reference Laboratories (NRL)

	Name of laboratory	Notes	Contact persons
1	UBA UniVie Austria	NRL	marina.froehlich@umweltbundesamt.at
2	NPL, UK	NRL	paul.quincey@npl.co.uk
3	UOC, Cypros		skleanthous@dli.mlsi.gov.cy
4	UBA_DE, Germany	NRL	elke.bieber@uba.de
5	NILU, Norway		Wenche.Aas@nilu.no
6	Empa, Switzerland	NRL	christoph.hueglin@empa.ch
7	INERIS, France	NRL	Olivier.FAVEZ@ineris.fr
8	ISCIII, Spain	NRL	rferndez@isciii.es
9	ENVS, Denmark	NRL	jakn@dmu.dk
10	GGD, Amsterdam		Theo.Hafkenscheid@rivm.nl
11	CZE, Czech republic		novakj@chmi.cz
12	IMI, Croatia		rgodec@imi.hr
13	IPHB, Serbia		zoran.sekulic@zdravlje.org.rs
14	VMM, Belgium	NRL	c.matheeussen@vmm.be
15	KAL, Slovenia		Gregor.Muri@gov.si
16	LRA, Portugal	NRL	susana.casimiro@apambiente.pt
17	ERLAP, EC-JRC	NRL	annette.borowiak@jrc.ec.europa.eu

2.2 Thermal-optical analysis

INSTRUMENT TYPE: All laboratories used the laboratory version of the Sunset analyser.

PROTOCOL: Thermal-optical analysis is a widely used technique to quantify TC, OC and EC in PM samples. In Europe two protocols are mainly used: the NIOSH protocol (and variations of it) [Peterson and Richard, 2002] and the EUSAAR_2 protocol [Cavalli et al., 2010]. Because of differences in temperature and length of the protocol steps, the two protocols are known to give significantly different results, with EC/TC ratio from NIOSH typically lower than that from EUSAAR_2. In absence of a general consensus by the scientific community on the definition of EC and of a reference material for it, it has not been possible yet to define a standard protocol. Thus, each participant was asked to analyze the samples with the protocol in-use in his laboratory. Seven laboratories applied variations of the NIOSH protocol, but all having the same value for highest temperature step in the He-mode of the analysis, i.e. 870°C (an example is reported in Table 3). The remaining ten laboratories applied the EUSAAR_2 protocol (Table 3). Transmittance was chosen by every participant to correct for pyrolysis, but four participants reported also reflectance-corrected results.

PUNCH SIZE and REPLICATES: All participants used sample punches of 1.5 cm², with the only exception of ERLAP which employed 1 cm² sample punches; two replicate measurements have been performed by all participants, only ENVS has performed one replicate only.
The analytical protocol and pyrolysis correction used, the punch size and the presence of replicate measurements are summarized in Table 2.

Table 2: List of the analytical protocol, optical correction for pyrolysis (Transmittance, T, Reflectance, R) used and punch size. Laboratories providing two replicate measurements are labeled with x.

	Name of laboratory	Protocol	Optical corr.	punch size cm^2	Replicates
1	UBA UniVie Austria	NIOSH	T/R	1.5	x
2	NPL, UK	NIOSH	T/R	1.5	x
3	UOC, Cypros	EUSAAR_2	T	1.5	x
4	UBA_DE, Germany	EUSAAR_2	T	1.5	x
5	NILU, Norway	EUSAAR_2	T	1.5	x
6	Empa, Switzerland	EUSAAR_2	T	1.5	x
7	INERIS, France	EUSAAR_2	T/R	1.5	x
8	ISCIII, Spain	NIOSH	T	1.5	x
9	ENVS, Denmark	EUSAAR_2	T	1.5	
10	GGD, Amsterdam	NIOSH	T	1.5	x
11	CZE, Czech republic	EUSAAR_2	T	1.5	x
12	IMI, Croatia	NIOSH	T	1.5	x
13	IPHB, Serbia	EUSAAR_2	T	1.5	x
14	VMM, Belgium	NIOSH	T	1.5	x
15	KAL, Slovenia	EUSAAR_2	T	1.5	x
16	LRA, Portugal	NIOSH	T	1.5	x
17	ERLAP, EC-JRC	EUSAAR_2	T/R	1	x

Table 3: Details of the two analytical protocols used by participants

	NIOSH		EUSAAR_2	
	Time S	Temp ºC	Time s	Temp ºC
Carrier gas				
Helium	70	310	120	200
Helium	60	475	150	300
Helium	60	615	180	450
Helium	90	870	180	650
Oxygen in Helium	45	550	120	500
Oxygen in Helium	45	625	120	550
Oxygen in Helium	45	700	70	700
Oxygen in Helium	45	775	80	850
Oxygen in Helium	120	890		
% Oxygen in Helium	2%		2%	

3 Data evaluation

The EU directive requires measurements of EC and OC in PM2.5 at rural background locations. But, in absence of a general consensus by the scientific community on the definition of a reference material for EC and, thus, of a standard analytical method, method performances (par 3.1) and laboratory performances (par. 3.2) are evaluated for TC and EC/TC ratio in the present comparison exercise. In fact, TC represents the most robust, and protocol-independent measure of TOA analysis; and EC/TC ratio is free from biases in the carbon determination and allows investigating possible biases in the OC/EC split determination among laboratories applying the same protocol.

All results are presented in Tables 1 and 2 of Annex 1 for TC (in µg cm^{-2}) and light transmittance-corrected EC/TC ratios.

On average, reported TC amounts ranged from 5.7 to 39.0 µg cm^{-2}, corresponding to atmospheric concentrations ranging from 1.2 to 8.3 µg m^{-3} collected for 24h with a face velocity of 54.1 cm s^{-1}. EC/TC ranged from 0.03 to 0.52, on average (including all observations regardless of the analytical protocol).

Figure 2 shows the correlation between TC general means (including all values) from NIOSH-like users and EUSAAR_2 users for the ten comparison samples. Errors bars are the standard deviation of means.
Linear regression indicates that TC_EUSAAR_2 = 0.99 x TC_NIOSH_like – 1.08 (R2=0.99), when including all values; when outliers are removed, TC_EUSAAR_2 = 0.99 x TC_NIOSH_like – 0.53 (R2=0.99).

There is a constant difference of 0.53 µgC cm^{-2} in the determination of TC between the two protocols over a TC range from 5 to 40 µgC cm^{-2}.

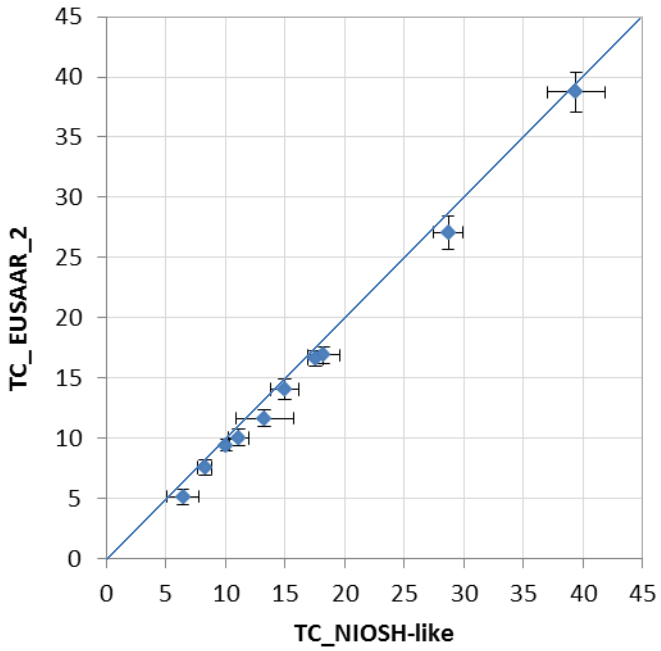


Figure 2: Correlation between TC general means (including all values) from NIOSH-like users and EUSAAR_2 users for the ten comparison samples. Errors bars are the standard deviation of means.

The two protocols differ for the highest temperature of the final step and its duration, i.e. 850°C for 80 s in the EUSAAR_2 protocol and 890°C for 120 s in the NIOSH-like protocol.

Based on the analysis performed at JRC applying the EUSAAR_2 protocol, the contribution of the EC4 fraction (at 850°C for 80 s) to the TC was calculated for all samples: AT-1: 2%; AT-2: 2%; CH-1: 10%; CH-2: 13%; HR-1: 2%; HR-2: 2%; CY-1: 1%; CY-2: 1%; FR-1: 5% and FR-2: 4%. With the exception of the CH-1 and CH-2 samples, the contribution of C evolving in the He-Ox phase at 850°C (EC4) was negligible for all samples, i.e. the totality of C evolved at T<850°C for the comparison aerosol samples. Furthermore, for all samples, EC4 carbon peak evolved completely well before the end of EC4 step. As C evolving –completely– at 850°C represented already a negligible fraction of TC, it was very unlikely that a significant residual C fraction still existed evolving at temperature of only 40 degree higher (NIOSH-like protocol reaches a temperature of 890 °C).

Furthermore, the comparability of thermal protocols (including EUSAAR_2) in the determination of TC has recently been assessed in the framework of a comparison exercise organised by Environment Canada. Twenty-seven samples were analysed using three different protocols, i.e. EUSAAR_2 by JRC, IMPROVE_A by DRI and Total900-envcan by EnvCan with the latter one having a temperature step at 900°C for 420 sec. The correlation observed between EUSAAR_2 and EnvCan for TC concentrations was excellent (R^2 = 0.94, slope = 0.999, intercept = 0.002 µg/m³).

In conclusion, all above observations strongly suggest that the observed constant difference of 0.53 µgC cm-2 between TC from the two protocols cannot be considered method-dependent. Therefore, the TC dataset is evaluated as a whole independently of the thermal protocol.

By contrary, as the split between OC and EC is an operational definition, potential differences in EC/TC are considered as protocol-dependent and, thus, the EC/TC dataset are evaluated separately for the two thermal protocols.

In the followings figures, results are ordered on the basis of the analytical thermal protocol used by the laboratories with results from laboratories using the NIOSH-like protocol first (i.e. laboratories 1, 2, 8, 10, 12, 14 and 16), followed by results from laboratories using the EUSAAR_2 protocol (i.e. laboratories 3, 4, 5, 6, 7, 9, 11, 13, 15, and 17).

3.1 Method performance: data evaluation description

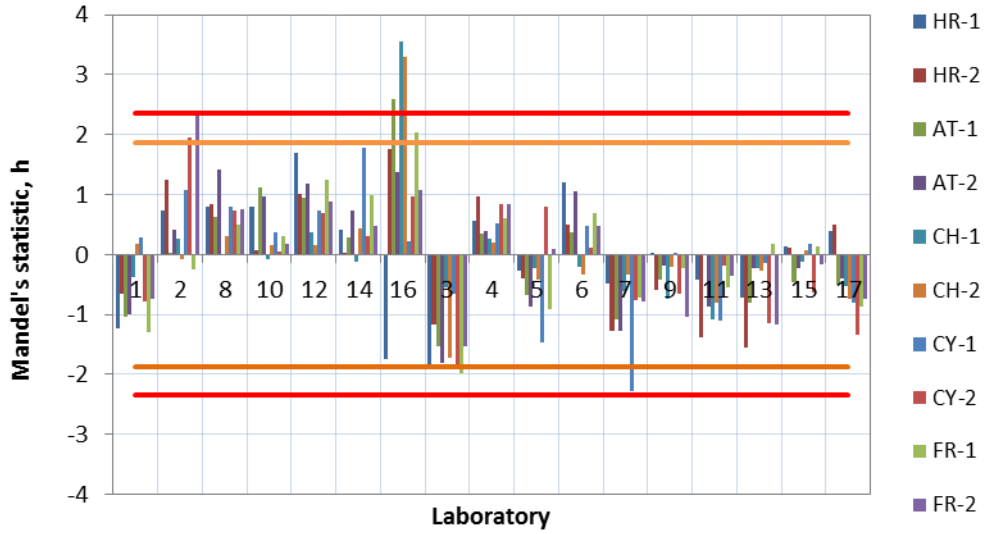
The consistency of the dataset is evaluated, at first graphically, by means of *Mandel's h* and *k* statistics [ISO5725-2], for possible outliers (i.e. observations greater than the critical value at 1% confidence level) or stragglers (i.e. observations greater than the critical value at 5% confidence level and less or equal to the critical value at 1% confidence level). The *Mandel's h* parameter describes the between-laboratory consistency and has been calculated for every laboratory and every sample; whereas the *Mandel's k* parameter estimates the within-laboratory consistency and has been calculated only for the laboratories that provided replicate measurements.
Furthermore G_1-Grubbs' and the Cochran's statistical tests are applied for testing the between-laboratory variability and the within-laboratory variability, respectively [ISO5725-2]. Based on the outcomes of above statistical treatments, outliers are discarded.
From the retained values and for each sample separately, the mean value, the repeatability and reproducibility standard deviations are calculated. Subsequently, the dependence of precision (i.e. repeatability and reproducibility standard deviations) upon the mean values is investigated and the functional relationship determined when it exists [ISO5725-2].

3.1.1 Results: Method performance for TC

In figure 3 the *Mandel's h* statistic values are presented grouped for each laboratory (panel a) and, separately, for each sample (panel b).
In the TC dataset, four outliers (lab/sample: 16/AT-1; 16/CH-1; 16/CH-2 and 2/FR-2) were identified of which three, all consistently with positive *h*, from lab 16. Furthermore, six stragglers (lab/sample: 3/HR-1; 7/CY-1; 2/CY-2; 3/CY-2; 3/FR-1 and 16/FR-1) were identified of which three, all consistently with negative *h*, from lab 3. For lab 3, four of the remaining observations showed *h* values close to the critical value for stragglers (i.e. 1.87).
Only the outlying observations 16/CH-1 and 16/CH-2 were confirmed as outliers by the Grubbs' test $G_.$.
Laboratories reported measurements of the external standard (e.g sucrose, phthalic acid): lab 1 and lab 3 underestimated and overestimated, respectively, the expected value by ≥10%.
For lab 3, this tendency cannot explain the identified stragglers. Lab 16 showed, on three replicates, an average recovery for the external standard of 99% but it consistently overestimated four comparison samples.

Laboratories showing biases shall carefully examine their procedures (particularly, determination and verification of the calibration constant, measurement of filter samples etc.) and identify appropriate corrective actions that are likely to prevent the recurrence of such results.

Panel a



Panel b

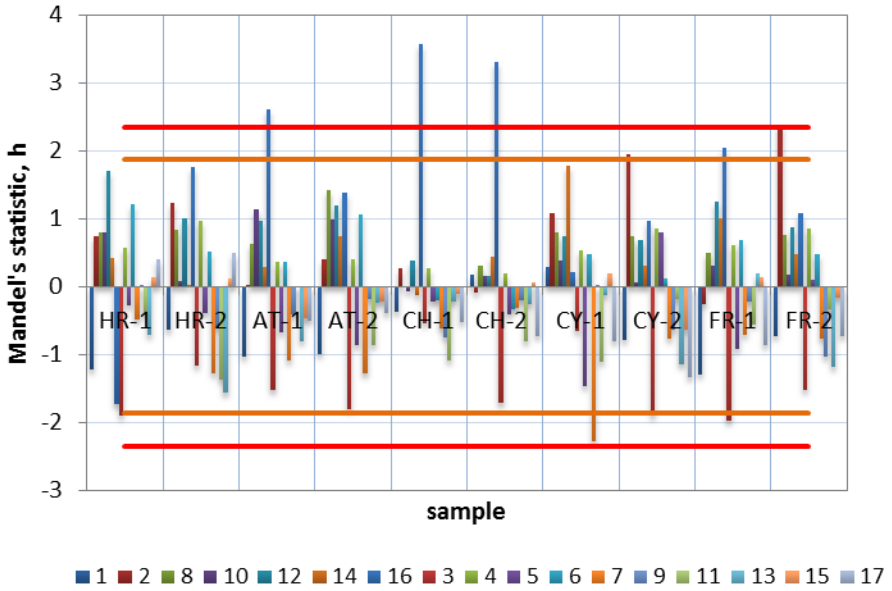
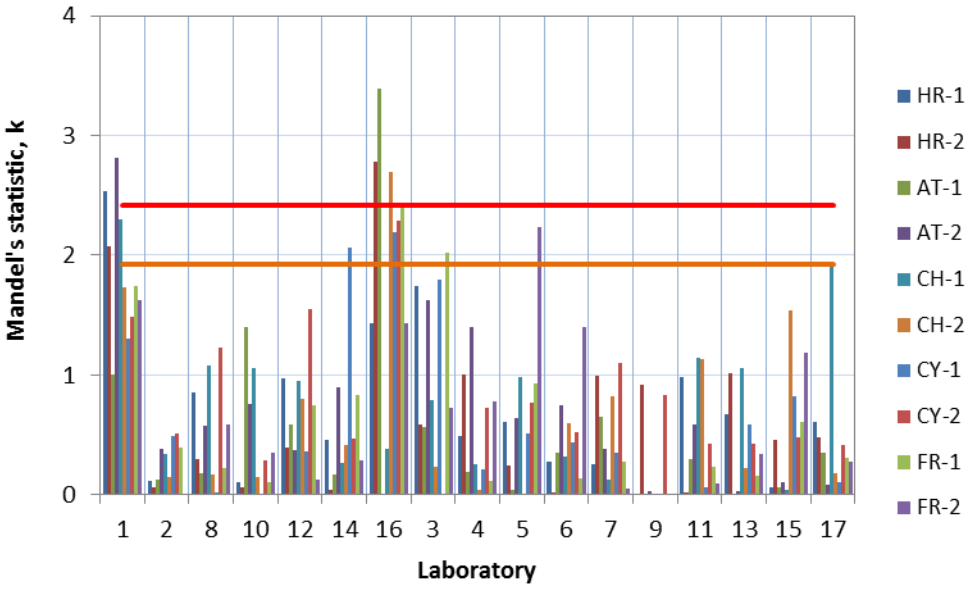


Figure 3. *Mandel's h* statistic values for between laboratory consistency on TC data, grouped by laboratory (panel a) and by sample (panel b). For 17 laboratories, *h* values should be < 2.35 at 1% significance level (red line) and < 1.87 at 5% significance level (orange line).

In figure 4 the *Mandel's k* statistic values are presented grouped for each laboratory (panel a) and, separately, for each sample (panel b). *Mandel's k* statistic values were calculated for all laboratories, except for lab 9, which provided a single measurement for each sample.
In the TC dataset, six outliers (lab/sample: 1/HR-1, 16/HR-2; 16/AT-1; 1/AT-2; 16/CH-2 and 16/FR-1) were identified of which two from lab 1 and the remaining 4 from the lab 16. Furthermore, seven stragglers (lab/sample: 1/HR-2; 1/CH-1; 14/CY-1; 16/CY-1; 16/CY-2; 3/FR-1 and 5 /FR-2) were identified of which two from lab 1 and two from lab 16. Only the outlying observation 16/AT-1 was confirmed as outlier by Cochran's test.

Panel a



Panel b

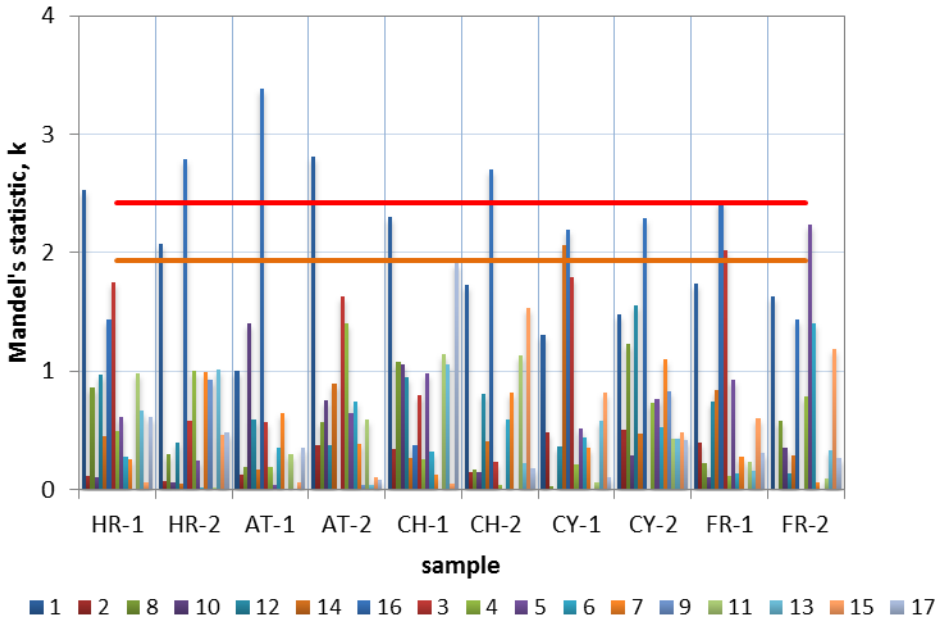


Figure 4. *Mandel's k* statistic values for within laboratory consistency on TC data, grouped by laboratory (panel a) and by sample (panel b). For 16 laboratories, *k* values should be < 2.42 at 1% significance level (red line) and < 1.93 at 5% significance level (orange line).

In conclusion, the outlying observations 16/CH-1, 16/CH-2 and 16/AT-1, confirmed as outliers by the statistical tests, were discarded from the dataset before further elaborations.

In general, the observed laboratory (between and within) inconsistencies did not depend on a specific sample (See panel b in figures 3 and 4). Localized sample heterogeneities/contaminations could not be excluded. But the prescribed scheme adopted to

distribute sub-samples to the laboratories is such that the occurrence of more stragglers or outliers for a single laboratory is indication of a poorer laboratory reproducibility or repeatability than that of the other laboratories.

From the retained values and for each sample separately, the mean value, the repeatability, s_r, and reproducibility, s_R, standard deviations were calculated. A dependence of precision upon the mean values was observed and the satisfactory weighted linear relationship has been established for both s_r and s_R as:

$s_r = 0.017 \times m + 0.227$;
and
$s_R = 0.038 \times m + 0.389$.

The smoothed values of s_r and s_R for the given m from the above relationship are reported as relative standard deviations in Table 4.

Table 4: Repeatability (s_r) and reproducibility (s_R) relative standard deviations for TC.

	General mean (µg/cm²)	s_r (%)	s_R (%)
HR-1	39.02	2.3	4.8
HR-2	27.75	2.5	5.2
AT-1	17.28	3.0	6.0
AT-2	16.97	3.1	6.1
CH-1	11.94	3.6	7.0
CH-2	5.43	5.9	10.9
CY-1	9.67	4.1	7.8
CY-2	7.90	4.6	8.7
FR-1	14.45	3.3	6.5
FR-2	10.43	3.9	7.5

3.1.2 Results: Method performance for EC/TC

Figure 5 shows the *Mandel's h* statistic values for EC/TC ratio calculated on the entire database and grouped for each sample. They revealed two distinct populations according to the used thermal protocol, i.e. NIOSH-like and EUSAAR_2, particularly for samples HR, CH and FR. In fact, most of the laboratories applying the NIOSH-like protocol showed negative *Mandel's h* statistic values, whereas laboratories applying the EUSAAR_2 protocol had positive *Mandel's h* statistic values. Consequently, the method performance statistics for EC/TC were evaluated separately for results from NIOSH-like protocol users and from EUSAAR_2 protocol users. Ten stragglers/outliers were identified when including all laboratories and both protocols.

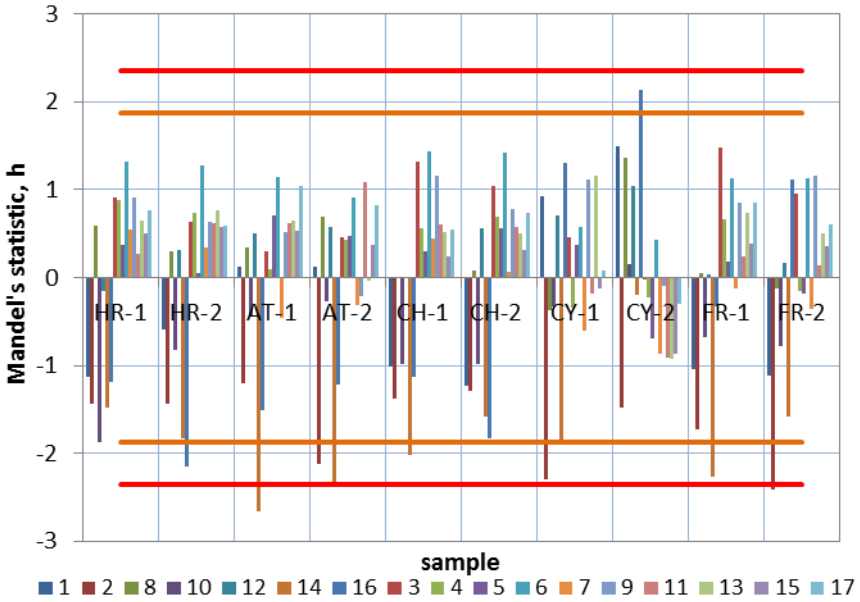
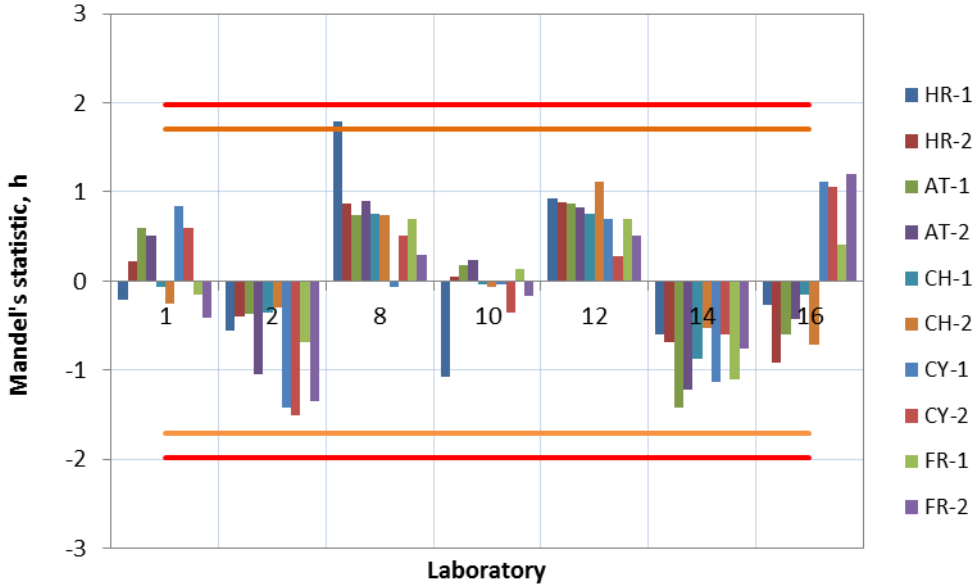


Figure 5. *Mandel's h* statistic values for between laboratory consistency on EC/TC ratio, grouped by sample. For 17 laboratories, *h* values should be < 2.35 at 1% significance level (red line) and < 1.87 at 5% significance level (orange line).

In figure 6 the *Mandel's h* statistic values for EC/TC ratio (grouped by laboratory) obtained from the NIOSH-like protocol users (panel a) and from the EUSAAR_2 protocol users (panel b) are presented. One straggler (lab/sample: 8/HR-1) was identified in the NIOSH-like EC/TC dataset and no outliers/stragglers in the EUSAAR_2 EC/TC dataset.
The identified straggler was not confirmed as straggler by the Grubbs' test G_1 when applied separately to results from NIOSH-like protocol users.
Comparing performances in figure 5 and figures 6 indicates an improved consistency (i.e. less variability) of the EC/TC dataset when a single thermal protocol is used. The number of outliers/stragglers is, in fact, much higher (i.e ten) when including all laboratories and both protocols.

In figure 7 the *Mandel's k* statistic values for EC/TC ratio (grouped by laboratory) obtained from the NIOSH-like protocol users (panel a) and from the EUSAAR_2 protocol users (panel b) are presented. In the EC/TC dataset from the NIOSH-like protocol, we identified four outliers (lab/sample: 8/HR-1; 8/CH-2; 1/CY-1 and 12/FR-2) and four stragglers (lab/sample: 16/HR-2; 16/AT-1; 1/CY-2; and 16/FR-1). Two outliers are from lab 8, and three stragglers from lab 16.
In the EC/TC dataset from the EUSAAR_2 protocol, two outliers (lab/sample: 9/HR-2; and 4/FR-1) and seven stragglers, of which three from lab 4 (lab/sample: 7/HR-1; 7/AT-1; 4/CH-1; 11/CY-1; 4 CY-2; 17/CY-2; and 4/FR-2) were identified.
Only two outliers (lab/sample: 8/HR-1 and 12/FR-2) were confirmed as straggler or outlier by Cochran's test when applied separately for results from NIOSH-like protocol users. These data have been discarded before further elaboration. No outlier was confirmed among the results from the EUSAAR_2 protocol users.

Panel a



Panel b

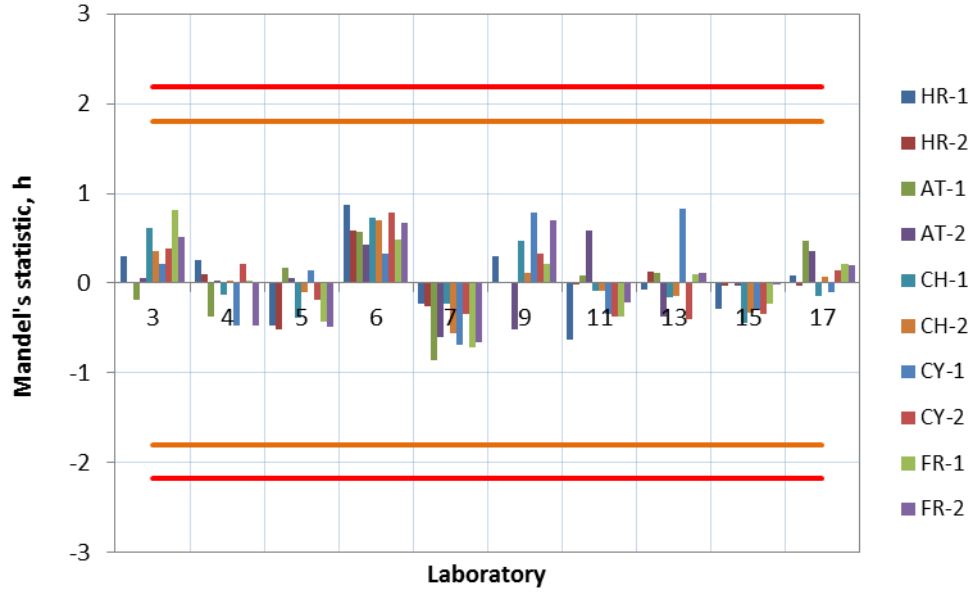
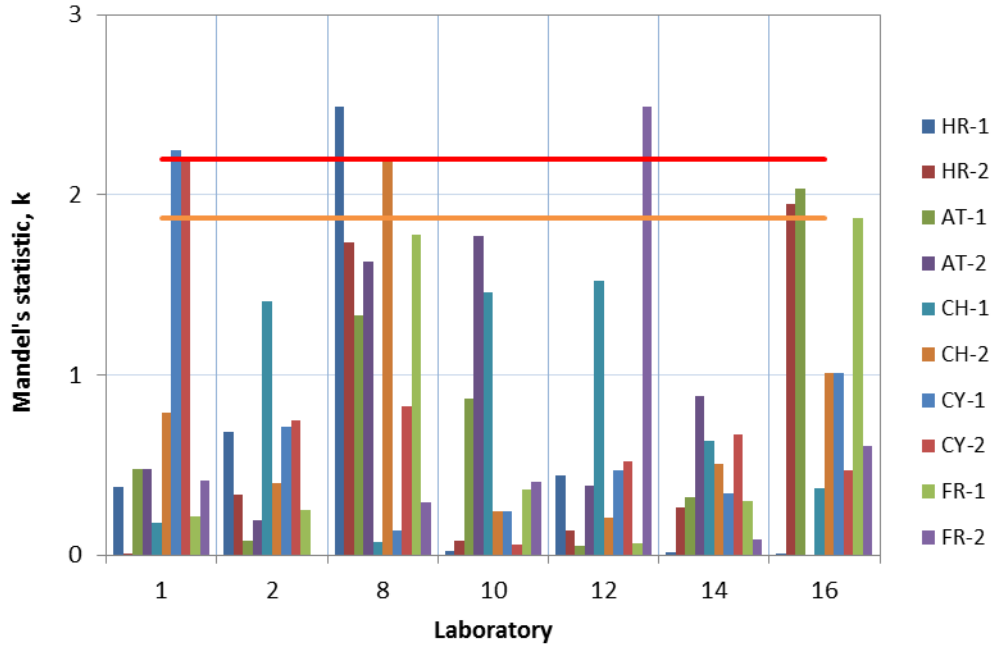


Figure 6. *Mandel's h* statistic values for between laboratory consistency on EC/TC ratio obtained from NIOSH-like protocol users (panel a) and from EUSAAR_2 protocol users (panel b), grouped by laboratory. For NIOSH-like protocol users (7 labs) *k* values should be < 1.98 at 1% significance level (red line) and < 1.71 at 5% significance level (orange line);for EUSAAR_2-protocol users (10 labs) *k* values should be < 2.18 at 1% significance level (red line) and < 1.80 at 5% significance level (orange line).

Panel a



Panel b

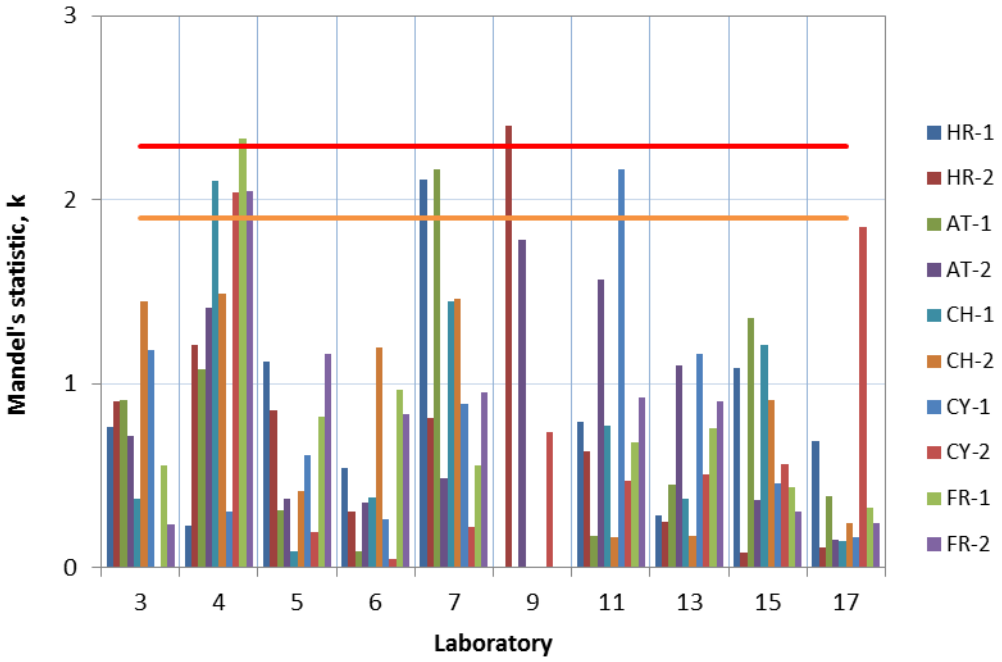


Figure 7. *Mandel's k* statistic values for within laboratory consistency on EC/TC ratio obtained from NIOSH-like protocol users (panel a) and from EUSAAR_2 protocol users (panel b), grouped by laboratory. For NIOSH-like protocol users (7 labs) *k* values should be < 2.20 at 1% significance level (red line) and < 1.87 at 5% significance level (orange line); for EUSAAR_2-protocol users (9 labs) *k* values should be < 2.29 at 1% significance level (red line) and < 1.90 at 5% significance level (orange line).

In general, the observed (between and within) laboratory inconsistencies did not depend on a specific sample. Localized sample heterogeneities/ contaminations cannot be excluded. But the prescribed scheme adopted to distribute sub-samples to the laboratories is such that the occurrence of more stragglers or outliers for a single laboratory indicates a poorer laboratory reproducibility/repeatability than that of the other laboratories.

From the retained values, for each sample and, separately for results from NIOSH-like protocol users and from EUSAAR_2 protocol users, the mean value, the repeatability, s_r, and reproducibility, s_R, standard deviations were calculated for EC/TC. The standard deviations s_r and s_R were not dependent on the EC/TC ratio and ranged (as relative standard deviations) from 2% to 10% and from 8% to 35%, respectively for the NIOSH-like protocol and from 2% to 14% and from 4% to 19% for the EUSAAR protocol over 9 of the 10 samples. Worse values for s_r and s_R were obtained for both protocols for the sample CY-2 because of a very low EC/TC ratio of 0.03 (see table 5 a and b). The higher values of s_R obtained for the NIOSH-like protocol could be caused by the number of variations of the NIOSH protocol used in this exercise as compared to the single version of the EUSAAR_2 protocol.

Table 5: Repeatability (s_r) and reproducibility (s_R) relative standard deviations for EC/TC obtained from NIOSH-like (a) and EUSAAR_2 (b) protocol users

a

NIOSH-like	General mean	s_r (%)	s_R (%)
HR-1	0.45	2.2	8.0
HR-2	0.38	6.2	14.3
AT-1	0.18	6.0	18.2
AT-2	0.22	2.2	21.9
CH-1	0.22	4.7	16.4
CH-2	0.19	9.8	22.6
CY-1	0.11	8.3	26.6
CY-2	0.05	11.7	55.5
FR-1	0.17	6.0	20.8
FR-2	0.11	8.6	34.6

b

EUSAAR_2	General mean	s_r (%)	s_R (%)
HR-1	0.56	2.1	4.0
HR-2	0.45	2.0	4.0
AT-1	0.21	3.0	6.7
AT-2	0.26	4.2	8.0
CH-1	0.30	2.9	7.4
CH-2	0.25	3.8	7.6
CY-1	0.12	9.2	13.4
CY-2	0.02	20.1	45.8
FR-1	0.22	3.6	9.0
FR-2	0.15	14.1	18.8

On average, the EC/TC ratios obtained by the EUSAAR_2 protocol were higher than those obtained by the NIOSH-like protocol by 23% (R2=0.98) when a transmittance was used to correct for pyrolysis. Four laboratories reported also EC/TC reflectance corrected, two

laboratories applying the NIOSH-like protocol and two applying the EUSAAR_2 protocol. Based on their results, the EC/TC ratios obtained by the EUSAAR_2 protocol were higher than those obtained by the NIOSH-like protocol by 30% (R2=0.98) when a reflectance was used to correct for pyrolysis. Furthermore, EC/TC reflectance-corrected ratios were, on average, higher than the transmittance-corrected ones by 14% (R2= 0.91) and by 20% (R2= 0.94) when the NIOSH-like protocol and the EUSAAR_2 protocol are used, respectively.

3.2 Laboratory performance: data evaluation description

- *Determining the assigned value*: Among the five methods described in the ISO 13528:2005(E) for determining the assigned value, the approach of the *consensus value from participants* was chosen, in absence of a reference or certified reference material. With this approach, the assigned value X for each test sample used in a round of proficiency testing scheme is the robust average calculated, with a recursive algorithm, from the results reported by all participant in the round (See ISO 13528:2005(E), Annex C).

- *Determining the standard deviation for proficiency assessment*: Among the five methods described in the ISO 13528:2005(E) for determining the standard deviation for proficiency assessment, σ*, the approach of calculating σ* *from data obtained in a round of a proficiency testing scheme* was chosen. With this approach, σ* is the robust standard deviation calculated, with a recursive algorithm, from the results reported by all participant in the round (See ISO 13528:2005(E), Annex C).
For TC, this approach was compared to that of the *prescribed value* derived from the requirement, i.e. DQO (i.e. expanded uncertainty, with a coverage factor of 2) of 25%, as in the EU Directive 2008/50/EC for PM at its limit value of 50 μg m^{-3}. Over the whole total carbon measurement range, σ* was calculated by linear interpolation between 12.5% at 199 μg cm^{-2} (corresponding at 50 μg m^{-3} when collected for 24h with a face velocity of 20.1 cm s^{-1}) and the limit of detection, i.e. 0.2 μg cm^{-2} at zero concentration level.
For EC/TC ratio, this approach was compared to that of a *perception value* defined as the level of performance that the inter-laboratory comparison coordinator would wish the participants to achieve, i.e. σ* of 15%.
For TC a single assigned value X and related σ* was calculated from the results of all participants, whereas for EC/TC ratio, two assigned values X and related σ* were calculated, i.e. from the results of participants applying the NIOSH protocol and, separately, from the results of those applying the EUSAAR_2 protocol.

- *z-score as estimate of each laboratory's bias*: *z*-scores were calculated to evaluate the capacity of the laboratory to comply with the limits defined by σ*.
The z-score is calculated as:

$$z = (x-X)/ \sigma^*$$

where x is the result from of the participant; X is the assigned value for the sample; and σ* is the standard deviation for proficiency assessment.
When a participant reports a result that gives rise to a bias greater than 3.0▪z or less than -3.0▪z, then the result is considered to give an "action signal". Likewise, a laboratory bias above 2.0▪ z or below -2.0▪z is considered to give a "warning signal". A laboratory bias between -2▪z and 2▪z is indication of a satisfactory performance.

Results can also be interpreted as percentage deviation from the assigned value, 100(x-X)/X. Thus, the warning and action signals, calculated as <-200▪σ*/X% and >200▪σ*/X%, <-300▪σ*/X% and >300▪σ*/X%, respectively, provide the percentage deviations from the assigned value corresponding to z-scores of – /+ 2 and -/+ 3.

3.2.1 Results: Laboratory performance for TC

The assigned values X, and the related standard deviations for proficiency assessment, σ*, calculated on the entire database for each sample, are reported in Table 3 of Annex 1. Following ISO13528, σ* were calculated i) *from data obtained in a round of a proficiency testing scheme,* σ^*_a and ii) from the *prescribed* DQO of 25% given for PM at its limit value of 50 μg m^{-3}, σ^*_b. For all assigned values, σ^*_a were smaller than σ^*_b.

Figure 8 shows z-scores calculated using σ^*_a. z-Scores less than -3 and greater than 3 indicate that the reported values deviated from the assigned value for more than +/- 14.8% for HR-1, 18.8% for HR-2, 19% for AT-1, 15.4% for AT-2, 19.9% for CH-1, 27.4% for CH-2, 13.1% for CY-1, 27.6% for CY-2, 21.7% for FR-1 and 27.0% for FR-2.

z-Scores less than -2 and greater than 2 indicated that the reported values deviated from the assigned value for more than +/- 9.8% for HR-1, 12.5% for HR-2, 12.6% for AT-1, 10.2% for AT-2, 13.2% for CH-1, 18.2% for CH-2, 8.7% for CY-1, 18.4% for CY-2, 14.4% for FR-1 and 18.0% for FR-2.

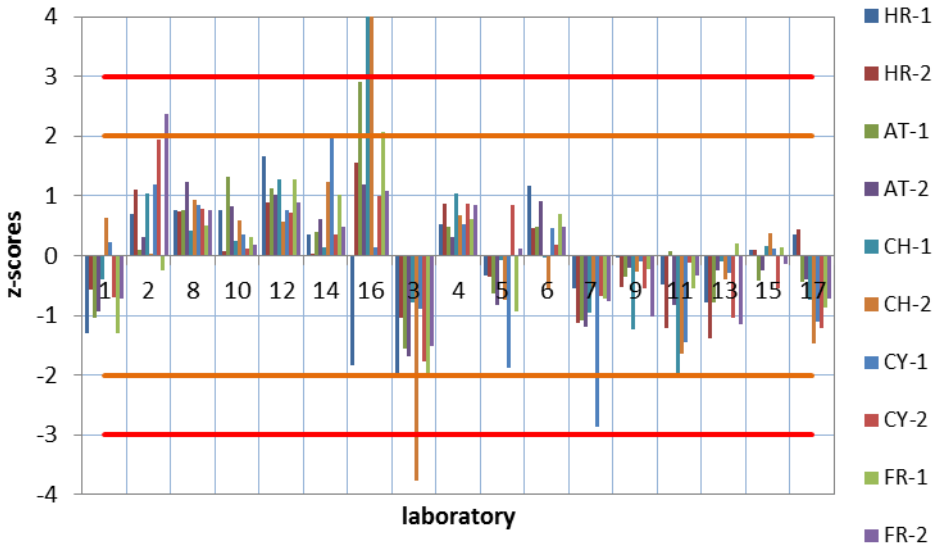


Figure 8. z-Scores for TC calculated using σ* *from data obtained in a round of a proficiency testing scheme*.

In the TC database, three outliers (lab/sample: 16/CH-1; 16/CH-2; and 3/CH-2) and six stragglers (lab/sample: 16/AT-1; 11/CH1; 14/CY-1; 7/CY-1; 16-FR-1 and 2/FR-2) were identified. Two outliers and two stragglers are from lab 16. For all samples, at least 11 laboratories showed deviation from the assigned values within +/- 1 σ^*_a (i.e. within 1 z-score).

For comparison, when applying σ^*_b, outliers were confirmed as not-complying with the directive DQO, whereas stragglers were identified as satisfactory values.

3.2.2 Results: Laboratory performance for EC/TC

The assigned values, X, and the related standard deviations for proficiency assessment, σ*, calculated separately from the results from NIOSH-like protocol and from EUSAAR_2 protocol for each sample, are reported in Table 4 and 5 of Annex 1. Following ISO13528, σ* were calculated *from data obtained in a round of a proficiency testing scheme*.

Figure 9 shows the z-scores calculated for the NIOSH-like protocol users (panel a) and, separately, for the EUSAAR_2 protocol user (panel b).

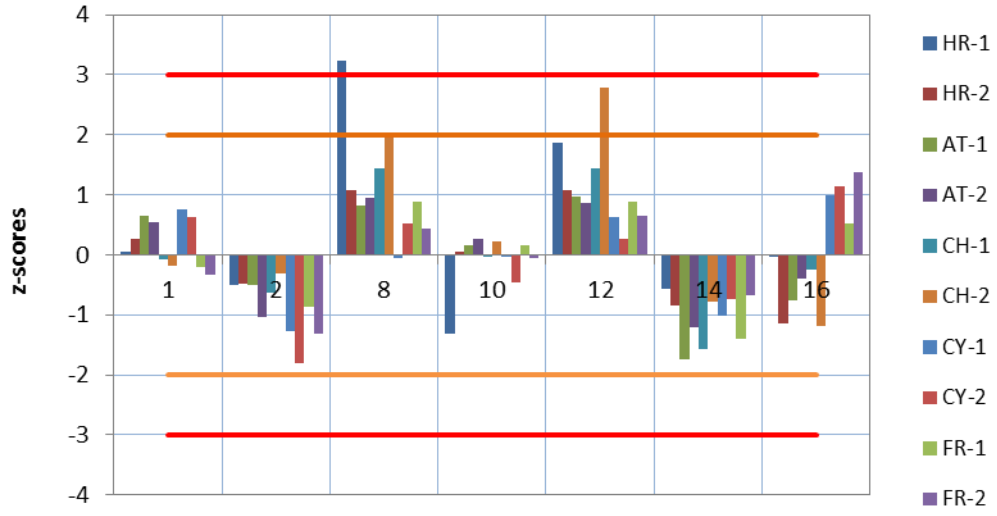
For NIOSH-like protocol users, z-scores less than -3 and greater than 3 indicated that the reported value deviated from the assigned value for more than +/- 21% for HR-1, 44% for HR-2, 51% for AT-1, 72% for AT-2, 44% for CH-1, 44% for CH-2, 86% for CY-1, 157% for CY-2, 67% for FR-1 and 114% for FR-2. Z-scores less than -2 and greater than 2 indicated that the reported values deviated from the assigned value for more than +/- 14% for HR-1, 29% for HR-2, 34% for AT-1, 48% for AT-2, 29% for CH-1, 29% for CH-2, 57% for CY-1, 104% for CY-2, 45% for FR-1 and 76% for FR-2.

For EUSAAR_2 protocol users, z-scores less than -3 and greater than 3 indicated that the reported value deviated from the assigned value for more than +/- 10% for HR-1, 4% for HR-2, 14% for AT-1, 23% for AT-2, 13% for CH-1, 13% for CH-2, 33% for CY-1, 133% for CY-2, 27% for FR-1 and 42% for FR-2. z-Scores less than -2 and greater than 2 indicated that the reported values deviated from the assigned value for more than +/- 7% for HR-1, 3% for HR-2, 9% for AT-1, 15% for AT-2, 9% for CH-1, 8% for CH-2, 22% for CY-1, 89% for CY-2, 18% for FR-1 and 28% for FR-2.

One straggler (lab/sample: 12/CH-2) and one outlier (lab/sample: 8/HR-1) were identified in the subset of data from the NIOSH protocol. Five stragglers (7/HR-2; 7/AT-1; 3/CH-1; 9/CH-1; 7/CH-2) and four outliers (lab/sample: 5/HR-2; 6/HR-2; 6/CH-1 and 6/ CH-2) have been identified in the subset of data from the EUSAAR_2 protocol.

For all samples, at least four out of seven NIOSH-like protocol users and seven out of ten EUSAAR_2 protocol users showed deviation from the assigned values within +/- 1 σ* (i.e. within 1 z-score).

Panel a



Panel b

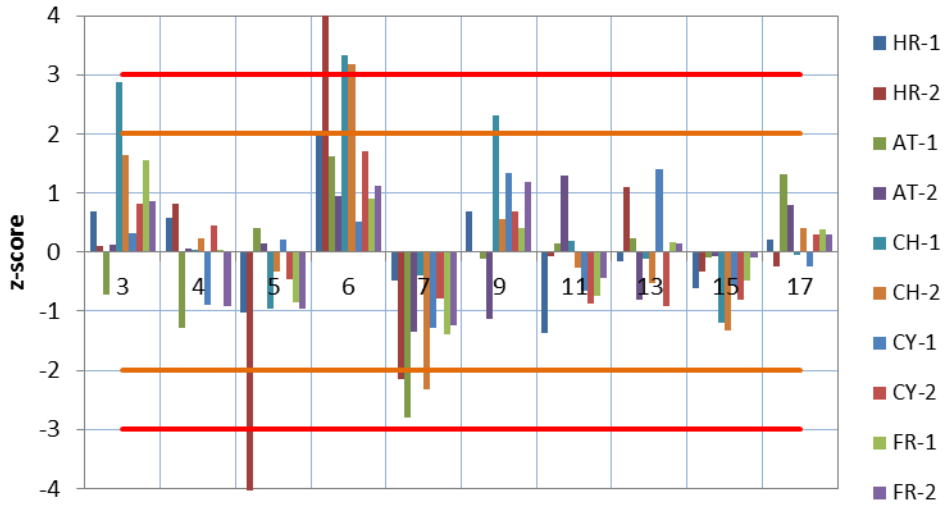
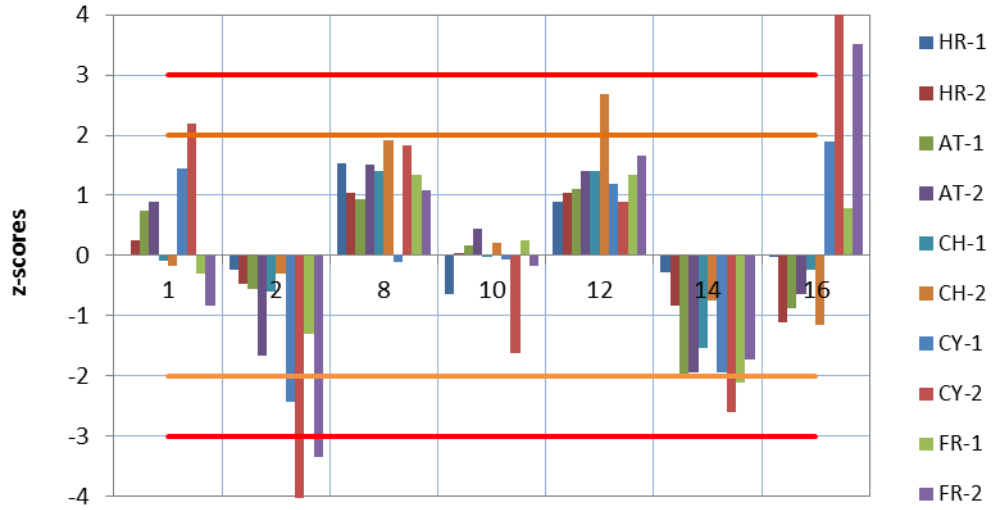


Figure 9. z-Scores for EC/TC ratio calculated using σ* *from data obtained in a round of a proficiency testing scheme* for the NIOSH-like protocol data sub-set (panel a) and the EUSAAR_2 protocol data sub-set (panel b).

Laboratory performances were evaluated, separately on the two data subsets, using as σ* a common level of performance that the inter laboratory comparison coordinator would wish participants to achieve, i.e. 15% (Figure 10). Under this condition, four outliers (2/CY-2; 16/CY-2; 2/FR-2 and 16/FR-2) and five stragglers (12/CH-2; 2/NPL; 1/CY-2; 14/CY-2; and 14/FR-1) were identified in the subset of data from the NIOSH-like protocol whereas one outlier (lab/sample: 7/CY-2) and six stragglers (lab/sample: 3, 7, 9, 11, 13, 15/CY-2), all of them at sample CY-2, were identified in the subset of data from the EUSAAR_2 protocol. Note that sample CY-2 had a very low EC/TC mean value (including all laboratories) of 0.03.

Panel a



Panel b

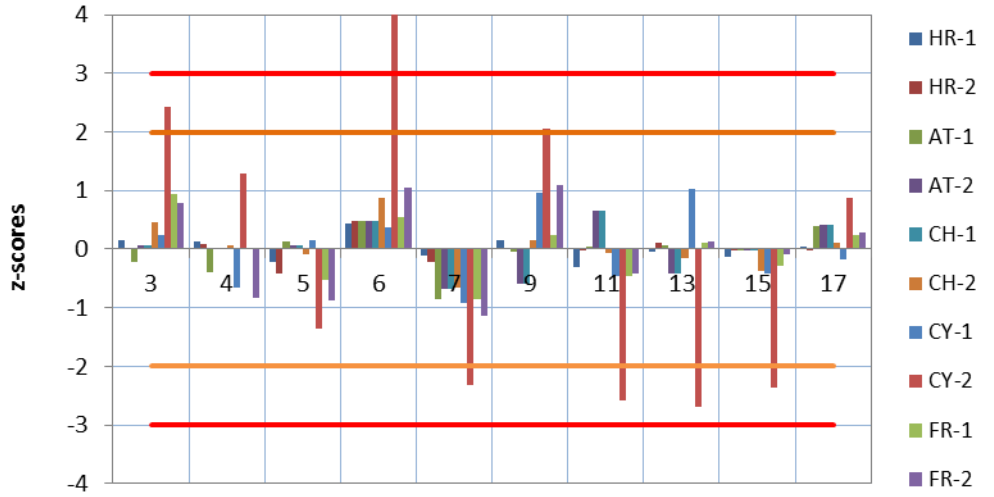


Figure 10. z-Scores for EC/TC ratio calculated using σ* *by perception, 15%* for the NIOSH-like protocol data sub-set (panel a) and the EUSAAR_2 protocol data sub-set (panel b).

4 Conclusions

The second AQUILA inter-laboratory comparison on the measurement of total carbon, organic carbon and elemental carbon was performed in 2011. The comparison involved 17 participants, all applying thermal-optical analysis (using the same type of analyzer from Sunset Laboratory Inc.) but two different analytical protocols, NIOSH (and variation of it) and EUSAAR_2.

Based on method performance statistics (i.e. *Mandel*'s *h* and *k* parameters and the G_1-Grubbs' and Cochran's statistical tests), good consistency was found for TC, although two outliers for reproducibility and one outlier for repeatability were identified (all from the same laboratory). For EC/TC, two outliers for repeatability were identified in the NIOSH-like protocol data sub-set. In general, the observed laboratory inconsistencies did not depend on a specific sample. Localized sample heterogeneities/contaminations could however not be excluded, but the prescribed scheme adopted to distribute sub-samples to the laboratories was such that the occurrence of more stragglers or outliers for a single laboratory is indication of a poorer laboratory reproducibility/repeatability than that of the other laboratories.
After elimination of these outliers, repeatability and reproducibility ranged (as relative standard deviation) for TC from 2% to 6% and from 5% to 11%, respectively. For EC/TC ratio repeatability and reproducibility ranged (as relative standard deviation) from 2% to 10% and from 8% to 35%, respectively for the NIOSH-like protocol and from 2% to 14% and from 4% to 19% for the EUSAAR_2 protocol. The higher values of s_R obtained for the NIOSH-like protocol could be at least partly caused by the number of variations of the NIOSH protocol used in this exercise as compared to the single version of the EUSAAR_2 protocol.

Furthermore, it was shown – based on z-scores – that three outliers were identified in the TC database when applying as the *standard deviation for proficiency assessment* calculated *from data obtained in a round of a proficiency testing scheme.* These outliers would also not comply with the DQO (i.e. expanded uncertainty, with a coverage factor of 2) of 25%, as in the EU Directive 2008/50/EC for PM at its limit value of 50 µg m^{-3}.
Laboratory performances were evaluated for EC/TC ratio, from the two data subsets provided by the NIOSH and EUSAAR_2 protocol users separately, using as σ* a common level of performance (i.e. 15%), that the inter-laboratory comparison coordinator would wish participants to achieve. Under this condition, four results were identified as outliers in the subset of data from the NIOSH-like protocol users, whereas one outlier was detected in the subset of data from the EUSAAR_2 protocol.

On average, the EC/TC ratios obtained by the EUSAAR_2 protocol were higher than those obtained by the NIOSH-like protocol by 23% (R2=0.98) when a transmittance was used to correct for pyrolysis. Whereas, the EC/TC ratios obtained by the EUSAAR_2 protocol were higher than those obtained by the NIOSH-like protocol by 30% (R2=0.98) when a reflectance was used to correct for pyrolysis (based on results from four laboratories only). Furthermore, EC/TC reflectance-corrected ratios were, on average, higher than the transmittance-corrected ones by 14% (R2= 0.91) and by 20% (R2= 0.94) when the NIOSH-like protocol and the EUSAAR_2 protocol are used, respectively.

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Annex 1.All results

Table 1: Total carbon (µg/cm^2) (only for sake of brevity results have been rounded to two decimal digits)

	HR-1	HR-2	AT-1	AT-2	CH-1	CH-2	CY-1	CY-2	FR-1	FR-2
1	35.34 37.3	27.60 25.91	16.39 16.11	15.97 16.42	11.34 12.05	6.17 5.60	9.86 9.77	7.34 7.37	13.19 12.98	9.52 9.97
2	40.39 40.53	29.70 29.63	17.59 17.39	17.40 17.19	12.93 12.75	5.55 5.62	10.43 10.01	9.10 9.42	14.03 14.34	12.65
3	36.32 34.25	26.27 25.62	16.11 15.22	16.01 15.10	11.18 11.60	3.61 3.72	8.57 10.11	6.58	11.58 13.15	9.26 8.76
4	39.8 40.4	29.8 28.7	18.0 17.8	17.7 16.9	12.9 12.8	5.91 5.93	9.85 10.0	8.26 8.73	15.1 15.0	10.9 11.5
5	38.12 38.85	27.28 27.01	16.71 16.65	16.48 16.12	12.22 11.70	5.19 5.19	9.14 8.70	8.22 8.71	13.12 13.84	11.29 9.76
6	41.56 41.23	28.52 28.54	17.64 18.19	17.59 18.01	11.91 12.08	5.14 5.43	9.73 10.10	8.15 7.82	15.12 15.23	11.36 10.40
7	37.91 38.21	26.34 25.23	16.69 15.68	16.08 15.86	11.22 11.39	5.10 5.50	8.65 8.35	7.72 7.02	13.81 13.59	9.73 9.69
8	41.09 40.07	28.87 29.2	18.07 18.36	18.25 17.93	12.63 12.06	6.09 6.01	10.07 10.09	8.03 8.81	15.06 14.89	10.94 11.34
9	39.06	27.35 26.32	16.99	16.84 16.82	11.03	5.44	9.68	7.19 7.72	14.21	9.47
10	40.66 40.53	27.83 27.9	19.92 17.73	17.53 17.95	11.93 12.49	5.84 5.91	9.86 9.87	7.85 8.03	14.81 14.73	10.48 10.72
11	38.78 37.61	25.63 25.61	17.22 17.68	16.46 16.13	10.11 10.71	5.01 4.46	9.08 9.13	7.90 7.63	13.78 13.95	10.08 10.14
12	42.93 41.77	29.52 29.08	18.16 19.08	17.80 18.01	13.27 12.77	6.06 5.67	9.89 10.20	7.89 8.88	16.06 15.48	11.29 11.20
13	37.21 38.01	25.91 24.78	16.51 16.52	16.78 16.80	11.66 12.22	5.43 5.32	9.85 9.35	7.24 6.97	14.71 14.59	9.22 9.45
14	39.56 40.10	27.75 27.80	17.69 17.95	17.30 17.80	12.05 12.19	6.10 6.30	11.47 9.70	7.97 8.27	15.18 15.83	10.77 10.97
15	39.34 39.27	28.18 27.66	16.98 16.88	16.82 16.77	12.15 12.13	5.39 6.13	10.12 9.41	7.31 7.61	14.83 14.36	9.88 10.68
16	34.75 36.46	28.91 32.02	17.93 23.23	18.05	18.78 18.58	10.22 8.91	10.72 8.84	7.85 9.31	15.66 17.55	10.94 11.92
17	39.44 40.16	28.24 28.78	17.16 16.61	16.64 16.68	10.92 11.93	4.87 4.87	9.30 9.21	7.11 6.84	13.41 13.65	9.65 9.84

Table 2: Elemental carbon / total carbon (only for sake of brevity results have been rounded to two decimal digits)

	HR-1	HR-2	AT-1	AT-2	CH-1	CH-2	CY-1	CY-2	FR-1	FR-2
1	0.46 0.45	0.39 0.39	0.20 0.21	0.25 0.25	0.22 0.22	0.16 0.18	0.12 0.15	0.07 0.05	0.16 0.16	0.09 0.10
2	0.42 0.45	0.35 0.36	0.17 0.17	0.21 0.21	0.19 0.21	0.17 0.18	0.06 0.07	0.01 0.00	0.13 0.14	 0.06
3	0.58 0.57	0.45 0.46	0.20 0.21	0.26 0.27	0.33 0.34	0.26 0.28	0.11 0.13	 0.03	0.25 0.26	0.17 0.16
4	0.57 0.57	0.45 0.47	0.20 0.21	0.25 0.27	0.28 0.31	0.25 0.27	0.11 0.11	0.02 0.04	0.21 0.24	0.10 0.16
5	0.55 0.53	0.42 0.43	0.22 0.22	0.26 0.27	0.28 0.28	0.25 0.25	0.12 0.13	0.02 0.02	0.20 0.21	0.11 0.14
6	0.60 0.59	0.48 0.49	0.23 0.23	0.28 0.28	0.34 0.34	0.28 0.30	0.13 0.12	0.04 0.04	0.25 0.23	0.16 0.18
7	0.57 0.54	0.44 0.45	0.18 0.20	0.24 0.23	0.28 0.30	0.24 0.22	0.10 0.11	0.01 0.02	0.19 0.20	0.14 0.11
8	0.51 0.60	0.47 0.41	0.20 0.22	0.27 0.28	0.27 0.27	0.20 0.26	0.11 0.11	0.06 0.06	0.21 0.19	0.13 0.12
9	0.58	0.44 0.47	0.21	0.22 0.25	0.33	0.26	0.14	0.03 0.03	0.23	0.17
10	0.41 0.41	0.38 0.38	0.18 0.19	0.24 0.23	0.23 0.21	0.18 0.19	0.11 0.11	0.04 0.04	0.17 0.17	0.12 0.10
11	0.54 0.53	0.45 0.46	0.21 0.22	0.30 0.27	0.30 0.29	0.25 0.25	0.13 0.09	0.01 0.02	0.20 0.21	0.12 0.15
12	0.50 0.52	0.44 0.44	0.21 0.21	0.27 0.27	0.26 0.28	0.25 0.25	0.13 0.13	0.06 0.05	0.20 0.20	0.10 0.18
13	0.56 0.56	0.46 0.46	0.21 0.22	0.25 0.24	0.30 0.29	0.25 0.25	0.15 0.13	0.01 0.02	0.23 0.22	0.14 0.16
14	0.43 0.43	0.33 0.34	0.13 0.13	0.16 0.15	0.18 0.17	0.17 0.15	0.07 0.08	0.03 0.03	0.11 0.12	0.08 0.08
15	0.56 0.54	0.45 0.45	0.22 0.21	0.26 0.26	0.29 0.27	0.25 0.23	0.12 0.11	0.02 0.01	0.21 0.21	0.14 0.15
16	0.45 0.45	0.35 0.28	0.17 0.14	0.2	0.21 0.22	0.14 0.16	0.15 0.13	0.08 0.07	0.17 0.20	0.18 0.16
17	0.57 0.56	0.45 0.45	0.22 0.23	0.28 0.28	0.29 0.30	0.26 0.26	0.12 0.11	0.03 0.02	0.23 0.23	0.16 0.15

Table 3: Assigned values and standard deviations for proficiency assessment, σ*(*from data obtained in a round of a proficiency testing scheme)* for TC.

	HR-1	HR-2	AT-1	AT-2	CH-1	CH-2	CY-1	CY-2	FR-1	FR-2
Assigned value, X	39.13	27.74	17.38	17.01	12.01	5.57	9.72	7.86	14.45	10.42
Standard deviation, σ*	1.92	1.74	1.10	0.87	0.80	0.51	0.42	0.72	1.04	0.94
Standard uncertainty of X	0.56	0.53	0.33	0.26	0.24	0.15	0.13	0.22	0.32	0.28

Table 4: Assigned values and standard deviations for proficiency assessment, σ*(*from data obtained in a round of a proficiency testing scheme)* for EC/TC from NIOSH-like protocol data set.

	HR-1	HR-2	AT-1	AT-2	CH-1	CH-2	CY-1	CY-2	FR-1	FR-2
Assigned value, X	0.45	0.38	0.18	0.22	0.22	0.18	0.11	0.05	0.17	0.11
Standard deviation, σ*	0.03	0.06	0.03	0.05	0.03	0.03	0.03	0.02	0.04	0.04
Standard uncertainty of X	0.02	0.03	0.01	0.03	0.02	0.01	0.01	0.01	0.02	0.02

Table 5: Assigned values and standard deviations for proficiency assessment, σ*(*from data obtained in a round of a proficiency testing scheme)* for EC/TC from EUSAAR_2 protocol data set.

	HR-1	HR-2	AT-1	AT-2	CH-1	CH-2	CY-1	CY-2	FR-1	FR-2
Assigned value, X	0.56	0.45	0.21	0.26	0.30	0.25	0.12	0.02	0.22	0.15
Standard deviation, σ*	0.02	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.02	0.02
Standard uncertainty of X	0.01	0.00	0.00	0.29	0.32	0.00	0.01	0.00	0.01	0.01

Annex 2. Justifications from participants regarding laboratory performance

Laboratory 3:
Upon reception of the samples (ACTRIS and AQUILA), the analysis was performed using as standards our sucrose as well as the phalate provided by JRC with very good recoveries. After the analysis of the samples a new calibration curve was done by diluting the phalate to low C levels (down to 0.7ugC) and a very good regression line was obtained with slope (experimental/theoretical values) of 0.97 and correlation coefficient r2 of 0.999.
In a communication with Dr. Cavalli she revealed us differences for several of our samples on average 12% (UoC values lower than 12%) and suggested the use of CO2. We ordered a new CO2 bottle and a new calibration curve was performed giving a slightly different slope: experimental value = 0.99 theoretical -0.8462, r2= 0.999. By applying the CO2 calibration curve, the differences between the old and new values become 9% for Actris samples (1.05-1.15) to 1.12 for AQUILA (1.06-1.20). We consider these changes as maximum as using phthalate provided by JRC or sucrose as standard changes are less than 4%.
Thus calibration issues cannot explain differences up to 35%. Factors such as sample in homogeneity or OC losses during transport should be also taken into consideration.

Laboratory 16:
After analyzing the intercomparison report we decided to review our procedures to determine the causes of the discrepancies verified in our results. We carefully retraced our steps and concluded that we had the b quality control problems with the blanck/zero.
The discrepancies are related with the preparation of the standard solution with milli Q water that contained a high amount of TOC, which then led to these disappointing results. In spite of this fact, the intercomparison allowed us to address some quality control issues that occurred and be aware in future COCE determinations.

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Abstract

The EC-JRC European Reference Laboratory for Air Pollution (ERLAP) has organized an inter-laboratory comparison for the measurement of total carbon (TC), elemental carbon (EC) and organic carbon (OC) in particulate matter collected on filters.
To this comparison seventeen European Union National Reference Laboratories for air quality or delegated organizations participated, all using thermal optical analysis with the same analyzer (Sunset Lab off-line carbon analyzer).

The aim of this comparison was to evaluate the performances of participants but also to study the effects of applying different thermal protocols, i.e. NIOSH and EUSAAR_2 protocols, currently in use in Europe for such analysis.

In absence of a general consensus by the scientific community on the definition of a reference material for EC and, thus, of a standard analytical method, method performances [ISO5725-2] and laboratory performances [ISO 13528:2005(E)] were evaluated for TC and EC/TC ratio in the present comparison exercise.

For TC, repeatability and reproducibility relative standard deviations ranged from 2% to 6% (s_r = 0.017 × m + 0.227) and from 5% to 11% (s_R = 0.038 × m + 0.389), respectively.
For EC/TC ratio, repeatability and reproducibility relative standard deviations ranged from 2% to 10% and from 8% to 35%, respectively for the NIOSH-like protocol, and from 2% to 14% and from 4% to 19%, respectively for the EUSAAR protocol. (No satisfactory dependence was found upon EC/TC ratio).

Furthermore, based on z-scores, three outliers were identified in the TC database when applying as *standard deviation for proficiency assessment,* σ*, that one calculated *from data obtained in a round of a proficiency testing scheme.* These outliers would also not comply with the DQO (i.e. expanded uncertainty, with a coverage factor of 2) of 25%, as in the EU Directive 2008/50/EC for PM at its limit value of 50 μg m^{-3}.

Laboratory performances were evaluated for EC/TC ratio, separately on the two data subsets from the NIOSH and EUSAAR_2 protocols using as σ* a common level of performance (i.e. 15%) that the inter-laboratory comparison coordinator would wish participants to achieve. Under this condition, four outliers were identified in the subset of data from the NIOSH-like protocol and one outlier in the subset of data from the EUSAAR_2 protocol.

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