EMEP/CCC-Report 1/2013

EMEP Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe

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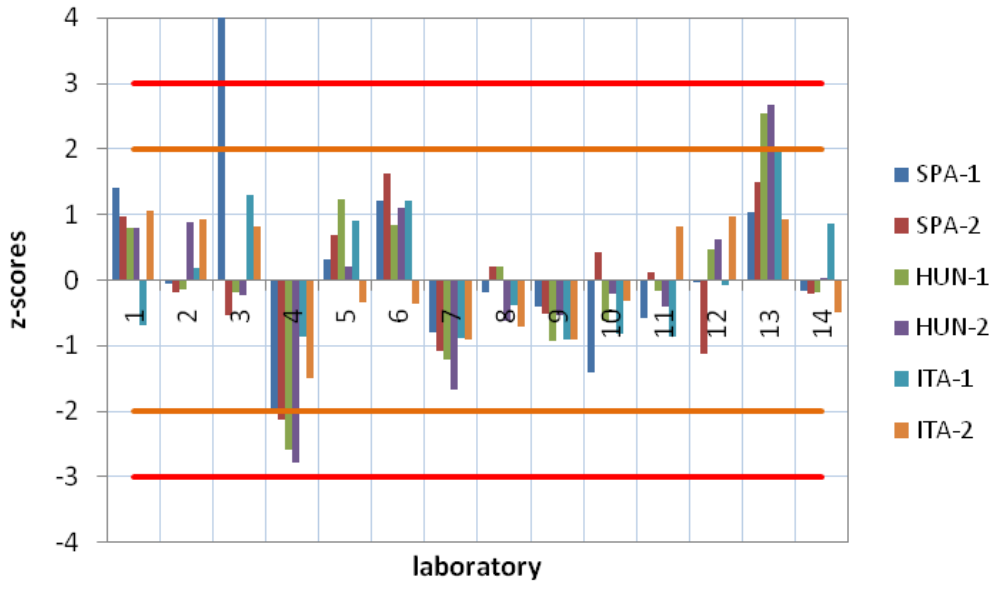

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Availability and quality of the EC and OC measurements within EMEP, including results of the fourth interlaboratory comparison of analytical methods for carbonaceous particulate matter within EMEP (2011)

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Contents

Page

Summary

Twelve sites reported concentrations of elemental carbon (EC) and organic carbon (OC) in atmospheric particulate matter to EBAS for 2010, which is the last year for which data from the EMEP (European Monitoring and Evaluation Program) monitoring network has been officially reported. Eleven of the twelve sites quantified EC and OC according to a thermal-optical method protocol. Further, ten of these twelve sites followed the recommended EUSAAR_2 analytical protocol, being an important step towards harmonized and comparable data for EC and OC within EMEP. The reported data were produced by 10 different institutes.

With the support of the EC funded project ACTRIS (Aerosol, Clouds and Trace Gas Research Infrastructure Network), the fourth interlaboratory comparison of analytical methods for carbonaceous particulate matter within EMEP was performed in 2011–2012. Fourteen laboratories responsible for ongoing, or in progress, measurement of OC, EC and TC at EMEP stations participated, applying the thermal or thermal-optical protocols they use on a regular basis for these analyses. The aim of the current comparison was to evaluate the performance of the methods and the participants according to the reference methods [ISO5725-2] and [ISO 13528:2005(E)], respectively.

In absence of suitable reference materials, the current inter comparison exercise was based on a test solution prepared by the Joint Research Centre of the European Commission (JRC), and test filter samples collected at three EMEP sites across Europe. Filter homogeneity was determined from dedicated filters sampled with each sampler.

For the determination of TC in test filters, the repeatability standard deviation (s_r) and reproducibility relative standard deviation (s_R) ranged from 3% to 6% and from 13% to 28%, respectively.

For EC/TC ratios in test filters, repeatability and reproducibility relative standard deviations ranged from 4% to 16% and from 12% to 33%, excluding methods with no optical correction for charring. The highest values of s_r and s_R for both TC and EC/TC were obtained for the test filters collected at IT04, which had high TC contents and low EC/TC values, rendering accurate analyses more difficult. However, the possibility that the test filters from IT04 used for the inter-comparison were less homogeneous than the filter dedicated to the homogeneity study cannot be completely excluded.

The study of the laboratories' performances with respect to determining TC in the test filters revealed one to three outliers, depending on the method applied to establish the *standard deviation for proficiency assessment* (σ*) used to calculate z-scores.

Regarding laboratories' performances in determining EC/TC ratios in the test filters, three outliers were also identified when using σ* = 15%, the common level

of performance that the interlaboratory comparison coordinator wished participants to achieve.
Three participants produced several outliers. These laboratories should carefully examine their procedures (i.e. in particular determination and verification of the calibration constant, checking the accuracy of the optical correction of charring) and identify appropriate corrective actions that are likely to prevent the recurrence of such results.

Availability and quality of the EC and OC measurements within EMEP, including results of the fourth interlaboratory comparison of analytical methods for carbonaceous particulate matter within EMEP (2011)

1. Introduction

Organic carbon (OC) and elemental carbon (EC) are prominent constituents of airborne particulate matter (PM) from the perspectives of health risks due to inhalation, impacts on climate change, and as indication of air pollution sources. These are reasons why the Quality Directive 2008/50/EC requires measurement of EC and OC in $PM_{2.5}$ at rural background locations in Europe. The 2010-2019 strategy of EMEP (European Monitoring and Evaluation Program) lists EC and OC (in PM_{10}) as core variables for the same reasons and has included these variables at EMEP level 2 sites.

The present report documents the current status of sampling and measurements of EC and OC as reported to EMEP for the year 2010, as well as the quality of EC and OC measurements within the EMEP monitoring network. The latter includes fourteen laboratories responsible for ongoing (i.e. those reporting for 2010), or in progress (those who have submitted data to EBAS for 2011 or plan to do so in the near future), measurement of OC, EC and TC at stations within the EMEP monitoring network, and which apply thermal-optical or thermal protocols for these analyses.

To assess the data comparability and get a picture of the method and laboratories' performance, interlaboratory comparisons have been organized by the Joint Research Centre of the European Commission (JRC) in agreement with the EMEP Chemical Coordinating Centre (CCC) at the Norwegian Institute for Air Research (NILU). So far four interlaboratory comparisons have been arranged. The present report is based on the 4th exercise organized in 2011-2012 with the support of the project ACTRIS funded by the European Commission.

2. Status of sampling and measurements of carbonaceous matter in PM within the EMEP network - 2010

The lack of comparable EC and OC data in Europe has hampered the possibility addressing the spatial and temporal variation of these variables on the regional scale. Exceptions are the EMEP EC and OC campaign (Yttri et al., 2007), and the CARBOSOL project (Pio et al., 2007), with data for the period 2002–2004, which can be used for such a purpose. More recent measurements are needed to get an overview of the current situation, and to validate the progress made with respect to model development.

An increased number of countries and sites have started reporting levels of EC and OC following the development of the EUSAAR protocol. Twelve sites

reported measurements of EC and OC for 2010, which is the most recent year of officially reported data, and which are two more than for 2009. See Table 2.1 for all sites reporting levels of EC and OC for 2010. In addition, total carbon (TC) was reported for the Hungarian site K-puszta (HU02). Note though that EC and OC data for the Slovenian site Iskrba (SI08) and the Polish site Diabla Gora (PL05) for 2010 are reported in Hjellbrekke and Fjæraa (2010) only and are not included in Table 2.1 for that reason.

We recognize that the quality of the EC and OC data reported to EMEP has improved with respect to sampling time and sampling frequency; i.e. these parameters are the same for consecutive years, which substantially reduces the uncertainties when comparing data from one year to the other. Also the data capture has improved, and the datasets include year-round measurements, making it possible to study seasonal variability.

Eleven of the twelve sites listed in Table 2.1 quantified EC and OC according to a thermal-optical method protocol. Further, ten of these twelve sites followed the recommended EUSAAR_2 analytical protocol, being an important step towards harmonized and comparable data for EC and OC within EMEP. A detailed description of the EUSAAR_2 protocol and its performance can be found in Cavalli et al. (2010). A SOP for EC and OC measurements has been finalized for inclusion in the EMEP manual, but has not yet been made available electronically. Effort concerning how to handle samples which are impacted by carbonate carbon are currently undertaken within the EU-funded project ACTRIS. Guidelines for how to deal with such samples will be developed based on the results obtained in ACTRIS and will subsequently be added to the SOP for EC and OC analyses.

Table 2.1: Sites reporting EC and OC for 2010, including size fractions and sampling period.

Site (Country)	EC	OC	PM_1	$PM_{2.5}$	PM_{10}	Period
Aspvreten (Sweden)	x	x			x	2008, 2009, 2010
Birkenes (Norway)	x	x		x	x	2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010
Finokalia (Greece)	x	x			x	2008, 2009, 2010
Harwell (UK)	x	x			x	2009, 2010
Hurdal (Norway)	x	x		x	x	2010,
Ispra (Italy)	x	x		x		2002[1)], 2003[2)], 2004[2)], 2005[2)], 2006, 2007, 2008, 2009, 2010
Košetice (Czech Rep.)	x	x		x		2009, 2010
Kårvatn (Norway)	x	x		x	x	2010
Melpitz (Germany)	x	x		x	x	2006, 2007, 2008, 2009, 2010
Montseny (Spain)	x	x		x	x	2007, 2008, 2009, 2010
Puy de Dôme (France)	x	x		x		2008, 2009, 2010
Vavihill (Sweden)	x	x			x	2008, 2009, 2010

1. EMEP EC and OC campaign
2. Both $PM_{2.5}$ and PM_{10}.

The EUSAAR_2 protocol has already been used for other site categories than rural background, and is one of the candidate methods to be tested for a standardized method for EC and OC measurements within CEN. With EMEP adopting the EUSAAR_2 protocol, we hope the experiences made by the EMEP community, and by others, will be a valuable asset which can be in favour of the choice of this protocol also within CEN, thus providing comparable EC and OC data for a wider range of site categories.

Particular concern should be made regarding EC and OC data obtained by other than thermal-optical analysis methodology, which do not account for charring of OC during analysis. For 2010, this concerns the German site Melpitz only, for which the EC concentration was grossly overestimated. However, thermal-optical analysis using the EUSAAR_2 protocol was initiated from July 2012 on at the Melpitz site.

Only the analytical part of the EUSAAR unified protocol is considered finalized at present. Comparable data, in particular for OC, require that both the analytical and the sampling protocol are harmonized, which currently is not the case. The final tests of the EUSAAR best affordable, "artefact-free" sampling train is currently being evaluated within the EU-funded project ACTRIS. The variability amongst the various sampling approaches currently used is apparent from the parameters listed in Table 2.2. Most sites sample for 24 hours, however the sampling time ranges from 48 hours to one week for low loading sites such as Birkenes and Puy de Dôme. Three sites (Aspvreten, Ispra and Vavihill) attempted to account for both positive and negative sampling artefacts, whereas one (Košetice) used the QBQ-approach (Quartz-behind-Quartz) to account for positive artefacts. Eight of the twelve sites did not address sampling artefacts on a regular basis, but some addressed the positive sampling artefacts based on results from intensive measurements periods.

Five of the twelve sites performed measurements of EC and OC in both PM_{10} and $PM_{2.5}$, hence providing valuable information on the size distribution of these variables, which also add to the understanding of sources and atmospheric processes.

A number of sites have reported EC and OC levels to EMEP (see: http://ebas.nilu.no) on a non regular basis; i.e. measurements are typically performed during EMEP intensive measurement periods (EIMPs), or during dedicated campaigns or projects such as the EMEP EC and OC campaign in 2002–2003. There are also EMEP sites at which filter samples are collected and analyzed with respect to EC and OC, but for which data are currently not reported to EMEP.

All institutes submitting EC, OC and TC data to EMEP are strongly encouraged to participate in relevant inter calibration exercises. In the following part of the current report, the results from the 4th interlaboratory comparison of analytical methods for carbonaceous particulate matter within EMEP are presented.

Table 2.2: Sampling equipment and analytical approach used at the sites reporting EC and OC to EMEP for 2010.

Site (Country)	Sampling time/ frequency	Filter face velocity	Sampling equipment	Analytical approach
Aspvreten (Sweden)	24 hr, every 3rd day	55 cm s^{-1}	Denuder/Backup filter pos/neg artifact	Sunset TOT (EUSAAR_2)
Birkenes (Norway)	168 hr, every 7th day	54 cm s^{-1}	Single filter (no correction)	Sunset TOT (EUSAAR_2)
Finokalia (Greece)	24 hr, every 2nd day	26 cm s^{-1}	Single filter (no correction)	Sunset TOT (EUSAAR_2)
Harwell (UK)	24 hr, daily	20 cm s^{-1}	Single filter (no correction)	Sunset TOT (Quartz)
Hurdal (Norway)	168 hr, every 7th day	54 cm s^{-1}	Single filter (no correction)	Sunset TOT (EUSAAR_2)
Ispra (Italy)	24 hr, daily	20 cm s^{-1}	Denuder/Backup filter Pos/neg artifact	Sunset TOT (EUSAAR_2)
Košetice (The Czech Rep.)	24 hours, every 6th day	20 cm s^{-1}	QBQ (pos. artifact)	Sunset TOT (EUSAAR_2)
Kårvatn (Norway)	168 hr, every 7th day	54 cm s^{-1}	Single filter (no correction)	Sunset TOT (EUSAAR_2)
Melpitz (Germany)	24 hr, daily	50 cm s^{-1}	Single filter (no correction)	VDI 2465 Part 2
Montseny (Spain)	24 hr, every 4th day	74 cm s^{-1}	Single filter (pos. artefact/camp)	Sunset TOT (EUSAAR_2)
Puy de Dôme (France)	48 hr, every 7th day	69 cm s^{-1}	Single filter (pos. artifact/camp)	Sunset TOT (EUSAAR_2)
Vavihill (Sweden)	72 hr, every 3rd day	55 cm s^{-1}	Denuder/Backup filter pos/neg artifact	DRI (EUSAAR_2)

3. EC and OC interlaboratory comparison – Organization

3.1 Samples

Samples for comparison were prepared by JRC and distributed to participants in October 2011. Results were to be delivered to the JRC by the end of November 2011.

3.1.1 Reference solution

A reference solution (phthalic acid solution) was prepared by JRC from 98% purity solid phthalic acid and ultra-pure water (18.2 mOhm resistivity). 3mL of this solution was distributed to each participant in closed brown glass flasks.

3.1.2 Filters, aliquots and filter homogeneity

In lack of suitable reference material for atmospheric OC and EC, the present interlaboratory comparison was based on ambient high-volume aerosol samples collected on 150 mm diameter quartz-fibre filters (Whatman QMA) at of the following EMEP sites:

- Montseny, Spain (SPA)
- K-puszta, Hungary (HUN)
- Ispra, Italy (ITA)

A total of six filter samples were collected during the month of September 2011 with the aim of having: i) a low probability of significant contribution from biomass burning emissions and ii) a higher stability of OC with ambient temperature quite close to room temperature. Upon receipt at JRC, filters were stored in a freezer at a temperature of -18 °C.

From each sample, punches of approximately 2.2×2.2 cm² or 1×1 cm² were cut and stored in closed Petri dishes. To help interpreting the consistency of results (i.e. between-laboratory and within laboratory consistencies), a code was assigned to the participants (Table 3.1) and filter punches cut from the filter according to a prescribed scheme (Figure 3.1).

Filters' homogeneity was investigated by JRC on a dedicated filter collected at each of the 3 sampling sites. Eight filter punches, in total, were taken along two perpendicular radii. The homogeneity was assessed as the relative standard deviation (% rsd) of the determination of TC and resulted in 5% for SPA, 1% for HUN and 2% for ITA. If sampling at each location occurred under repeatable conditions, then we can infer that the filters used for the interlaboratory comparison had a similar homogeneity. However, these values represent only an upper limit of the between-aliquot standard deviation (i.e. filter homogeneity). In fact, the procedure used here for homogeneity checks did not account for the JRC 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).

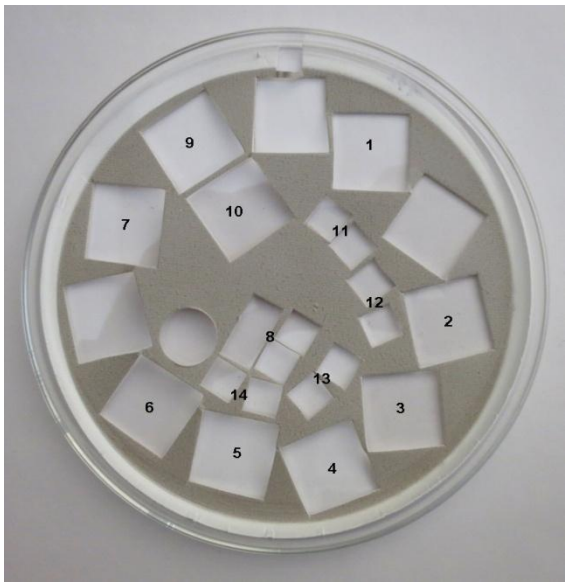


Figure 3.1: Distribution of the aliquots provided to each participant (see Table 3.1).

3.2 Participants

In accordance with the EMEP policy, results are presented in such a way that participants can be identified (Table 3.1). The Hydrometeorological Institute of Slovenia (SI01L), which produces and reports OC and EC data from Iskrba (SI08), and the Institute of Environmental Protection (PL02L), which produces and reports OC and EC data from Diabla Gora (PL05), did not participate in this interlaboratory comparison.

Table 3.1: List of participants in the 4th interlaboratory comparison of analytical methods for carbonaceous particulate matter within EMEP.

Code	Laboratory acronym	EMEP Lab. code	EMEP Station(s)
1	LGGE	FR04L	FR0030R
2	NILU	NO01L	NO0001R, NO0039R, NO0056R
3	UniBe		CH0001R
4	Tropos	DE08L	DE0044R
5	EMPA	CH01L	CH0002R, CH0005R
6	ULund	SE04L	SE0011R
7	UoC	GR02L	GR0002R
8	JRC	IT04L	IT0004R
9	CHMI	CZ03L	CZ0003R
10	UPAC	HU02L	HU0002R
11	BHam	GB04L	GB0036
12	ISCIII	ES01L	ES0009R
13	CNR-IIA	IT01L	IT0001R
14	UBA-DE	DE03L	DE0002R, DE0003R, DE0007R, DE0008R

Note: Full name and addresses for the participants can be found in Annex 2.

3.3 Analytical methods and protocols

INSTRUMENT TYPES:
Almost all participants used a Sunset Laboratory OC/EC Lab Instrument with the following exceptions:

- Lab 4: Behr C50 IRF Carbon Analyser
- Lab 6: DRI Model 2001A OC/EC Thermal-Optical Carbon Analyzer
- Lab 10: Astro Model 2100 TOC Analyser

Correction for charring is not possible with the instrument used by Lab. 4, and not applicable to the analyses performed by Lab. 10.

PROTOCOLS:
In Europe, mainly two protocols are used to quantify total carbon (TC), or OC and EC in PM samples:

- the NIOSH protocol (and variations of it) [Peterson and Richard, 2002], and
- the EUSAAR_2 protocol [Cavalli et al., 2010].

Analyses can also be performed using single step protocols (TC only), or the VDI 2 step protocol (VDI 2465, Part 2, 1999). Details concerning the various protocols used in the inter comparison are listed in Table 3.2.

Although EMEP has adopted EUSAAR_2 as the standard thermal protocol for EC and OC analyses, each participant was asked to analyze the comparison samples with the protocol used in its laboratory to produce data from its EMEP stations (Table 3.3). Eleven laboratories applied the EUSAAR_2 protocol. Transmittance was chosen by these laboratories to correct for pyrolysis, whereas two of them also reported reflectance-corrected results. One laboratory (Lab. 12) applied a variation of the NIOSH protocol (i.e. the default NIOSH-like protocol provided with the Sunset laboratory analyser), having a temperature of 870 °C for the highest temperature step in the He-mode of the analysis. One laboratory (Lab. 4) applied the VDI thermal method without correction for pyrolysis. One laboratory (Lab. 10) determined only total carbon using the TOC method.

Table 3.2: Details for the analytical protocols used by the inter comparison participants.

Carrier gas	EUSAAR_2		NIOSH 5040		VDI2465(2)		TOC	
	Time (s)	Temp (ºC)	Time (s)	Temp (ºC)	Time (s)	Temp (ºC)	Time (s)	Temp (ºC)
He	120	200	70	310	600	650		
He	150	300	60	475				
He	180	450	60	615				
He	180	650	90	870				
O_2 / He	120	500	45	550	600	650	300	680
O_2 / He	120	550	45	625				
O_2 / He	70	700	45	700				
O_2 / He	80	850	45	775				
O_2 / He	120	200	120	890				
% O_2 in He	2%		2%		100%		100%	

Table 3.3: List of the analytical protocol, optical correction for pyrolysis (Transmittance (T), Reflectance (R), Not Applied (N/A) used, punch size and number of replicates.

Code	Name of laboratory	Protocol	Optical corr.	punch size cm^2	Replicates
1	LGGE	EUSAAR_2	T/R	1.50	2
2	NILU	EUSAAR_2	T	1.00	3
3	UniBe	EUSAAR_2	T	1.50	2
4	Tropos	VDI2465(2)	N/A	0.7854	4
5	EMPA	EUSAAR_2	T	1.00	4
6	ULund	EUSAAR_2	T	0.5	1 or 2
7	UoC	EUSAAR_2	T	ND	2
8	JRC	EUSAAR_2	T/R	1.00	4
9	CHMI	EUSAAR_2	T	1.50	2
10	UPAC	TOC	N/A	0.785-3.077	4
11	BHam	EUSAAR_2	T	1	2
12	ISCIII	QUARTZ	T	1	2
13	CNR-IIA	EUSAAR_2	T	1	2
14	UBA-DE	EUSAAR_2	T	1	2

Note: Analytical method deviating from the EUSAAR_2 protocol are highlighted in different colour.

4. Data evaluation

4.1 Phthalic acid test solution

4.1.1 Determining the assigned value

The value assigned to the C content of the test phthalic acid solution was derived from the masses of phthalic acid and water used to prepare the solution (ISO 13528:2005(E).

4.1.2 Determining the uncertainty of the assigned value

The uncertainty of the assigned value was estimated by combining the uncertainties associated with gravimetric and volumetric measurements according to the law of propagation of errors (ISO 13528:2005(E).

4.1.3 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 determination *by perception* was chosen. With this approach, σ* is defined from the level of performance that the interlaboratory comparison coordinator would wish the participants to achieve (10%) as:

$\sigma^* = 0.1 / 3.$

z-scores were calculated to evaluate the capacity of each participant to comply with the limits defined by σ*.

The z-score is calculated as:

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

where x is the result from 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, the result is considered to give an "action signal". Likewise, a laboratory bias above 2×z or below -2*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 $<-200*\sigma^*/X\%$ and $>200*\sigma^*/X\%$, $<-300*\sigma^*/X\%$ and $>300*\sigma^*/X\%$, respectively, provide the percentage deviations from the assigned value corresponding to z-scores of ± 2 and ± 3.

4.2 TC and EC/TC in test filters

In the present comparison exercise, Method performances (4.2.1.) and laboratory performances (4.2.2.) were evaluated for the TC content and the EC/TC ratio. TC represents the most robust and protocol-independent result of TOA analyses; and the EC/TC ratio is free from biases in the total carbon determination and allows investigating possible biases in the OC/EC split determination among laboratories applying the same protocol.

As samples are exposed for more than 3 min at temperatures above 500 °C in an oxidizing atmosphere for all analytical protocols, there are no technical reasons for which the various protocols used in this comparison should result in different total carbon values. Potential differences in TC are thus considered as random and the dataset for TC is evaluated as a whole.

In contrast, the split between OC and EC is an operational definition and potential differences in the EC/TC ratio are considered to be protocol-dependent. It would have been more appropriate to evaluate separately EC/TC ratio subsets according to the protocol employed, but subsets including only one laboratory each are not statistically significant. Thus, the EC/TC ratio dataset is evaluated as a whole too.

4.2.1 Method performance

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 its critical value at 1% confidence level) or stragglers (i.e. observations greater than its critical value at 5% confidence level and less or equal to its 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. Critical values for *Mandel's k* indicators (i.e.

the determination of outliers and stragglers) vary upon the number of replicate measurements. In this comparison exercise, laboratories provided a variable number of replicates, thus *Mandel's k* were calculated for an average case of two replicates.

Furthermore, the G_1-Grubbs' statistical test is applied for testing the between-laboratory variability [ISO5725-2]. Based on the outcomes of above Mandel's statistics, 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].

4.2.2 Laboratory performance

– *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 62.5 μg cm^{-2} (corresponding to 50 μg m^{-3} when collected for 24h with a filter face velocity of 47.2 cm s^{-1}) and the limit of detection, i.e. 0.2 μg cm^{-2} at zero concentration level.

For the EC/TC ratio, this approach was compared to that of a *perception value* defined as the level of performance that the interlaboratory comparison coordinator would wish the participants to achieve, i.e. 15%.

For both TC and EC/TC ratio a single assigned value X and related σ* was calculated from the results of all participants.

– *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* as described in 4.1.3.

5. Results

All results are presented in Tables A1, A2, and A3 (Annex 1) for the test solution (µg C μL^{-1}), TC (in µg cm^{-2}), and light transmittance-corrected EC/TC ratios in test filters, respectively.

5.1 Test solution

The assigned value and uncertainty for the carbon content of the test solution prepared by JRC were 1.52 ± 0.01 µgC μL^{-1}.

Eleven among fourteen participants reported measurements of the test solution (Table A1). Figure 5.1 show that participants 1, 7 and 13 had z-scores larger than 3 or less than -3 (outliers). Lab. 1 and 13 underestimated the expected value by 23% and 13%, respectively; whereas lab. 7 overestimated the expected value by 11%. All other laboratories determined the carbon content of the reference solution with deviations from the expected value within ±10%. Possible reasons for these outliers can also include errors in the test solution handling (e.g. pipetting), which have no impact on the routine analysis of aerosol samples, but may affect the calibration of the instrument (if performed with a standard solution).

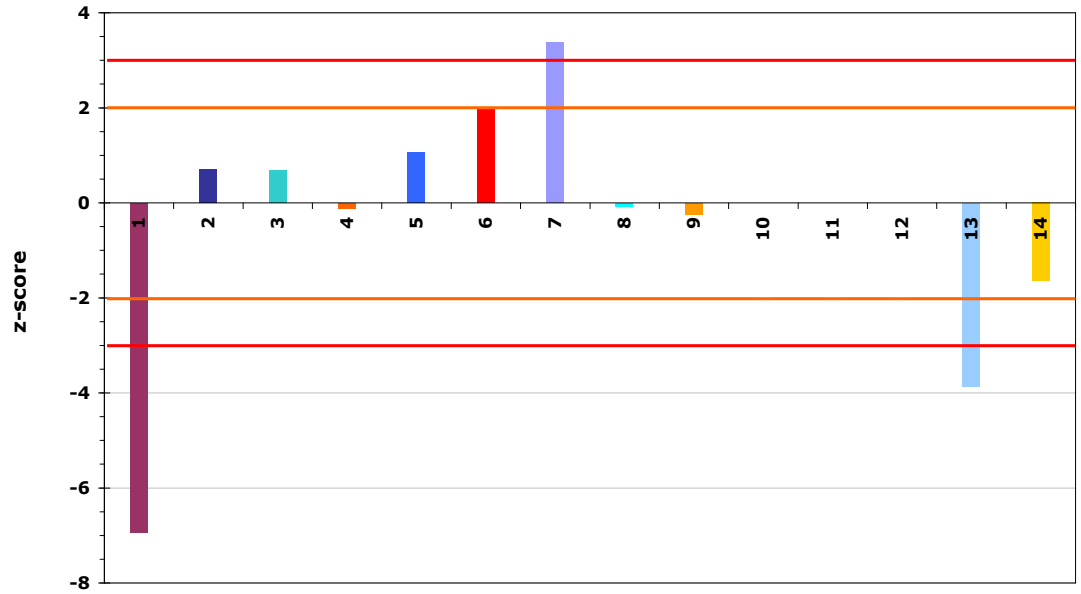


Figure 5.1: z-scores for the determination of the reference solution carbon content. Participants 10, 11, and 12 did not report.

5.2 Test filter punches

On average, reported TC amounts ranged from 8.4 to 37.2 µg cm^{-2}, corresponding to atmospheric concentrations ranging from 4.8 to 21.5 µg m^{-3} when assuming a 24 hour sampling time and a filter face velocity of 20 cm s^{-1}. EC/TC ratios ranged from 0.02 to 0.14 on average (including all observations regardless of the analytical protocol).

5.2.1 Method performance

5.2.1.1 Method performance for TC

5.2.1.1.1.1 Reproducibility

The *Mandel's h* statistic values are presented as sorted by (a) laboratory and (b) sample in Figure 5.2. One outlier (lab/sample: 3/SPA-1) and six stragglers (4/SPA-2; 4/HUN-1; 13/HUN-1; 4/HUN-2; 13/HUN-2; and 13/ITA-1) were identified. The outlier was confirmed as such by the G_1-Grubbs' test. Consistently negative *h* values correspond to the three stragglers from lab. 4, while consistently positive *h* values are associated with the stragglers from lab. 13. Laboratory 13, which also was an outlier for the determination of the test solution C content, overestimated TC in the test filter samples by 27%, on average.

5.2.1.1.1.2 Repeatability

The *Mandel's k* statistic values are presented as sorted by (a) laboratory, and (b) by sample in Figure 5.3. *Mandel's k* statistic values were calculated for all laboratories (lab. 6 provided replicates for only two samples).

In the TC filter content dataset, five outliers (lab/sample: 10/SPA-1, 12/SPA-2; 5/HUN-1; 10/HUN-2; and 13/ITA-2) and one straggler (lab/sample: 12/ITA-1) were identified.

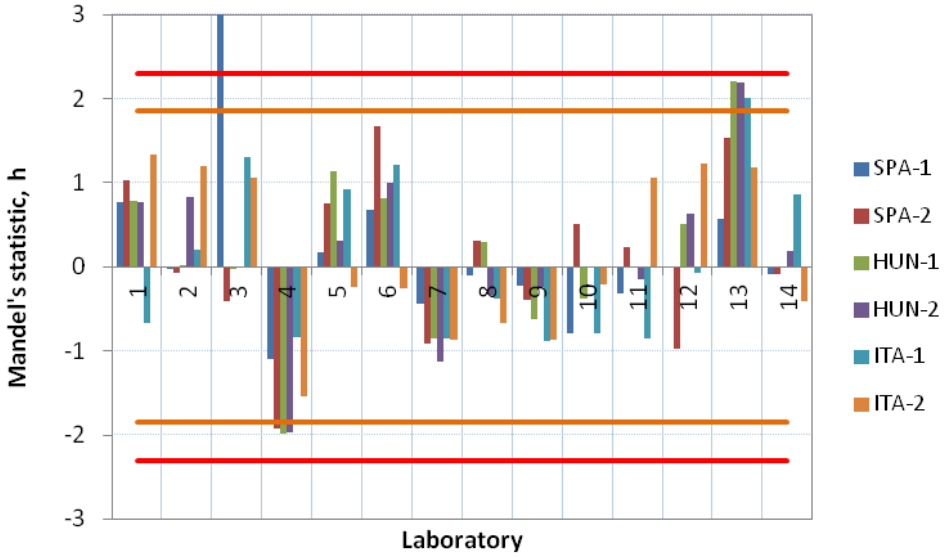
5.2.1.1.1.3 Mean values and standard deviations

All outlying values (from both Mandel's h and k statistics) were discarded from the dataset. From the retained values and for each sample separately, the mean value, the repeatability standard deviation, s_r, and reproducibility standard deviation, s_R, were calculated. The standard deviations s_r and s_R were not dependent on the TC filter content and ranged (as relative standard deviations) from 3% to 6% and from 13% to 28% (Table 5.1).

Table 5.1: Mean, repeatability (s_r) and reproducibility (s_R) relative standard deviations for TC filter contents.

	General mean (µg/cm²)	s_r (%)	s_R (%)
SPA-1	7.82	5.6	14.9
SPA-2	14.64	3.6	13.5
HUN-1	17.23	3.1	15.5
HUN-2	20.29	3.0	12.7
ITA-1	36.46	5.3	23.6
ITA-2	29.20	2.9	28.3

Panel a



Panel b

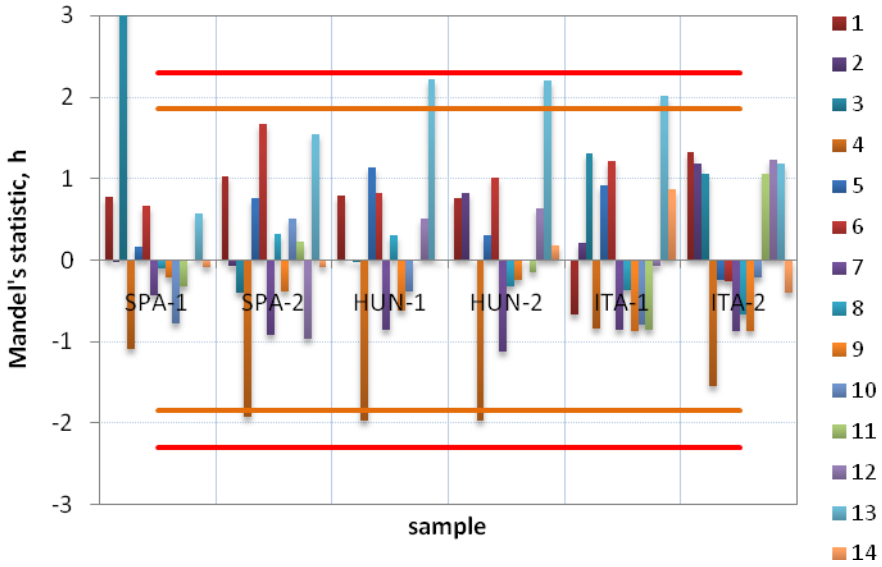
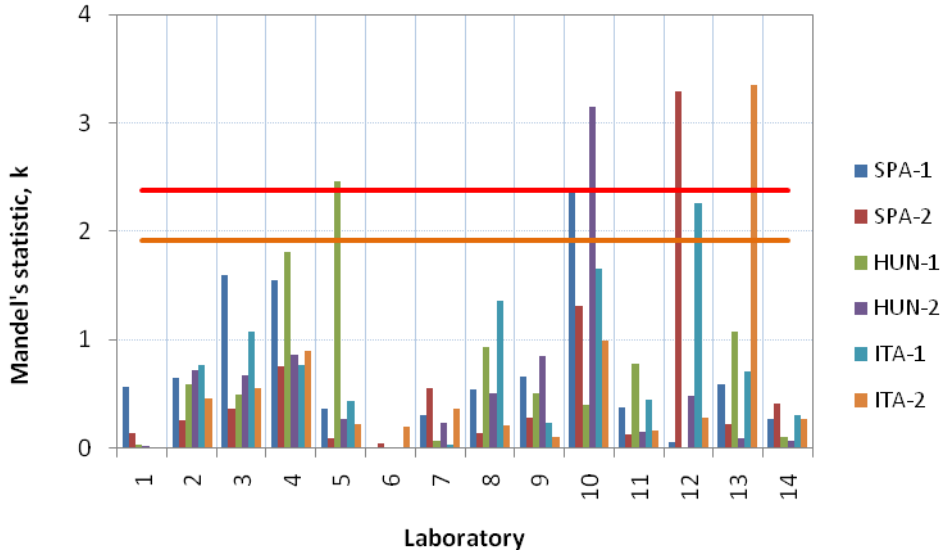


Figure 5.2: Mandel's h statistic values for between-laboratory consistency on TC data, grouped by laboratory (panel a) and by sample (panel b). For 14 laboratories, h values should be < 2.30 at 1% significance level (red line) and < 1.85 at 5% significance level (orange line).

Panel a



Panel b

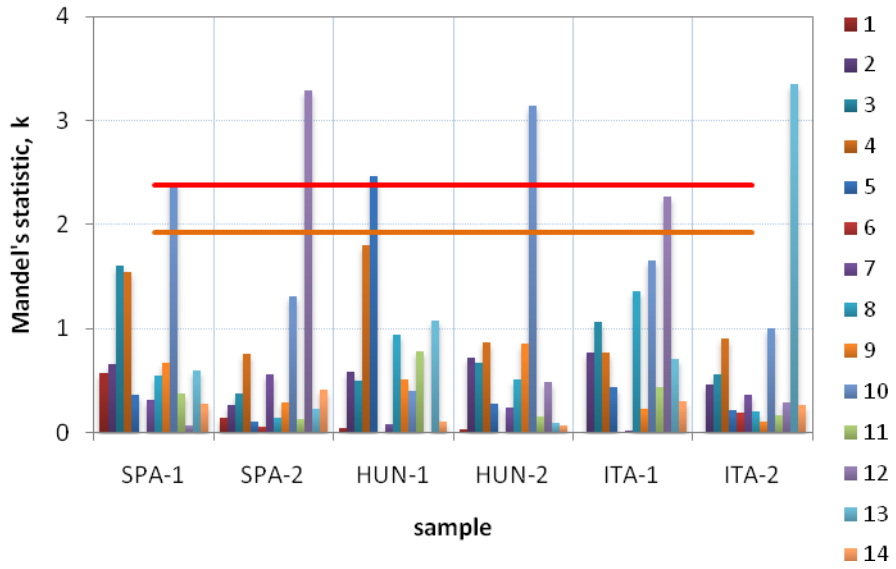


Figure 5.3: Mandel's k statistic values for between-laboratory consistency on TC data, grouped by laboratory (panel a) and by sample (panel b). For 13 laboratories and 2 replicates, k values should be < 2.38 at 1% significance level (red line) and < 1.92 at 5% significance level (orange line).

The reproducibility relative standard deviation is particularly high for ITA-1 and ITA-2 samples, even after exclusion of outliers. This might be due to their high TC contents (i.e. 36.46 and 29.20 μg/cm^2, respectively), but it might also indicate a poorer homogeneity of the two comparison filters compared to 2% as in the filter dedicated to the filter homogeneity determination. Between-laboratory inconsistencies identified for these two samples could at least partly be due to filter heterogeneity or high TC values. For the remaining samples, the observed laboratory (between and within) inconsistencies did not depend on a specific sample (See panel b in figures 5.3 and 5.4). Although (localized) sample heterogeneities/contaminations could not be excluded, the homogeneity tests performed on dedicated filters do not support this hypothesis, and the recurrence of stragglers or outliers for a single laboratory (ITA-1 and ITA-2 samples excluded) probably indicate an unsatisfactory laboratory reproducibility or repeatability as compared to the other laboratories.

5.2.1.2 Method performance for EC/TC

EC/TC ratios measured by lab. 4, i.e. applying an analytical method without correction for pyrolysis, were substatnially higher (by a factor of 1.6 to 5.7) than the average values calculated including all laboratories. To avoid biasing the evaluation of method performance for EC/TC, values from lab. 4 were therefore discarded. Note also that lab. 10 did not determine EC.

5.2.1.2.1 Reproducibility

Figure 5.4 shows the *Mandel's h* statistic values for EC/TC ratios calculated for the entire database for each laboratory (panel a) and for each sample (panel b). One outlier (lab/sample: 13/ITA-2) and one straggler (lab/sample: 13/ITA-1) were identified. The outlier only was confirmed as such by the Grubbs' test G_1.

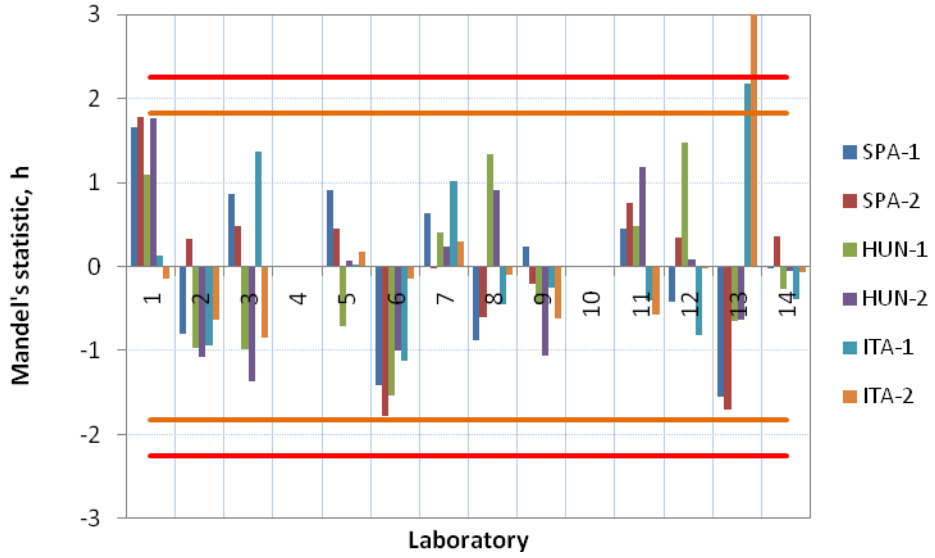
5.2.1.2.2 Repeatability

In Figure 5.5 the *Mandel's k* statistic values are presented grouped for each laboratory (panel a) and for each sample (panel b). *Mandel's k* statistic values were calculated for all laboratories (lab 6 provided replicates for two samples only). In the EC/TC dataset, three outliers (lab/sample: 12/SPA-2; 3/ITA-1 and 13/ITA-2) and two stragglers (lab/sample: 14/SPA-2; and 9/HUN-2) were identified.

5.2.1.3 Averages and standard deviations

All outlying values were discarded from the dataset. From the retained values, for each sample, the mean value, the repeatability standard deviation, s_r, and the reproducibility standard deviation, s_R, 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 4% to 16% and from 12% to 33% (Table 5.2).

Panel a



Panel b

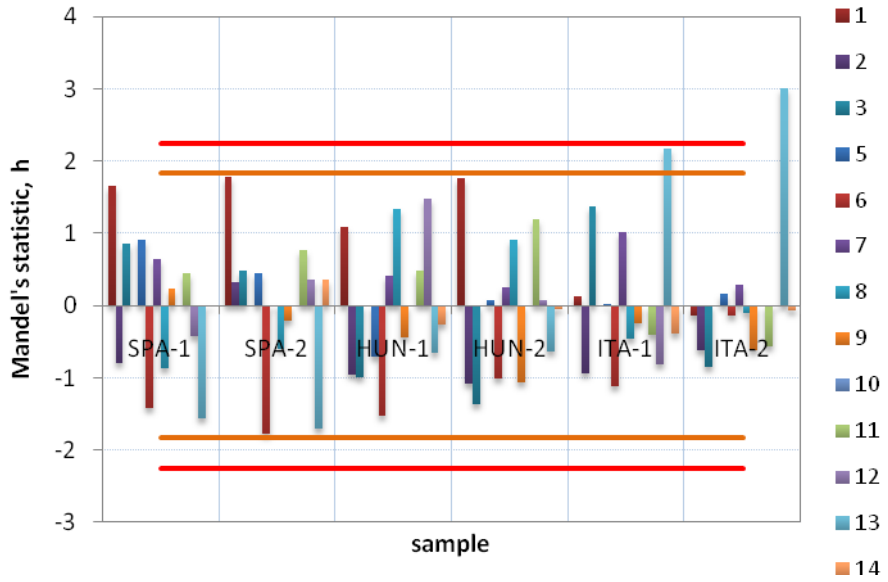
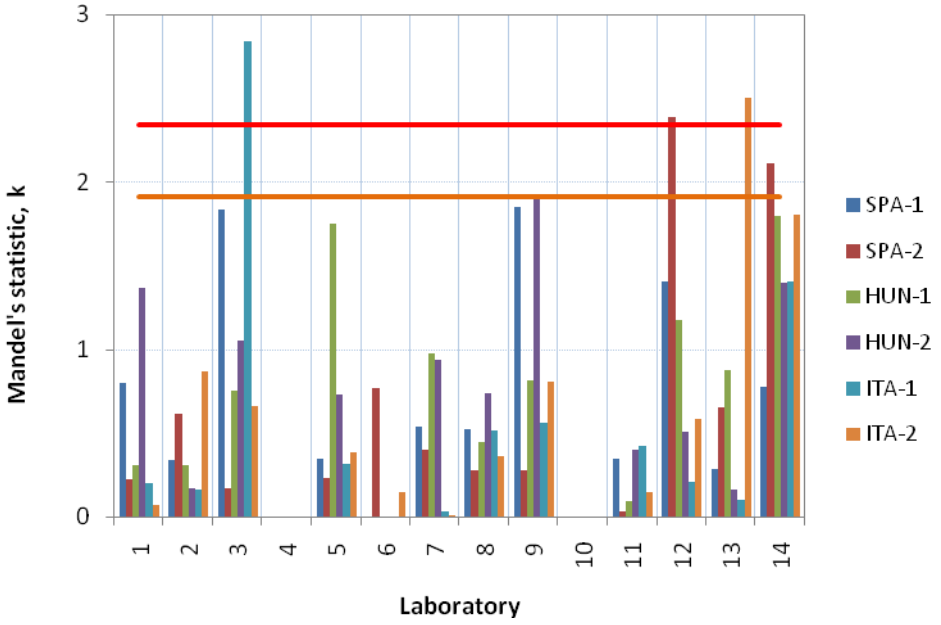


Figure 5.4: Mandel's h statistic values for between-laboratory consistency on EC/TC ratios obtained from the entire database, grouped by laboratory (panel a) and by sample (panel b). For 12 laboratories h values should be < 2.25 at 1% significance level (red line) and < 1.83 at 5% significance level (orange line).

Panel a



Panel b

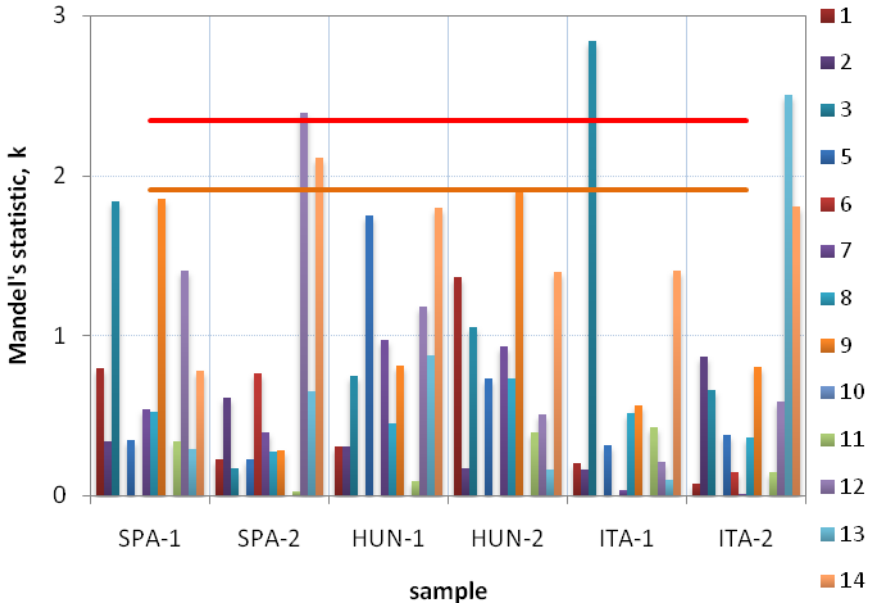


Figure 5.5: Mandel's k statistic values for between-laboratory consistency on EC/TC ratio obtained from the entire database, grouped by laboratory (panel a) and by sample (panel b). For 11 laboratories k and two replicates values should be < 2.34 at 1% significance level (red line) and < 1.91 at 5% significance level (orange line).

Table 5.2: Mean, repeatability (s_r) and reproducibility (s_R) relative standard deviations for EC/TC ratios in filter samples.

	General mean	s_r (%)	s_R (%)
SPA-1	0.11	7.9%	15.4%
SPA-2	0.14	4.4%	14.9%
HUN-1	0.10	5.7%	12.2%
HUN-2	0.09	5.7%	12.0%
ITA-1	0.04	11.5%	26.3%
ITA-2	0.01	15.7%	32.5%

Repeatability and reproducibility relative standard deviation are particularly high for ITA-1 and ITA-2 samples, even after exclusion of outliers. This might be due to their very low EC/TC ratio values (i.e. 0.04 and 0.01, respectively), but it might also indicate a poorer homogeneity of the two comparison filters compared to 2% as observed in the filter dedicated to the filter homogeneity determination. Thus, between- and within- laboratory inconsistencies identified for these two samples could be at least partly due to filter heterogeneities. For the remaining samples, the observed laboratory (between and within) inconsistencies did not depend on a specific sample (See panel b in Figures 5.3 and 5.4). Though localized sample heterogeneities/contaminations could not be excluded, the homogeneity tests performed on dedicated filters do not support this hypothesis and the recurrence of stragglers or outliers for a single laboratory (for samples other than ITA-1 and ITA-2) probably indicate an unsatisfactory laboratory reproducibility or repeatability as compared to the other laboratories.

5.2.2 Laboratory performance

5.2.2.1 Laboratory performance for TC determination

Following ISO13528, σ* were calculated (a) *from data obtained in a round of a proficiency testing scheme* (σ^*_a) and (b) from the *prescribed* DQO of 25% given for PM at its limit value of 50 μg m^{-3} (σ^*_b).

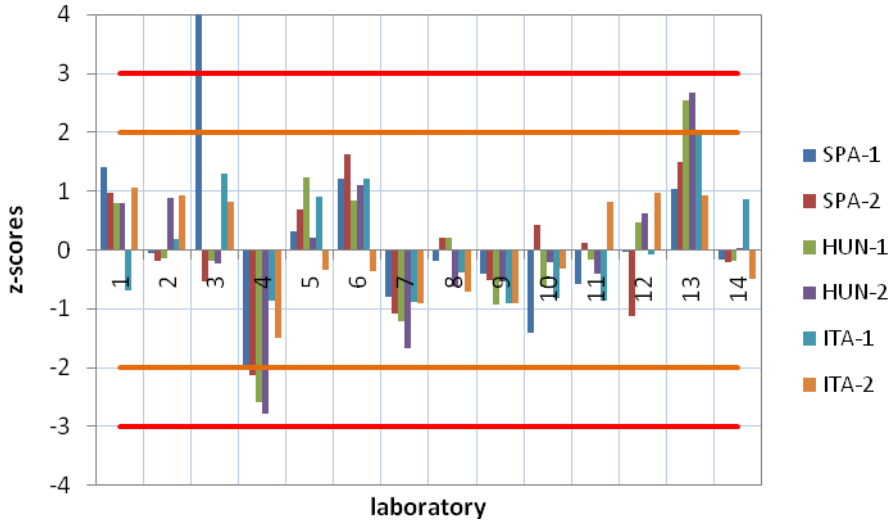
The assigned values X, their standard deviations, and the related standard deviations for proficiency assessment, σ^*_a, calculated based on the entire database for each sample, are reported in Table A4 of Annex 1. Figure 5.6 (panel a) shows z-scores calculated using σ^*_a. z-scores less than -3 and greater than 3 indicate reported values that deviate from the assigned value by more than ± 43.8% for SPA-1, 35.9% for SPA-2, 35.9% for HUN-1, 26.2% for HUN-2, 73.4% for ITA-1 and 90.8% for ITA-2. z-scores less than -2 and greater than 2 indicate reported values that deviate from the assigned value for more than ± 29.2% for SPA-1, 23.9% for SPA-2, 23.9% for HUN-1, 17.5% for HUN-2, 48.9% for ITA-1 and 60.5% for ITA-2.

In the TC database there are one outlier (lab/sample: 3/SPA-1) and six stragglers (lab/ sample: 4/SPA-2; 4/HUN-1; 4/HUN-2; 13/HUN-1; 13/HUN-2 and 13/ITA-1). All stragglers come from two laboratories. For all samples, at least

eight out of fourteen laboratories showed deviation from the assigned values within ± 1 σ^*_a (i.e. within 1 z-score).

Using σ^*_b as standard deviations for proficiency assessment, two additional outliers (lab/ sample: 13/ITA-1 and 4/ITA-2) and eleven additional stragglers were identified. Indeed, σ^*_a was greater than σ^*_b for all assigned values but HUN-2. In total three values (lab/sample: 3/SPA-1, 13/ITA-1 and 4/ITA-2) would not comply with the DQO of 25%, as in the EU Directive 2008/50/EC for PM at its limit value of 50 µg m^{-3}.

Panel a



Panel b

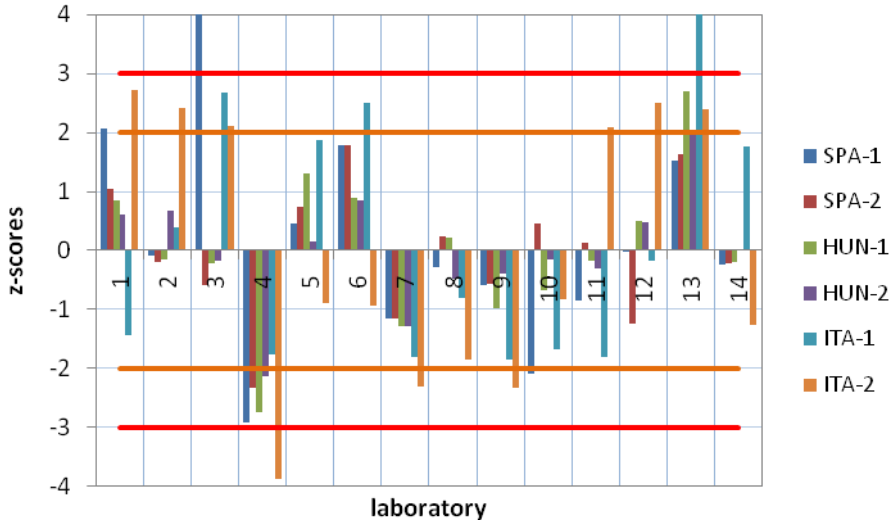


Figure 5.6: z-scores for TC calculated using σ^*_a from data obtained in a round of a proficiency testing scheme (panel a) and the prescribed σ^*_b value (panel b).

5.2.2.2 Laboratory performance for the determination of EC/TC

σ* were calculated (a) *from data obtained in a round of a proficiency testing scheme,* (σ^*_a) and (b) from the *prescribed* DQO of 25%, like for PM at its limit value of 50 µg m^{-3} (σ^*_b) in the Directive EC/50/2008.

The assigned values, X, their standard deviations, and the related standard deviations for proficiency assessment, σ^*_a, are reported in Table A5 of Annex 1.

z-scores (Figure 5.7) less than -3 and greater than 3 indicated that the reported value deviated from the assigned value for more than ± 50.2% for SPA-1; 25.9% for SPA-2; 36.7% for HUN-1; 39.4% for HUN-2; 64.0% for ITA-1 and 121.9% for ITA-2. z-scores less than -2 and greater than 2 indicated that the reported values deviated from the assigned value for more than ± 33.5% for SPA-1; 17.3% for SPA-2; 24.5% for HUN-1; 26.2% for HUN-2; 42.7% for ITA-1 and 81.3% for ITA-2.

Four outliers (lab/sample: 6/SPA-2; 13/SPA-2; 13/ITA-1; and 13/ITA-2) and three stragglers (lab/sample: 1/SPA-2; 3/ITA-1; and 7/ITA-1) were identified.

For all samples, at least six out of twelve showed deviation from the assigned values within ± 1 σ^*_a (i.e. within 1 z-score).

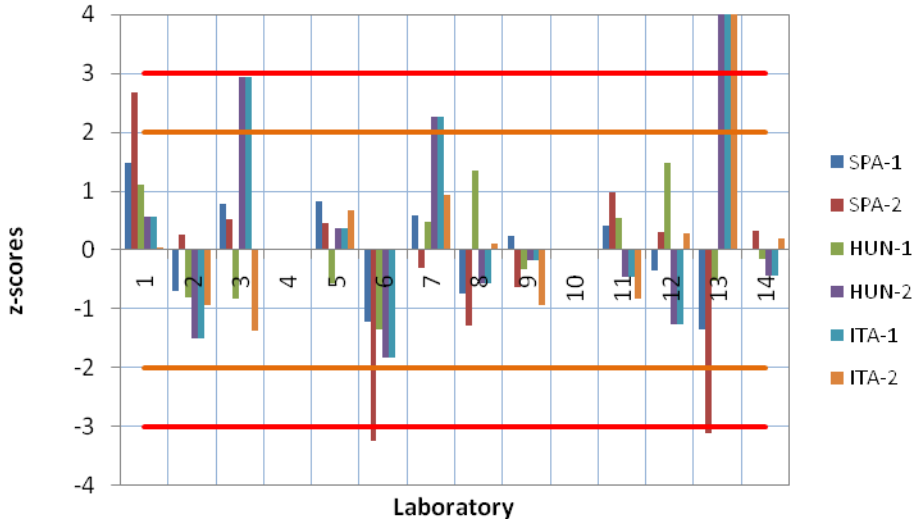


Figure 5.7: z-scores for EC/TC ratios calculated using σ^*_a from data obtained in a round of a proficiency testing scheme.

Laboratories' performances were also evaluated using as σ^*_b a level of performance that the interlaboratory comparison coordinator would wish the participants to achieve, i.e. 15%. Under this condition, we identified only 3 outliers (lab/sample: 13/ITA-1; 3/ITA-2 and 13/ITA-2), but 7 stragglers (all for ITA-1 and ITA-2), since the level of performance (i.e σ^*_b) set by the coordinator (15%) is by far more stringent than that derived from *data in a round of a proficiency testing scheme* (i.e. σ^*_a) for samples ITA-1 and ITA-2.

6. Conclusions

Based on Mandel's *h* and *k* parameters and the G_1-Grubbs'statistical test analyses, thermal and thermal-optical methods generally show a satisfactory level of performance for the determination of TC in the test filters, although one outlier for reproducibility and five outliers for repeatability (among 84 values) were identified. Thermal-optical methods (i.e. methods including optical correction of charring) also show a satisfactory level of performance for the determination of EC/TC: one outlier for reproducibility and three outliers for repeatability were identified (among 72 values).

After elimination of outliers, repeatability and reproducibility of TC measurements ranged (as relative standard deviation) from 3% to 6% and from 13% to 28%, respectively. For the determination of EC/TC ratios, repeatability and reproducibility ranged (as relative standard deviation) from 4% to 16% and from 12% to 33%.

Repeatability and reproducibility relative standard deviations were particularly high for TC (reproducibility only) and EC/TC for the ITA-1 and ITA-2 samples, even after exclusion of outliers. This might be due to a poorer homogeneity of the two test filters compared to the homogeneity of 2% determined for the dedicated filter. It might also indicate that errors in the determination of TC are larger in filters where the TC content is high (i.e.. 36.5 and 29.2 μg cm^{-2} for ITA-1 and ITA-2, respectively), and that errors in the determination of EC/TC get larger in filters where EC/TC ratios are very low (i.e. 0.04 and 0.01 in ITA-1 and ITA-2, respectively).

Four participants produced several outliers or stragglers in the determination of TC in the other (i.e. non-ITA filters) test filters. This indicates an unsatisfactory laboratory reproducibility or repeatability as compared to the other laboratories.

Laboratories' performances were further tested based on the analysis of z-scores. For the determination of TC in test filters, 1 to 3 outliers were identified (depending on the method used to determine the *standard deviation for proficiency assessment*). The participants that produced these outliers were already identified by Mandel's statistics. The analysis of the laboratories' performances for determining EC/TC ratios in the test filters revealed four outliers when using as σ* the *standard deviation for proficiency assessment* to calculate z-scores. Three of these outliers were produced by the same participant, already identified by the other statistical tests.

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

7. References

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Annex 1

Results

Table A1: Total carbon content (µgC µL^{-1}) of the phthalic acid test solution determined by 11 of the 14 participants.

Participant #	Replicate #1	Replicate #2	Replicate #3	Replicate #4	Replicate #5	Replicate #6	Replicate #7	Replicate #8	Replicate #9
1	1.13	1.18	1.20						
2	1.56	1.54	1.57						
3	1.55								
4	1.47	1.50	1.57	1.59	1.44				
5	1.57	1.56	1.60	1.56	1.58				
6	1.55	1.67	1.64						
7	1.78	1.70	1.60						
8	1.50	1.50	1.50	1.49	1.56	1.54			
9	1.42	1.49	1.51	1.60	1.45	1.53	1.56		
10									
11									
12									
13	1.36	1.25	1.29	1.39	1.33	1.27	1.26	1.37	1.39
14	1.47	1.48	1.38	1.42					

Table A2: Total carbon content (µg cm^{-2}) of the six test filters determined by the 14 participants.

Participant #	SPA-1	SPA-2	HUN-1	HUN-2	ITA-1	ITA-2
1	9.44 9.90	16.54 16.32	19.57 19.54	22.12 22.08	30.39 30.38	40.89 40.87
2	7.96 8.33 7.59	14.15 14.35 14.71	17.16 17.85 17.59	23.06 22.18 21.48	39.94 37.66 37.24	40.64 39.23 39.26
3	15.16 13.88	14.07 13.49	17.76 17.29 17.23	19.75 20.79	46.75 49.63	39.35 37.98
4	6.45 6.44 5.25 4.72	11.52 11.79 10.54 10.01	13.46 11.69 11.19 13.00	15.74 16.88 15.31 14.62	29.87 29.99 26.84 29.09	17.14 18.95 15.23 16.31
5	8.18 8.39 8.60 8.48	15.81 16.02 15.96	19.69 22.17 19.60	21.37 20.82 20.88 20.91	45.61 44.55 43.99 42.94	28.01 27.32 27.93 28.51
6	9.45	17.58 17.66	19.64	22.66	47.41	27.97 27.37 27.41
7	6.98 7.23	13.28 12.41	15.25 15.31	17.83 17.46	28.73 28.78	22.10 23.00
8	7.70 8.26 7.62 7.65	14.93 15.13 15.31 15.07	17.56 18.75 18.15 18.69	19.37 20.00 18.79 19.92	31.35 34.41 44.86 37.53	24.67 23.82 24.11 24.34
9	7.30 7.83	13.59 14.03	16.10 15.67	20.38 19.05	28.88 28.28	22.37 22.62
10	5.78 4.87 8.01 6.81	14.46 16.49	16.54 16.25 16.72	23.49 18.84 16.10 22.72	29.44 32.45 26.15	26.75 29.21
11	7.51 7.21	15.05 14.85	17.80 17.14	20.06 19.82	29.40 28.22	38.38 38.78
12	8.00 8.05	10.17 15.30	18.84 18.84	21.42 22.17	38.89 32.79	39.70 40.40
13	9.47 9.00	17.55 17.20	23.73 22.83	25.40 25.54	53.58 55.48	35.49 43.80
14	7.94 7.73	14.7 14.1	17.5 17.4	20.8 20.7	44.7 43.9	26.7 26.1

*Table A3: Elemental carbon / total carbon ratio (all * 100) in the six test filters determined by 13 of the 14 participants.*

Participant #	SPA-1	SPA-2	HUN-1	HUN-2	ITA-1	ITA-2
1	13.55 14.72	17.48 17.77	11.69 11.43	10.97 9.92	3.83 4.07	1.45 1.42
2	9.92 9.72 10.41	14.06 14.70 15.16	9.32 8.96 9.21	7.50 7.62 7.68	2.78 2.97 2.71	1.21 0.71 0.71
3	14.14 11.46	15.08 14.86	8.63 9.29 9.50	7.72 6.91	3.53 6.96	0.78 0.47
4	14.26 12.89 20.57 25.42	14.35 12.47 24.48 19.68	19.43 27.12 24.22 19.08	25.54 21.92 17.83 25.38	17.88 15.04 12.78 15.98	10.21 17.31 11.16
5	13.08 13.09 12.46 13.99	14.99 14.65 15.03	10.13 8.24 10.02	8.35 8.77 9.15 9.39	3.52 3.96 4.02 4.12	1.79 1.67 1.92 1.69
6	8.99	9.84 10.82	8.50	7.68	2.64	1.39 1.46 1.09
7	12.82 12.04	14.20 13.69	11.18 10.35	9.29 8.57	4.90 4.86	1.94 1.94
8	10.06 09.14 10.01 10.42	12.50 13.08 12.73 12.67	11.68 11.94 11.60 12.20	9.07 9.60 9.67 10.04	3.52 3.05 2.82 3.66	1.40 1.44 1.42 1.65
9	10.40 13.11	13.72 13.37	9.42 10.12	8.36 6.88	3.21 3.89	0.69 1.06
10	-	-	-	-	-	-
11	12.37 11.87	15.51 15.55	10.89 10.81	10.20 9.72	3.65 3.14	0.98 0.91
12	9.63 11.68	13.18 16.21	12.53 11.52	8.96 8.57	2.83 3.08	1.44 1.71
13	8.98 8.56	10.88 10.06	9.90 9.15	8.11 7.99	6.03 6.15	5.64 4.47
14	11.91 10.77	13.38 16.06	9.22 10.75	8.10 9.18	2.56 4.25	1.10 1.94

Table A4: Assigned values and standard deviations for proficiency assessment, σ (*from data obtained in a round of a proficiency testing scheme) *for TC filter content (µg/cm^2).*

	SPA-1	SPA-2	HUN-1	HUN-2	ITA-1	ITA-2
Assigned value, X	8.02	17.73	17.84	20.66	36.61	30.96
Standard deviation, σ*	0.79	1.63	2.01	2.36	4.34	3.64
Standard uncertainty of X	0.39	0.59	0.71	0.60	2.99	3.13

Table A5: Assigned values and standard deviations for proficiency assessment, σ (*from data obtained in a round of a proficiency testing scheme) *for EC/TC (all * 100) in filter samples.*

	SPA-1	SPA-2	HUN-1	HUN-2	ITA-1	ITA-2
Assigned value, X	11.32	14.32	10.18	8.61	3.63	1.41
Standard deviation, σ*	1.89	1.24	1.25	1.13	0.78	0.57
Standard uncertainty of X	0.68	0.45	0.45	0.41	0.28	0.21

Annex 2

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5- EMPA, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland

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7- UoC, University of Crete, Environmental Chemical Processes Laboratory, POBox 2208, 71003 Voutes, Heraklion, Greece

8- JRC, European Commission, Joint Research Centre, Institute for Environment and Sustainability, via Fermi 2749, I-21027 Ispra (VA), Italy

9- CHMI, Czech Hydrometeorological Institute, Na Sabatce 17, CZE-143 06, Praha 4-Komorany, Czech Republic

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11- BHam, University of Birmingham, Division of Environmental Health & Risk Management, School of Geography, Earth & Environmental Sciences, Edgbaston, Birmingham B15 2TT, United Kingdom

12- ISCIII, Instituto de Salud Carlos III, Atmospheric Pollution Department, Centro Nacional de Sanidad Ambiental, Ctra. Majadahonda-Pozuelo Km. 2, 28220 Majadahonda (Madrid), Spain

13- CNR-IIA, National Research Council - Institute for Atmospheric Pollution, Via Salaria Km. 29.300, CP 10 - 00016 - Monterotondo Stazione – ROMA, Italy

14- UBA-DE, Umweltbundesamt / Federal Environment Agency, Air Pollution Monitoring Network, Paul-Ehrlich-Str. 29, D-63225 Langen, Germany