Results of the inter-laboratory comparison exercise for TC and EC measurements (ref.: OCEC-2018-1)

Summary

The European Centre for Aerosol Calibration (ECAC) under ACTRIS-2 completed in March 2018 an inter-laboratory comparison for the measurement of total carbon (TC), elemental carbon (EC) and organic carbon (OC) in particulate matter collected on filters. The aim of this comparison was to evaluate the performances of the measurement method (i.e. reproducibility and repeatability) and of individual laboratories (bias and variability).

This exercise was based on ambient $PM_{2.5}$ aerosol samples collected on quartz fiber filters at a regional background site in Italy. A solution of phthalic acid prepared at JRC-ERLAP (the inter-laboratory comparison exercise coordinator) was also distributed.

Twenty-one laboratories participated in this exercise running the EUSAAR_2 protocol as their usual thermal-optical protocol with their usual analytical instrument. Among those, seventeen are responsible for the aerosol chemical speciation at the EMEP or ACTRIS stations located in their countries (i.e. Germany, Switzerland, Greece, Finland, Norway, Poland, Czech Republic, Cyprus, Spain, Sweden, The Netherlands, Germany, and Italy).

Measurement method performance: for TC determination, repeatability and reproducibility relative standard deviations ranged from **2 %** to **7 %** and from **5 %** to **12 %** (as one relative standard deviation), respectively. For the determination of the EC/TC ratio, repeatability and reproducibility relative standard deviations ranged from **3 %** to **8 %** and from **12 %** to **17 %**, respectively.

Based on last seven inter-laboratory comparisons, repeatability and reproducibility standard deviations show an inverse dependence on TC loadings and EC/TC ratios becoming exponentially poorer toward lower TC contents i.e. <10 µgC / cm² and EC/TC ratios i.e. <0.07, respectively.

Laboratory performance: for both TC loadings and EC/TC ratios, laboratories' performances were assessed in terms of z-scores, calculating the *standard deviation for proficiency assessment* (σ^*) *from the data obtained in the round of the proficiency testing scheme.*

The assigned values for TC loadings and EC/TC ratios in the test samples were calculated as the robust average values among all participants. The assigned value for the concentration of phthalic acid was determined from primary gravimetric and volumetric measurements.
For TC loadings, fourteen outliers –mainly from two participants– and one straggler were identified; 86% of all entries were within 10% from the assigned TC concentration value.

Regarding EC/TC ratios, four outliers and eight stragglers -from a few participants- were identified. 57% of all entries were within 10% of the assigned value and 89% were within the 25% of the assigned value.

Although the contribution of localized sample heterogeneities and/or contaminations to biased data cannot be totally excluded, the random scheme adopted to distribute sub-samples was such that the recurrence of stragglers or outliers (more than two) for single laboratories most probably indicated an unsatisfactory laboratory performance as compared to the other participants. Laboratories showing unsatisfactory precision (both in terms of repeatability and reproducibility) or significant and/or systematic biases for several test samples shall carefully examine their operating procedures and instrumental set-up and identify appropriate corrective actions with the help of ECAC staff if needed.

In addition, on the basis of results from the present inter-laboratory comparison and for the purpose of harmonizing TC, OC and EC air mass concentrations reported into the EBAS database, statistics, i.e. percentage bias and variability, were calculated for TC, OC and EC determination for each participant.

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 related to inhalation and indication of air pollution sources. For these reasons requirements for measuring EC and OC in $PM_{2.5}$ at rural background locations have been included in the Air Quality Directive 2008/50/EC.

The Directive states that measurements should be made in a manner consistent with those of the cooperative programme for monitoring and evaluation of the long range transmission of air pollutants in Europe (EMEP). Thermal-optical analysis has been recognized as the most suitable method for the determination of EC and OC collected on filters and the thermal protocol EUSAAR_2 with a transmittance optical correction for pyrolysis has been recently selected as the European standard thermal protocol (EN16909:2017).

The *European center for aerosol calibration* within the European project ACTRIS-2 has organized in February-March 2018 an inter-laboratory comparison exercise (ILCE) (ref. OCEC-2018-1) among twenty-one applicants including, among others, laboratories in charge of OC and EC measurements at EMEP/ACTRIS station in Germany, Switzerland, Greece, Finland, Norway, Poland, Czech Republic, Cyprus, Spain, Sweden, The Netherlands, Germany, and Italy.

The Senate Department for the Environment, Transport and Climate Protection of Berlin, the University of California-Davis and the Air Quality Agency of Paris also participated.

1 Organization

1.1 Samples, sub-samples and sub-sample homogeneity

In lack of suitable certified reference material for atmospheric OC and EC, this ILCE made use of ambient (outdoor) $PM_{2.5}$ aerosol collected with high-volume samplers on quartz fiber filters at the rural site of Ispra, Italy. Filters (Pallflex, 2500 QAT) were stored in a refrigerator.

Aliquots of ca. 3.6 cm x 1.8 cm, or of 1.6 cm dia. randomly punched out from the test filter samples were distributed to participants according to their needs to allow them to triplicate measurements.

The homogeneity of the test samples was investigated by ERLAP on one of the test samples. Ten subsamples of 1 cm^2 were taken along two perpendicular axes across the filter surface and analysed for their TC, OC and EC contents. The filter homogeneity was assessed as the standard deviation of the average of the 10 replicate analyses. This leads to an upper limit for the filter homogeneity since it includes the repeatability of the ERLAP laboratory (< 3 and 5% for TC and EC, respectively). The homogeneity was better than 4 and 3% for TC and EC/TC, respectively. If sampling occurred under repeatable conditions, it can be assumed that the remaining test samples had similar homogeneities.

An aqueous solution of phthalic acid was also distributed to the participants to assess the uncertainty of the instrument calibration constant determination. The solution was prepared by dissolving a precisely known mass of pure phthalic acid (≥ 99.5%) in a precisely known volume of ultra-pure water (resistivity ≥18.2 MΩ cm).

1.2 Participants

Participants were selected among applicants to ECAC choosing (in the interest for the scientific community) in a first place laboratories which submit TC and EC data to the EBAS database and laboratories which could most benefit from the outcome of this exercise in term of their expertise development.

The list of the twenty-one participants is reported in Table 1. For brevity, the number assigned to each participant will be used in the remainder of the document.

Table 1: List of participants in the inter-laboratory comparison 2018-1, and contact persons

Code	Participant	Acronym	Contact
1	Leibniz Institute of Tropospheric Research	TROPOS	spindler@tropos.de
2	Swiss Federal Laboratories for Materials Science and Technology	EMPA	andrea.fischer@empa.ch; christoph.hueglin@empa.ch
3	National Centre for Scientific Research "Demokritos"	ERL	ldiapouli@ipta.demokritos.gr
4	University of Helsinki	SMEARII	liine.heikkinen@helsinki.fi; mikael.ehn@helsinki.fi
5	Senate Department for the Environment, Transport and Climate Protection	SenUVK	sebastian.clemen@senuvk.berlin.de
7	NILU-Norwegian Institute for Air Research	NILU	Key@nilu.no
8	University of California-Davis	UCDavis	ktrzepla@ucdavis.edu
9	Institute of Environmental Engineering Polish Academy of Sciences	IPIS	barbara.mathews@ipis.zabrze.pl
10	Global Change Research Institute AS CR v. v. i.	CzechGlobe	mbengue.s@czechglobe.cz
11	AIRPARIF	AIRPARIF	chadia.kebbi@airparif.fr
12	University of Birmingham	Bham	z.shi@bham.ac.uk
13	The Cyprus Institute	CYI	k.oikonomou@cyi.ac.cy; i.hafez@cyi.ac.cy ; j.sciare@cyi.ac.cy
14	University of Crete, Chemistry Department	ECPL_UOC	c_theodosi@chemistry.uoc.gr
15	IDAEA - CSIC	IDAEA - CSIC	noemi.perez@idaea.csic.es; Andres.alastuey@idaea.csic.es
16	Lund University, Nuclear physics	Lund-Uni	Patrik.nilsson@design.lth.se; adam.kristensson@design.lth.se
17	GGD Amsterdam	GDD Amsterdam	ppanteliadis@ggd.amsterdam.nl
18	Umweltbundesamt	UBA_DE	elke.bieber@uba.de
19	Slovenian Environment Agency	SEA	judita.burger@gov.si
20	Czech Hydrometeorological Institute	CHMI	Adela.holubova@chmi.cz; milan.vana@chmi.cz
21	Wojewódzki Inspektorat Ochrony Środowiska we Wrocławiu Pracownia Laboratorium z siedzibą w Jeleniej Górze	JGORA-PIOS	izabela.kaluzinska@jgora.pios.gov.pl
22	European Commission, DG-JRC	ERLAP	fabrizia.cavalli@ec.europa.eu

1.3 Sample shipment and reporting of results

Test samples were shipped to all participants (except the "local" participant, 22) on 9th February 2018 via courier at ambient temperature without temperature record, in closed petri dishes. Participants were asked to report TC and EC concentrations, in µg C cm^{-2} units with three decimal digits, from three replicates of test ambient $PM_{2.5}$ samples, by the end of March 2018. In addition, participants were asked to report the OC content of 10 µl of a phthalic acid solution (µg / 10 µl) precisely prepared and traceable to primary measurements.

1.4 Thermal-optical analysis

The thermal protocol EUSAAR_2 [Cavalli et al., 2010] with a transmittance optical correction for pyrolysis has been recently selected as the European standard thermal protocol for the measurements of TC, OC and EC in PM samples (EN16909:2017). In this exercise all participants applied it.

Nineteen laboratories operated a Sunset carbon analyser- of which two, labs 4 and 10, used the semi-continuous model with NDIR detector. Two laboratories, i.e. 12 and 16, operated a DRI carbon analyser, the 12 with an NDIR detector.

2 Data evaluation

Ambient PM filter samples: In absence of suitable certified reference material for atmospheric TC, OC and EC deposited on filters, the *measurement method performance* (par. 2.1) and *laboratory performances* (par. 2.2) were evaluated using atmospheric $PM_{2.5}$ collected on filters as test samples.

In this report we focus on the *TC loadings* (in µg cm^{-2}) and *EC/TC ratios* reported by each participants for each test sample. TC represents the most robust (and protocol-independent) output of TOA analyses, while EC/TC ratios are free from biases in the total carbon determination calibration, and reflect possible differences in the OC/EC split determination among participants. On average, reported TC loadings ranged from 6.7 to 23 µg cm^{-2}, corresponding to atmospheric concentrations ranging from 1.2 to 5.5 µg m^{-3} collected for 24h at a face velocity of 54 cm s^{-1}. EC/TC ranged on average from 0.09 to 0.24. All submitted results (in µg cm^{-2}) for TC, EC, OC (calculated as OC = TC-EC) and EC/TC ratio are presented in tables in Annex 1.

Aqueous solution of phthalic acid: This solution was used to assess the uncertainty of the instrument calibration constant determination. Results were analysed in terms of percentage differences from the assigned value.

Assigned values:

As ambient PM collected on filters was used as test samples, the true values for *TC and EC/TC loadings* were not known. The assigned value and its standard uncertainty for TC loading and EC/TC ratio on each test filter was calculated as the robust average among values from all participants (see Par 2.2).

For the *phthalic acid solution,* the assigned OC concentration value was calculated from the water volume used to make the solution, the mass of phthalic acid dissolved in this water volume, and the chemical formula of phthalic. The assigned value was 1.57 gC l^{-1} (traceable to primary measurements) with an expanded combined relative uncertainty (k = 2) of 1.0%.

2.1 TEST FILTER SAMPLES - Method performance

2.1.1 Data evaluation description

The assessment of the *method performance* aims at deriving, from the results of the present exercise, the precisions of the measurement method in terms of repeatability and reproducibility standard deviations. For this, the consistency of the dataset is evaluated by means of Cochran's test and Grubbs' test [ISO5725-2] for possible outliers (i.e. observations greater than the critical value at the 99% confidence level) or stragglers (i.e. observations greater than the critical value at the 95% confidence level but less or equal to the critical value at the 99% confidence level). Cochran's test verifies the within-laboratory consistency (repeatability). The critical values for *Cochran's test* (i.e. outlier and straggler) vary upon the number of participants and the number of replicate measurements. In this comparison exercise, all twenty-one laboratories provided three replicates for every sample except labs 4 (for IPR1, IPR3 and IPRP5 samples), 10 (for IPR27) and 16 (for IPR1, IPR5 and IPR27). However, Cochran's critical values for three replicates were used for all test samples, i.e. 0.318 (outlier) and 0.261 (straggler).

For each test filter separately, Cochran's criterion is applied to test the consistency of the highest standard deviation value among those reported by all laboratories. After the removal of the outlier(s), if any, the test is repeated on the remaining standard deviations values.

Grubb's test verifies the between-laboratory consistency (reproducibility) and is applied to test, at the first place, the significance of the largest observation (or two as for G_2), and then the significance of the smallest observation (or two as for G_2). For an inter-laboratory comparison among twenty-one participants, the critical values for Grubb's test are 3.031 and 0.376 -outliers for G_1 and G_2, respectively- and 2.733 and 0.455 -stragglers for G_1 and G_2, respectively.

Based on the outcomes of above statistical analyses (Grubbs' and Cochran's tests), outliers are discarded for the calculation of the mean value, the method repeatability and reproducibility standard deviations. Subsequently, the dependence of precision (i.e. repeatability and reproducibility) upon the mean values is investigated [ISO5725-2].

2.1.2 Results: Method performance for TC

Within-laboratory consistency. In Figure 1, the standard deviations on the three replicates reported by each laboratory for each test samples are presented grouped by laboratory. Cochran's test identifies as outliers 10/IPR1, 14/IPR3, 14/IPR5, 10/IPR7, 8/IPR30 and 10/IPR30 (laboratory/sample) and 14/IPR19 as straggler (laboratory/sample).

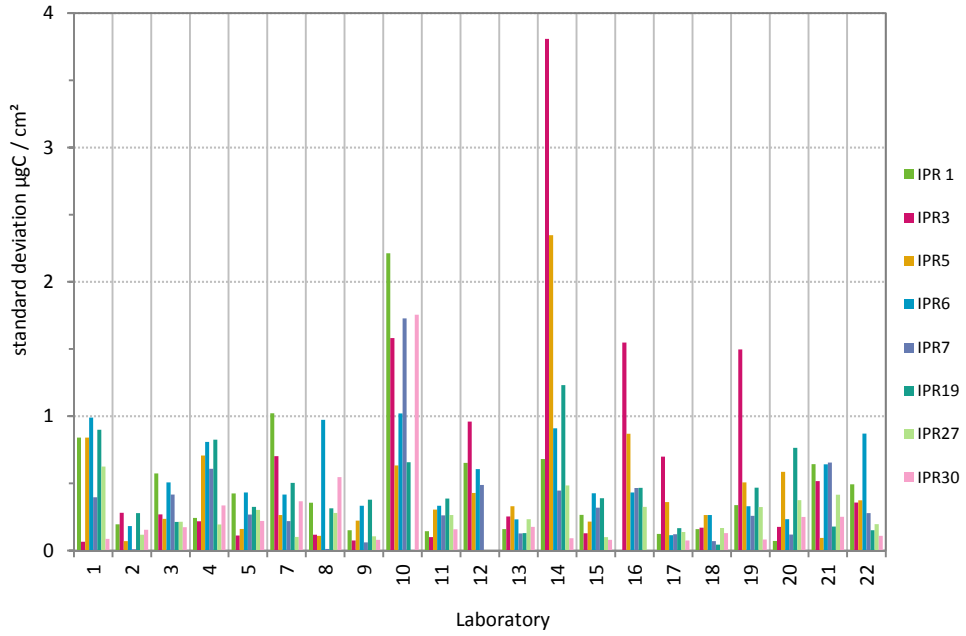


Figure 1. Standard deviation on the three replicates reported for each test filters, grouped by laboratory.

Between-laboratory consistency. In Figure 2, the average values from the replicates reported by each laboratory for each test sample are presented.

The G_1 and G_2 Grubbs' tests identifies as outliers 10/IPR1, 22/IPR1, 10/IPR3, 14/IPR3, 10/IPR5, 4/IPR6, 10/IPR6, 17/IPR6, 10/IPR19, 14/IPR19, 10/IPR27 and 14/IPR27, and as stragglers 10/IPR7, 14/IPR7, 21/IPR7 10/IPR30 and 14/IPR30.

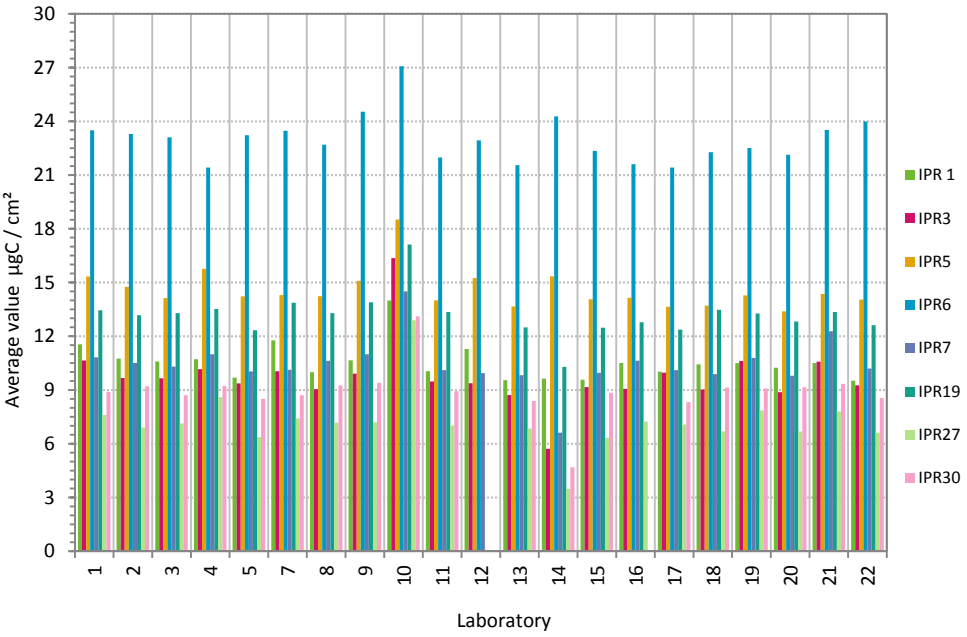


Figure 2. TC average values from three replicates reported by laboratories for each test sample, grouped by laboratory.

Localized sample heterogeneities or contaminations cannot rigorously be excluded, but the occurrence of several stragglers and/or outliers from a single laboratory (case of labs 10 and 14) most probably suggests unsatisfactory laboratory precision for the determination of the TC loadings as compared to the other laboratories.

The entries identified as outliers by the statistical tests were discarded from the dataset, and from the retained values and for each sample separately, the mean value, the method repeatability (*sr*) and reproducibility (*sR*) standard deviations were calculated. The general means and values of *sr* and *sR* for the eight test filter samples are listed in Table 2. Both repeatability (less evident) and reproducibility relative standard deviations tend to have an inverse dependence on TC.

Table 2: General mean, repeatability (*sr*) and reproducibility (*sR*) standard and relative standard deviations for TC.

test sample	general mean	sr		sR	
	µgC / cm²	µgC / cm²	%	µgC / cm²	%
IPR 1	10.41	0.48	4.6	0.76	7.3
IPR3	9.60	0.63	6.5	0.79	8.2
IPR5	14.31	0.40	2.8	0.69	4.9
IPR6	22.94	0.57	2.5	0.99	4.3
IPR7	10.23	0.34	3.3	1.07	10.4
IPR19	13.10	0.45	3.4	0.62	4.7
IPR27	7.14	0.28	3.9	0.62	8.6
ISP30	8.65	0.19	2.2	1.09	12.6

Combining the repeatability and reproducibility relative standard deviations for the EUSAAR_2 protocol obtained during the previous ILCEs and the present one, we observe that the method precision (both *sr* and *sR*) for TC measurement becomes exponentially poorer toward lower TC contents i.e. < 10 µgC / cm² (Fig. 3).

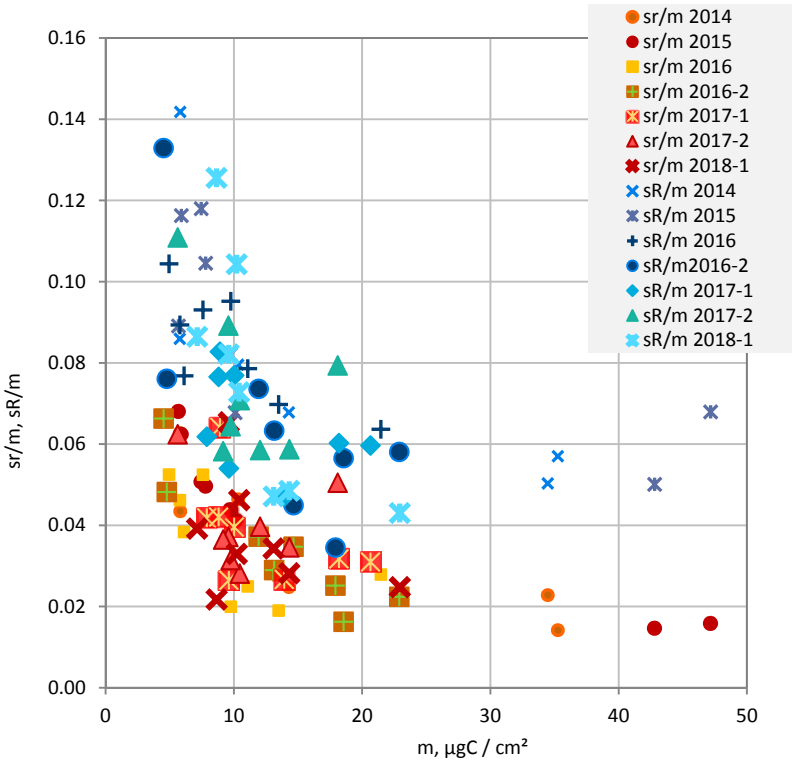


Figure 3. Repeatability and reproducibility relative standard deviation for the EUSAAR_2 protocol for TC measurement obtained during the previous inter-laboratory comparisons and the present one.

2.1.3 Results: Method performance for EC / TC

Within-laboratory consistency. In Figure 4, the standard deviations of the replicates reported for each test samples are presented grouped by laboratory. Cochran's test identifies 14/IPR3, 16/IPR3, 10/IPR5, 4/IPR19, 15/IPR19, 15/IPR27, 16/IPR27, 19/IPR27, 20/IPR27 as outliers (laboratory/sample) and no stragglers.

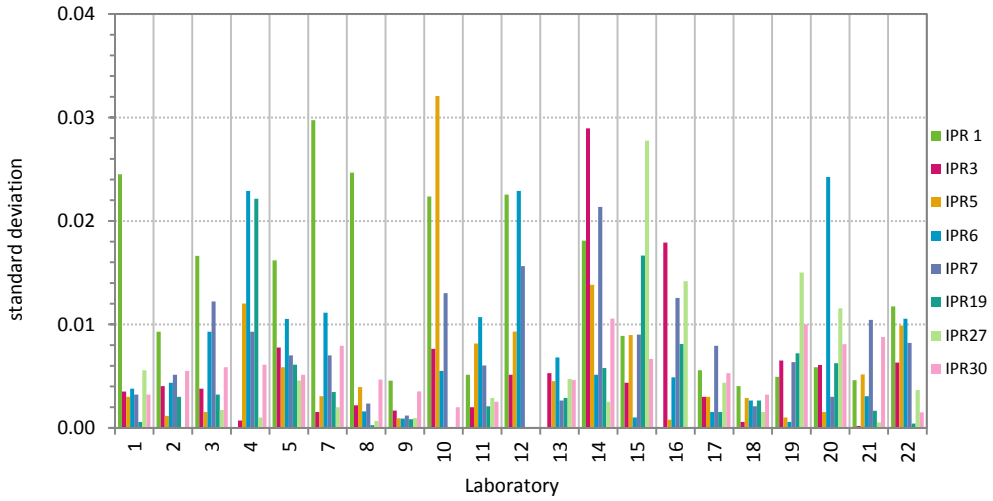


Figure 4. Standard deviation on the replicates reported for each test filters, grouped by laboratory.

Between-laboratory consistency. In Figure 5 the EC/TC ratio average values from the replicates reported by all laboratories for each test sample are presented grouped by laboratory. Grubbs' test identifies the entries 14/IPR6 and 16/IPR6 as stragglers and no outliers.

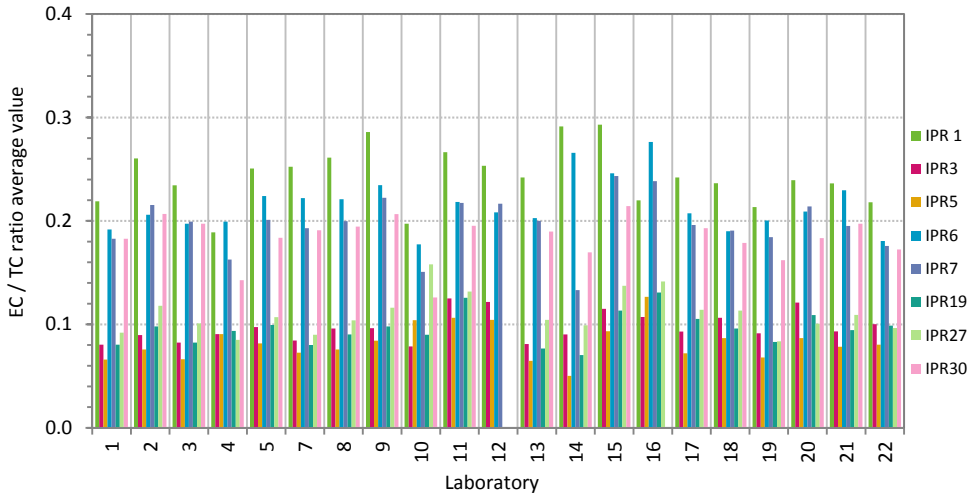


Figure 5. EC/TC average ratios from the replicates reported by laboratories for each test sample, grouped by laboratory.

The entries identified as outliers by the statistical tests are discarded from the dataset, and the mean value, the repeatability (*sr*) and the reproducibility (*sR*) standard deviations for EC/TC are calculated for each sample from the retained values (Table 3). Both repeatability (less evident) and reproducibility relative standard deviations tend to have an inverse dependence on EC/TC ratio.

Table 3: General mean, repeatability (*sr*) and reproducibility (*sR*) standard and relative standard deviations for EC/TC.

test sample	general mean	sr		sR	
			%		%
IPR 1	0.24	0.02	6.2	0.03	12.3
IPR3	0.10	0.00	4.7	0.02	15.5
IPR5	0.08	0.01	7.7	0.02	21.2
IPR6	0.21	0.01	4.9	0.03	12.5
IPR7	0.20	0.01	4.7	0.03	14.1
IPR19	0.09	0.00	4.2	0.02	17.1
IPR27	0.11	0.00	2.8	0.01	13.7
ISP30	0.18	0.01	3.3	0.02	12.2

Combining the repeatability and reproducibility relative standard deviation for the EUSAAR_2 protocol obtained during the previous four ILCEs and the present one, we observe that the method precision (both *sr* and *sR*) for EC/TC ratio measurement can become poorer at lower EC/TC ratios, i.e. < 0.07 (Fig. 6).

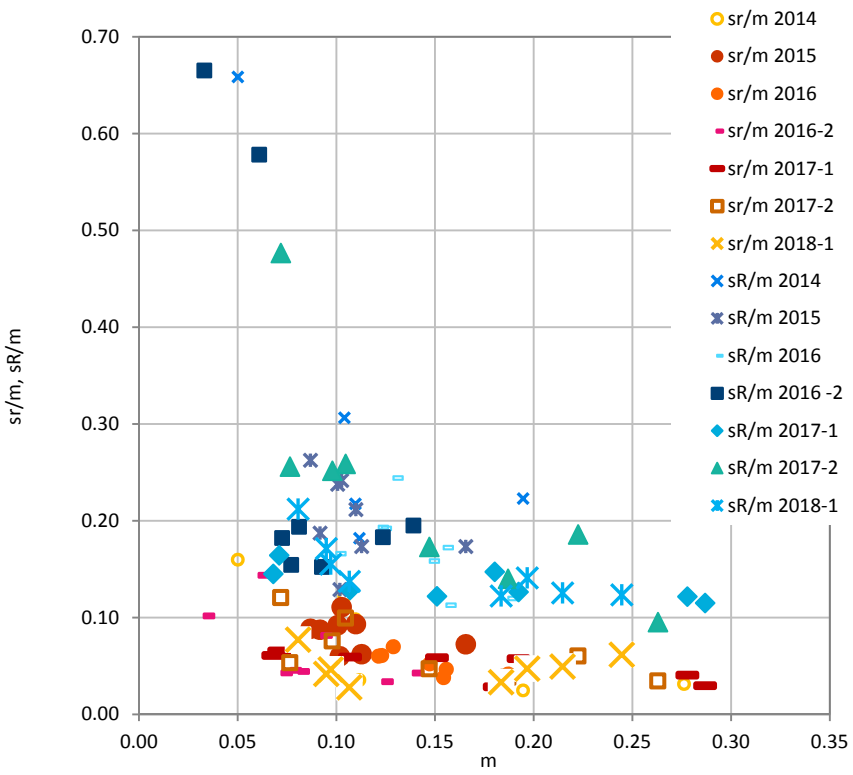


Figure 6. Repeatability and reproducibility relative standard deviation for the EUSAAR_2 protocol for EC/TC measurement obtained during the previous inter-laboratory comparisons and the present one.

2.2 FILTER TEST SAMPLES - Laboratory performance

2.2.1 Data evaluation description

The assessment of the *laboratory performance* aims at describing the laboratory bias compared to the assigned value associated with its standard deviation. Each participant's performance is determined in terms of *z-scores,* a measure of the deviation from the assigned value. To calculate *z-scores*, an assigned value and its standard deviation have to be determined for each test sample.

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

- *Determining the standard deviation for proficiency assessment*: Among the available methods 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 participants (See ISO 13528:2005(E), Annex C).

These approaches might become statistically ineffective [ISO 13528:2015 (E)], for example, if the number of participant is lower than twenty. To verify their reliability the robust mean and its standard deviation were also calculated applying the Q/Hampel method (ISO 13528:2015 (E)). The values obtained do not significantly differ from those obtained by the *consensus value from participant results*, in Table 8, which are then used for the following elaboration.

For each laboratory and test sample, the *z-score* was calculated as:

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

where x_i is the result from the participant i; X is the assigned value for the sample; and σ^* is the standard deviation for proficiency assessment.

When a participant reports an entry that produces a bias greater than +3 z or less than -3 z (i.e. deviating from the assigned value for more than 3 standard deviations), this entry is considered to give an "action signal". Likewise, a laboratory bias above +2 z or below -2 z (i.e. deviating from the assigned value for more than 2 but less than 3 standard deviations) is considered to give a "warning signal". A laboratory bias between -2 z and +2 z indicates a satisfactory laboratory performance with respect to the standard deviation for proficiency assessment.

In addition, on the basis of results from the present inter-laboratory comparison and for the purpose of harmonizing TC, OC and EC air mass concentrations reported into the EBAS database, statistics, i.e. percentage bias and variability, were calculated for TC, OC and EC determination for each participant. Methods and results are in Annex 2.

2.2.2 Results: Laboratory performance for TC

The assigned values X and the related standard deviations for proficiency assessment σ* calculated from the entire database for each sample, are reported in Table 4. Following ISO13528, σ* were calculated *from data obtained in a round of a proficiency testing scheme*.

Table 4: Assigned values and standard deviations for proficiency assessment σ* *from data obtained in a round of a proficiency testing scheme* for TC.

		IPR 1	IPR3	IPR5	IPR6	IPR7	IPR19	IPR27	IPR30
assigned value	µg/cm2	10.4	9.6	14.4	22.9	10.3	13.1	7.1	8.9
standard	µg/cm2	0.8	0.7	0.7	1.1	0.5	0.6	0.6	0.4
deviation	%	7.2	7.2	5.1	4.8	5.2	4.8	8.9	5.0
2σ*	%	14	14	10	10	10	10	18	10
3σ*	%	22	22	15	15	16	14	27	15

Figure 7 shows z-scores calculated from σ*. Fourteen outliers, 10/IPR1, 10/IPR3, 14/IPR3, 10/IPR5, 10/IPR6, 10/IPR7, 14/IPR7, 21/IPR7, 10/IPR19, 14/IPR19, 10/IPR27, 14/IPR27, 10/IPR30 and 14/IPR30 (lab/sample) –mainly from two participants– and one straggler, 4/IPR27, are identified.

For each sample, thirteen to fifteen out of twenty-one participants show deviations from the assigned values within +/- 1 σ* as listed in Table 8 (i.e. within 1 z-score). 86% of all entries are within 10% from the assigned value.
A few participants show the systematic tendency (i.e. for all test samples and larger than ± 5%, on average) of overestimating –i.e. lab 10 - or underestimating –i.e. lab 13 - the assigned TC concentrations.
A contribution of filter heterogeneities to poor laboratory performances cannot be completely excluded. However, participants showing large (|z-scores|> 2) and/or systematic biases shall carefully examine their procedures and identify appropriate corrective actions that are likely to prevent the recurrence of such results in the future. A more accurate determination of the instrument's calibration constant (e.g. implementing CO_2 calibration where possible) would probably reduce the observed variability in TC determination.

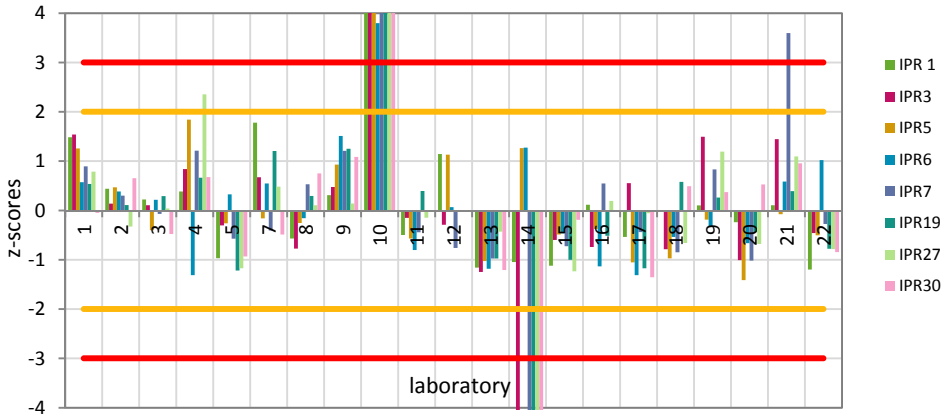


Figure 7. z-scores for TC calculated using σ* *from data obtained in a round of a proficiency testing scheme*. The scale is set from -4 to +4.

2.2.3 Results: Laboratory performance for EC/TC

The assigned values, X, and the related standard deviations for proficiency assessment, σ*, are reported in Table 5. Following ISO13528, σ* are calculated *from data obtained in a round of a proficiency testing scheme* including all participants.
The corresponding z-scores are shown in Figure 8.

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.

		IPR 1	IPR3	IPR5	IPR6	IPR7	IPR19	IPR27	IPR30
assigned value	ratio	0.24	0.10	0.08	0.21	0.20	0.09	0.11	0.19
standard	ratio	0.03	0.01	0.02	0.02	0.02	0.02	0.02	0.01
deviation	%	12	14	19	10	12	16	15	7
2σ*	%	24	27	39	20	24	32	30	15
3σ*	%	36	41	58	30	37	49	45	22

Four outliers – 16/IPR6, 10/IPR27, 4/IPR30 and 10/IPR30 (lab/sample) - and eight stragglers – 11/IPR3, 12/IPR3, 16/IPR5, 14/IPR6, 14/IPR7, 11/IPR19, 16/IPR19 and 16/IPR27 - (lab/sample) are identified. For each sample, eleven to sixteen out of twenty-one laboratories

show deviations from the assigned values within +/- 1 σ* as listed in Table 5 (i.e. within 1 z-score).
57% of all entries are within 10% of the assigned value and 89% are within the 25% of the assigned value.
A few participants show the systematic tendency (i.e. for all test samples and larger than ± 5%, on average) of overestimating – i.e. lab 9 and 11 and 15 - or underestimating – i.e. lab 1 and 19 - the assigned EC/TC ratio.
A contribution of filter heterogeneities to poor laboratory performances cannot be completely excluded. However, participants showing large (|z-scores|> 2) and/or systematic biases shall carefully examine their procedures and identify appropriate corrective actions that are likely to prevent the recurrence of such results in the future. A more solid and stable in time instrument set-up in terms of i) laser stability; ii) FID response in He and He/O_2 phases; iii) temperature calibration and iv) transit time would correct such performances and reduce the observed variability in EC/TC ratio determination.

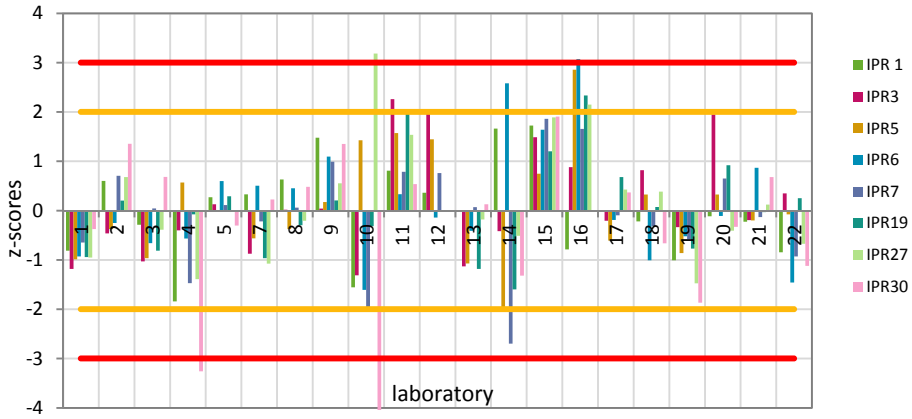


Figure 8. z-scores for EC/TC ratio calculated using σ* *from data obtained in a round of a proficiency testing scheme*. The scale is set from -4 to +4.

2.3 PHTHALIC ACID SOLUTION – Percentage differences

Participants were asked to report the OC content of 10 µl of phthalic acid solution. This included the analysis of samples prepared by spiking a pre-cleaned filter punch with 10 µl solution. This is the procedure normally used by laboratories to determine and verify the FID calibration constant.
Figure 9 shows the percentage differences from the assigned value (1.57 ± 0.02 gC l^{-1}, calculated from primary mass and water volume measurements) for each participant. Fourteen laboratories out of twenty laboratories reported OC deviating from the assigned value by less than ±5%. Since each phthalic acid solution flask was not checked individually, contaminations cannot be completely excluded.
This exercise did not aim at identifying systematic tendency of a laboratory to underestimate or overestimate the C content of analysed samples but rather to highlight the potential uncertainty (and variability) that can affect carbon determination, when the spiking procedure is applied to determine the FID calibration constant.

It is recommended to implement the calibration with CO_2 injections where possible, or to carefully revise the accuracy of all steps involved in the external solution spiking procedure (calibration of the pipette volume, complete deposition of the volume onto a punch filter, drying etc.).

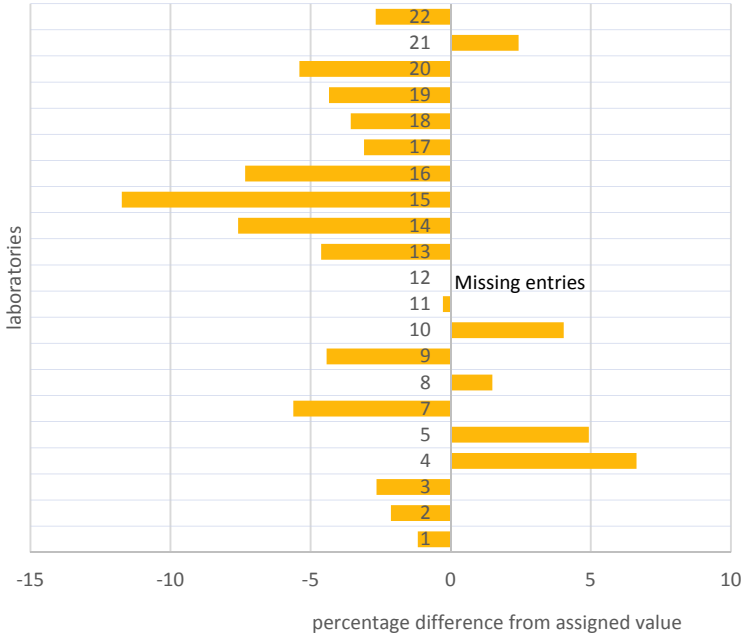


Figure 9. Phthalic acid solution –percentage differences from the assigned value, i.e. the C concentration of the test solution calculated from the mass of phthalic acid and the volume of ultra-pure water used to make the solution.

Conclusions

This inter-laboratory comparison involved twenty-one participants all applying thermal-optical analyses and the EUSAAR_2 protocol.
The measurement method ***repeatability and reproducibility for TC*** ranged from **2 % to 7 %** and from **5 % to 12 %** (as one relative standard deviation), respectively.
For the ***EC/TC ratio, repeatability and reproducibility*** ranged from **3 %** to **8 %** and from **12 %** to **17 %**, respectively.
Combining the repeatability (sr) and reproducibility (sR) relative standard deviation for the EUSAAR_2 protocol obtained during the previous ILCEs and the present one, we observed that the method precision (both sr and sR) becomes exponentially poorer toward lower TC contents i.e. <10 µgC / cm² and EC/TC ratio. i.e. <0.07.
Although the contribution of localized sample heterogeneities and /or contaminations to biased data cannot be totally excluded, the random scheme adopted to distribute sub-samples was such that the recurrence of stragglers or outliers for single laboratories most probably indicates an unsatisfactory laboratory precision as compared to the other participants.

Still in absence of a suitable certified reference material for atmospheric OC and EC, the tests samples used to assess laboratories' performance consisted of atmospheric PM deposited on filters. The assigned values for TC loadings and EC/TC ratios in the test samples were calculated as robust averages among all participants.

Laboratory performances were assessed for both TC loadings and EC/TC ratios determinations based on z-scores, applying as assigned values and standard deviation for proficiency assessment the ones calculated from data obtained in a round of a proficiency testing scheme.
For TC loadings, fourteen outliers –mainly from two participants– and one straggler were identified; 86% of all entries were within 10% from the assigned TC concentration value. A few participants show the systematic tendency (i.e. for all test samples and larger than + or – 5% on average) of overestimating –i.e. lab 10 - or underestimating –i.e. lab 13 - the assigned TC concentrations. Participants showing large (|z-scores|> 2) and/or systematic biases shall carefully examine their procedures and identify appropriate corrective actions that are likely to prevent the recurrence of such results in the future. A more accurate determination of the instrument's calibration constant (e.g. implementing CO_2 calibration where possible) would correct this tendency.
Regarding EC/TC ratios, four outliers and eight stragglers from a few participants, were identified. 57% of all entries were within 10% of the assigned value and 89% were within the 25% of the assigned value. A few participants show the systematic tendency (i.e. for all test samples and larger than + or – 5%, on average) of overestimating –i.e. labs 9, 11 and 15 - or underestimating –i.e. labs 1 and 19 - the assigned EC/TC ratio. Participants showing large (|z-scores|> 2) and/or systematic biases shall carefully examine their procedures and identify appropriate corrective actions that are likely to prevent the recurrence of such results in the future. A more solid and stable in time instrument set-up in terms of i) laser stability; ii) FID response in He and He/O_2 phases; iii) temperature calibration and iv) transit time would correct this behavior and reduce the observed variability in EC/TC ratio determination.
In addition, on the basis of results from the present inter-laboratory comparison and for the purpose of harmonizing TC, OC and EC air mass concentrations reported into the EBAS database,

statistics, i.e. percentage bias and variability, were calculated for TC, OC and EC determination for each participant.

References

EU Directive 2008/50/EC on ambient air and cleaner air for Europe.

FprCEN/TR 16243. Ambient air quality - Guide for the measurement of elemental carbon (EC) and organic carbon (OC) deposited on filters. CEN, Brussels, 2011.

EN 16909. Ambient air – Measurement of elemental carbon (EC) and organic carbon (OC) collected on filters. CEN, Brussels, 2017.

Cavalli F., Putaud J., Viana M., Yttri K., Genberg J., Toward a Standardised Thermal-Optical Protocol for Measuring Atmospheric Organic and Elemental Carbon: The EUSAAR Protocol. Atmospheric Measurement Techniques 3 (1); p. 79-89, 2010.

ISO 13528. Statistical methods for use in proficiency testing by inter-laboratory comparisons. ISO, Geneva, 2005.

ISO 13528. Statistical methods for use in proficiency testing by inter-laboratory comparisons. ISO, Geneva, 2015.

ISO 5725-2. Accuracy (trueness and precision) of measurement methods and results -- Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method. ISO, Geneva, 1994.

Annex 1. Numerical results reported by participants

Table 1: Total carbon loadings (µg/cm^2)

Laboratory	IPR1	IPR3	IPR5	IPR6	IPR7	IPR19	IPR27	IPR30
1	11.117	10.596	15.366	24.634	10.589	12.972	7.993	8.941
	12.512	10.627	16.162	23.034	10.605	14.482	7.939	8.800
	11.003	10.721	14.482	22.826	11.284	12.883	6.885	8.958
2	10.944	9.983	14.822	23.187	10.513	13.497	6.933	9.072
	10.768	9.610	14.779	23.179	10.496	13.014	6.773	9.377
	10.553	9.432	14.684	23.498	10.512	13.015	7.003	9.183
3	11.251	9.401	14.328	22.689	10.151	13.163	7.356	8.851
	10.332	9.618	14.181	22.944	9.994	13.536	7.122	8.763
	10.195	9.937	13.866	23.667	10.781	13.169	6.927	8.516
4	NaN	NaN	15.264	21.093	11.136	14.145	8.589	9.425
	10.887	10.315	NaN	22.331	11.524	13.842	8.405	8.833
	10.544	10.007	16.264	20.810	10.330	12.588	8.794	9.405
5	9.651	9.483	14.143	23.523	9.837	12.406	6.244	8.646
	9.292	9.259	14.413	23.418	10.341	12.619	6.712	8.628
	10.138	9.363	14.128	22.727	9.933	11.981	6.147	8.256
7	12.200	9.410	14.500	23.800	10.300	13.800	7.350	8.290
	10.600	9.930	14.000	23.000	10.200	13.400	7.530	8.850
	12.500	10.800	14.400	23.600	9.880	14.400	7.360	8.980
8	10.315	8.969	14.113	21.949	10.631	13.082	6.875	8.744
	10.058	9.178	14.255	22.328	10.643	13.140	7.220	9.831
	9.611	8.980	14.329	23.792	10.620	13.654	7.430	9.187
9	10.815	9.977	14.915	24.202	10.925	14.222	7.305	9.493
	10.514	9.922	15.345	24.868	11.024	13.984	7.094	9.362
	10.644	9.829	15.031	24.535	11.036	13.481	7.195	9.349
10	13.369	15.135	18.825	28.066	14.414	17.791	12.887	11.952
	16.448	15.811	18.925	27.101	12.827	17.084	NaN	15.130
	12.156	18.149	17.781	26.027	16.279	16.478	NaN	12.250
11	10.117	9.519	13.962	21.622	10.331	12.968	6.908	9.094
	10.147	9.361	14.323	22.285	10.172	13.353	7.316	8.780
	9.884	9.545	13.718	22.020	9.820	13.742	6.822	8.904
12	11.998	8.296	15.697	22.736	10.024	NaN	NaN	NaN
	11.152	9.711	15.192	22.457	10.374	NaN	NaN	NaN
	10.715	10.126	14.845	23.619	9.410	NaN	NaN	NaN
13	9.495	8.997	14.024	21.779	9.681	12.361	6.723	8.210
	9.728	8.506	13.371	21.315	9.854	12.621	7.105	8.562
	9.423	8.637	13.609	21.567	9.931	12.487	6.683	8.390
14	9.634	5.715	15.342	24.270	6.619	10.286	3.482	4.680
	10.959	12.393	13.947	23.245	5.772	8.925	4.447	4.863
	10.019	5.880	10.764	22.457	6.445	7.829	3.889	4.775
15	9.877	9.265	13.883	22.577	9.609	12.245	6.272	8.776
	9.483	9.207	14.301	22.610	10.022	12.253	6.444	8.808
	9.371	9.018	14.001	21.855	10.237	12.924	6.270	8.928
16	NaN	8.210	NaN	21.150	10.450	13.270	7.460	NaN
	10.510	10.850	13.530	22.010	10.300	12.340	7.000	NaN
	NaN	8.130	14.760	21.660	11.170	12.730	NaN	NaN
17	9.878	10.677	14.064	21.292	10.130	12.551	7.130	8.341
	10.071	9.935	13.451	21.521	9.977	12.227	6.914	8.241
	10.110	9.280	13.429	21.421	10.218	12.317	7.172	8.388
18	10.592	9.229	13.578	22.175	9.963	13.522	6.735	9.149
	10.274	8.939	14.013	22.569	9.882	13.454	6.506	9.004

	10.418	8.928	13.534	22.066	9.823	13.439	6.832	9.264
19	10.160	9.182	14.866	22.592	10.702	13.779	8.140	9.018
	10.509	12.169	13.943	22.776	10.590	12.860	7.507	9.062
	10.836	10.497	14.039	22.136	11.084	13.171	7.939	9.178
20	10.286	9.054	13.458	22.012	9.872	13.682	7.066	8.927
	10.160	8.885	12.767	21.974	9.862	12.593	6.653	9.113
	10.283	8.702	13.933	22.395	9.660	12.207	6.317	9.423
21	9.980	11.171	14.330	23.450	13.030	13.310	7.550	9.580
	11.220	10.200	14.470	24.180	11.970	13.550	7.570	9.370
	10.308	10.377	14.290	22.900	11.833	13.200	8.280	9.080
22	10.079	9.656	13.619	24.989	10.250	12.559	6.480	8.495
	9.335	9.166	14.301	23.599	9.896	12.787	6.840	8.476
	9.146	8.960	14.225	23.386	10.445	12.501	6.524	8.674

Table 2: Elemental carbon / total carbon (ratios)

Laboratory	IPR1	IPR3	IPR5	IPR6	IPR7	IPR19	IPR27	IPR30
1	0.195	0.077	0.063	0.196	0.179	0.080	0.097	0.179
	0.218	0.080	0.069	0.189	0.184	0.080	0.086	0.184
	0.244	0.084	0.066	0.190	0.185	0.081	0.093	0.185
2	0.250	0.086	0.077	0.209	0.221	0.098	0.118	0.201
	0.268	0.089	0.075	0.208	0.214	0.101	0.118	0.207
	0.263	0.094	0.075	0.201	0.211	0.095	0.118	0.212
3	0.219	0.085	0.065	0.193	0.202	0.080	0.102	0.195
	0.232	0.084	0.068	0.191	0.210	0.081	0.099	0.204
	0.252	0.078	0.066	0.208	0.186	0.086	0.102	0.193
4	NaN	NaN	0.082	0.192	0.160	0.084	0.084	0.136
	0.189	0.091	NaN	0.181	0.155	0.119	0.086	0.148
	0.189	0.090	0.099	0.225	0.173	0.078	0.085	0.144
5	0.259	0.095	0.086	0.235	0.209	0.106	0.111	0.188
	0.261	0.106	0.075	0.214	0.198	0.094	0.108	0.185
	0.232	0.091	0.084	0.223	0.196	0.098	0.102	0.178
7	0.248	0.086	0.070	0.232	0.190	0.078	0.090	0.197
	0.284	0.083	0.072	0.210	0.188	0.084	0.092	0.194
	0.225	0.084	0.076	0.224	0.201	0.078	0.088	0.182
8	0.233	0.093	0.080	0.222	0.200	0.090	0.105	0.198
	0.280	0.097	0.072	0.221	0.202	0.090	0.103	0.197
	0.270	0.097	0.076	0.219	0.197	0.091	0.104	0.189
9	0.281	0.098	0.084	0.235	0.221	0.099	0.117	0.210
	0.290	0.094	0.085	0.234	0.223	0.097	0.116	0.207
	0.286	0.097	0.083	0.234	0.223	0.098	0.115	0.203
10	0.202	0.077	0.084	0.171	0.150	0.090	0.158	0.128
	0.173	0.072	0.141	0.180	0.164	0.090	NaN	0.124
	0.217	0.087	0.087	0.181	0.138	0.090	NaN	0.126
11	0.265	0.127	0.110	0.225	0.218	0.128	0.135	0.193
	0.272	0.125	0.112	0.206	0.211	0.124	0.130	0.198
	0.262	0.123	0.097	0.224	0.223	0.125	0.130	0.195
12	0.230	0.126	0.115	0.201	0.231	NaN	NaN	NaN
	0.255	0.123	0.100	0.234	0.219	NaN	NaN	NaN
	0.275	0.116	0.098	0.190	0.200	NaN	NaN	NaN
13	0.242	0.085	0.069	0.208	0.198	0.080	0.108	0.187
	0.242	0.075	0.060	0.195	0.199	0.075	0.099	0.187
	0.242	0.083	0.065	0.205	0.203	0.075	0.106	0.195
14	0.291	0.090	0.050	0.266	0.133	0.070	0.099	0.170
	0.261	0.038	0.046	0.256	0.155	0.081	0.101	0.179
	0.259	0.085	0.072	0.262	0.113	0.080	0.104	0.191
15	0.283	0.118	0.083	0.246	0.234	0.108	0.112	0.211
	0.296	0.117	0.098	0.247	0.244	0.132	0.133	0.222
	0.300	0.110	0.099	0.245	0.252	0.100	0.167	0.210
16	NaN	0.088	NaN	0.271	0.251	0.134	0.151	NaN
	0.220	0.111	0.127	0.276	0.239	0.122	0.131	NaN
	NaN	0.123	0.126	0.281	0.226	0.137	NaN	NaN
17	0.248	0.090	0.069	0.209	0.193	0.105	0.111	0.189
	0.241	0.096	0.072	0.207	0.205	0.104	0.119	0.191
	0.237	0.093	0.075	0.206	0.190	0.107	0.112	0.199
18	0.237	0.106	0.090	0.191	0.193	0.093	0.112	0.175
	0.240	0.106	0.085	0.187	0.190	0.098	0.115	0.181
	0.232	0.107	0.085	0.192	0.189	0.097	0.113	0.180
19	0.219	0.091	0.067	0.200	0.188	0.077	0.075	0.152

	0.210	0.098	0.069	0.200	0.188	0.081	0.075	0.162
	0.211	0.085	0.068	0.201	0.177	0.091	0.101	0.172
20	0.235	0.117	0.087	0.223	0.217	0.102	0.094	0.188
	0.237	0.118	0.085	0.223	0.214	0.111	0.094	0.188
	0.246	0.128	0.088	0.181	0.211	0.114	0.114	0.174
21	0.241	0.093	0.080	0.233	0.197	0.094	0.109	0.190
	0.233	0.093	0.083	0.227	0.184	0.093	0.110	0.207
	0.234	0.093	0.073	0.229	0.204	0.096	0.109	0.195
22	0.205	0.094	0.089	0.188	0.185	0.099	0.096	0.172
	0.227	0.100	0.069	0.185	0.172	0.099	0.093	0.171
	0.222	0.107	0.083	0.168	0.170	0.098	0.100	0.174

Table 3: Elemental carbon loadings (μg/cm^2)

Laboratory	IPR1	IPR3	IPR5	IPR6	IPR7	IPR19	IPR27	IPR30
1	2.167	0.819	0.972	4.822	1.900	1.035	0.774	1.604
	2.727	0.852	1.121	4.357	1.952	1.160	0.680	1.617
	2.689	0.902	0.961	4.343	2.083	1.042	0.638	1.658
2	2.737	0.860	1.140	4.851	2.322	1.321	0.816	1.827
	2.890	0.860	1.114	4.831	2.246	1.308	0.799	1.827
	2.773	0.883	1.106	4.732	2.213	1.235	0.828	1.939
3	2.462	0.794	0.934	4.371	2.055	1.059	0.752	1.722
	2.399	0.804	0.958	4.386	2.095	1.103	0.708	1.785
	2.572	0.774	0.915	4.914	2.005	1.133	0.707	1.646
4	NaN	NaN	1.243	4.058	1.786	1.189	0.726	1.243
	2.054	0.940	NaN	4.039	1.790	1.641	0.721	1.308
	2.084	0.900	1.592	4.675	1.790	0.985	0.746	1.358
5	2.501	0.898	1.220	5.528	2.057	1.311	0.690	1.623
	2.422	0.978	1.074	5.023	2.045	1.191	0.722	1.599
	2.356	0.850	1.190	5.072	1.945	1.179	0.628	1.470
7	3.020	0.810	1.010	5.510	1.960	1.070	0.660	1.630
	3.000	0.830	1.000	4.820	1.920	1.180	0.690	1.720
	2.810	0.900	1.090	5.270	1.990	1.120	0.650	1.630
8	2.406	0.838	1.124	4.880	2.124	1.178	0.720	1.730
	2.816	0.895	1.023	4.939	2.151	1.187	0.747	1.933
	2.598	0.869	1.082	5.215	2.096	1.236	0.769	1.738
9	3.041	0.973	1.258	5.697	2.414	1.402	0.855	1.995
	3.052	0.936	1.307	5.809	2.457	1.358	0.819	1.935
	3.045	0.951	1.253	5.753	2.462	1.327	0.831	1.899
10	2.696	1.164	1.587	4.795	2.169	1.606	1.214	1.527
	2.855	1.139	2.661	4.874	2.104	1.542	1.005	1.885
	2.641	1.144	1.552	4.720	2.253	1.477	NaN	1.542
11	2.680	1.212	1.537	4.868	2.249	1.662	0.932	1.755
	2.762	1.171	1.602	4.584	2.148	1.658	0.953	1.739
	2.585	1.173	1.334	4.942	2.192	1.724	0.914	1.734
12	2.765	1.049	1.809	4.570	2.321	NaN	NaN	NaN
	2.842	1.195	1.517	5.261	2.272	NaN	NaN	NaN
	2.943	1.179	1.458	4.494	1.883	NaN	NaN	NaN
13	2.299	0.760	0.966	4.527	1.917	0.992	0.729	1.533
	2.352	0.640	0.806	4.160	1.960	0.946	0.704	1.601
	2.277	0.717	0.889	4.429	2.019	0.940	0.706	1.639
14	2.806	0.516	0.769	6.452	0.881	0.723	0.345	0.794
	2.858	0.469	0.648	5.942	0.897	0.720	0.448	0.873
	2.595	0.502	0.776	5.879	0.726	0.626	0.404	0.911
15	2.797	1.095	1.158	5.546	2.249	1.323	0.705	1.853
	2.810	1.081	1.395	5.580	2.449	1.621	0.859	1.959
	2.809	0.995	1.391	5.346	2.577	1.287	1.045	1.871
16	NaN	0.720	NaN	5.740	2.620	1.780	1.130	NaN
	2.310	1.200	1.720	6.080	2.460	1.500	0.920	NaN
	NaN	1.000	1.860	6.090	2.520	1.740	NaN	NaN
17	2.450	0.963	0.976	4.442	1.958	1.321	0.795	1.573
	2.432	0.958	0.974	4.457	2.049	1.266	0.822	1.571
	2.399	0.867	1.006	4.410	1.939	1.318	0.800	1.669
18	2.510	0.977	1.219	4.236	1.920	1.251	0.754	1.600
	2.462	0.950	1.196	4.221	1.875	1.319	0.750	1.628
	2.414	0.960	1.148	4.241	1.859	1.305	0.774	1.663
19	2.225	0.840	1.002	4.520	2.016	1.058	0.613	1.368

	2.211	1.190	0.959	4.562	1.991	1.038	0.561	1.466
	2.282	0.887	0.952	4.443	1.965	1.196	0.799	1.577
20	2.415	1.057	1.173	4.906	2.146	1.396	0.665	1.678
	2.412	1.050	1.084	4.897	2.108	1.393	0.626	1.713
	2.527	1.116	1.228	4.042	2.042	1.393	0.718	1.636
21	2.410	1.059	1.140	5.460	2.570	1.250	0.820	1.820
	2.668	0.971	1.200	5.480	2.200	1.260	0.830	1.940
	2.349	1.015	1.040	5.230	2.395	1.270	0.825	1.770
22	2.065	0.909	1.209	4.694	1.899	1.243	0.623	1.457
	2.123	0.915	0.993	4.372	1.700	1.266	0.636	1.453
	2.029	0.956	1.179	3.939	1.780	1.228	0.654	1.510

Table 4: Organic carbon [OC = TC-EC loadings] (μg/cm^2)

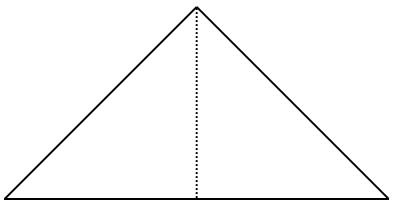
Laboratory	IPR1	IPR3	IPR5	IPR6	IPR7	IPR19	IPR27	IPR30
1	8.95	9.78	14.39	19.81	8.69	11.94	7.22	7.34
	9.79	9.78	15.04	18.68	8.65	13.32	7.26	7.18
	8.31	9.82	13.52	18.48	9.20	11.84	6.25	7.30
2	8.21	9.12	13.68	18.34	8.19	12.18	6.12	7.25
	7.88	8.75	13.67	18.35	8.25	11.71	5.97	7.55
	7.78	8.55	13.58	18.77	8.30	11.78	6.18	7.24
3	8.79	8.61	13.39	18.32	8.10	12.10	6.60	7.13
	7.93	8.81	13.22	18.56	7.90	12.43	6.41	6.98
	7.62	9.16	12.95	18.75	8.78	12.04	6.22	6.87
4	NaN	NaN	14.02	17.04	9.35	12.96	7.86	8.18
	8.83	9.38	NaN	18.29	9.73	12.20	7.68	7.53
	8.46	9.11	14.67	16.14	8.54	11.60	8.05	8.05
5	7.15	8.59	12.92	18.00	7.78	11.10	5.55	7.02
	6.87	8.28	13.34	18.40	8.30	11.43	5.99	7.03
	7.78	8.51	12.94	17.66	7.99	10.80	5.52	6.79
7	9.18	8.60	13.49	18.29	8.34	12.73	6.69	6.66
	7.60	9.10	13.00	18.18	8.28	12.22	6.84	7.13
	9.69	9.90	13.31	18.33	7.89	13.28	6.71	7.35
8	7.91	8.13	12.99	17.07	8.51	11.90	6.16	7.01
	7.24	8.28	13.23	17.39	8.49	11.95	6.47	7.90
	7.01	8.11	13.25	18.58	8.52	12.42	6.66	7.45
9	7.77	9.00	13.66	18.51	8.51	12.82	6.45	7.50
	7.46	8.99	14.04	19.06	8.57	12.63	6.27	7.43
	7.60	8.88	13.78	18.78	8.57	12.15	6.36	7.45
	10.67	13.97	17.24	23.27	12.25	16.18	11.67	10.42
	13.59	14.67	16.26	22.23	10.72	15.54	NaN	13.24
	9.51	17.00	16.23	21.31	14.03	15.00	NaN	10.71
11	7.44	8.31	12.43	16.75	8.08	11.31	5.98	7.34
	7.39	8.19	12.72	17.70	8.02	11.70	6.36	7.04
	7.30	8.37	12.38	17.08	7.63	12.02	5.91	7.17
12	9.23	7.25	13.89	18.17	7.70	NaN	NaN	NaN
	8.31	8.52	13.68	17.20	8.10	NaN	NaN	NaN
	7.77	8.95	13.39	19.13	7.53	NaN	NaN	NaN
13	7.20	8.24	13.06	17.25	7.76	11.37	5.99	6.68
	7.38	7.87	12.57	17.16	7.89	11.68	6.40	6.96
	7.15	7.92	12.72	17.14	7.91	11.55	5.98	6.75
14	6.83	5.20	14.57	17.82	5.74	9.56	3.14	3.89
	8.10	11.92	13.30	17.30	4.88	8.21	4.00	3.99
	7.42	5.38	9.99	16.58	5.72	7.20	3.48	3.86
15	7.08	8.17	12.73	17.03	7.36	10.92	5.57	6.92
	6.67	8.13	12.91	17.03	7.57	10.63	5.59	6.85
	6.56	8.02	12.61	16.51	7.66	11.64	5.23	7.06
16	NaN	7.49	NaN	15.41	7.83	11.49	6.33	NaN
	8.20	9.65	11.81	15.93	7.84	10.84	6.08	NaN
	NaN	7.13	12.90	15.57	8.65	10.99	NaN	NaN
17	7.43	9.71	13.09	16.85	8.17	11.23	6.34	6.77
	7.64	8.98	12.48	17.06	7.93	10.96	6.09	6.67
	7.71	8.41	12.42	17.01	8.28	11.00	6.37	6.72
18	8.08	8.25	12.36	17.94	8.04	12.27	5.98	7.55
	7.81	7.99	12.82	18.35	8.01	12.14	5.76	7.38
	8.00	7.97	12.39	17.83	7.96	12.13	6.06	7.60
19	7.94	8.34	13.86	18.07	8.69	12.72	7.53	7.65

	8.30	10.98	12.98	18.21	8.60	11.82	6.95	7.60
	8.55	9.61	13.09	17.69	9.12	11.98	7.14	7.60
20	7.87	8.00	12.29	17.11	7.73	12.29	6.40	7.25
	7.75	7.84	11.68	17.08	7.75	11.20	6.03	7.40
	7.76	7.59	12.71	18.35	7.62	10.81	5.60	7.79
21	7.57	10.11	13.19	17.99	10.46	12.06	6.73	7.76
	8.55	9.23	13.27	18.70	9.77	12.29	6.74	7.43
	7.96	9.36	13.25	17.67	9.44	11.93	7.46	7.31
22	8.01	8.75	12.41	20.30	8.35	11.32	5.86	7.04
	7.21	8.25	13.31	19.23	8.20	11.52	6.20	7.02
	7.12	8.00	13.05	19.45	8.67	11.27	5.87	7.16

Annex 2. QA measures

Calculation of QA variability = Random errors (2RSD)

It is assumed that laboratories taking part in inter-laboratory comparisons will obtain results near the expected ones when this bias is removed, and that the differences between expected and obtained results more often will be close to zero than not. Based upon this assumption, a triangular distribution can be used to quantify the random errors in the laboratory results (Eurachem, 2000; EMEP CCC report 6/2003).



The triangle distribution is symmetric with a baseline 2a. The height in the triangle will be 1/a when the triangle area equals 1. The standard uncertainty is given by

$$u(x) = \frac{a}{\sqrt{6}} \qquad (1)$$

The distance from –a to a (i.e. 2a) is called the range. When applied on the inter-laboratory comparison results, the range equals the distance between the largest and smallest of the differences between expected and found concentrations. L and T represent the laboratories' and the expected concentrations respectively, and D is the difference:

$$D_i = L_i - T_i \qquad (2)$$

The range (2a) is then the difference between the highest and minimum differences (D_{max} – D_{min}) and the uncertainty $u(D)$, for the differences becomes

$$u(D) = \frac{\left(D_{\max} - D_{\min}\right)}{\left(2 \cdot \sqrt{6}\right)}. \qquad (3)$$

and more than 95 % of the data will be within $\pm 2 \cdot u(D)$. The QA variability is defined as the relative standard deviation (RSD) given by the 95% confidence limit, thus:

$$\text{QA variability} = 2 \cdot RSD = \frac{2 \cdot u(D) \cdot 100}{\frac{\sum_{i=1}^{n} T_i}{n}}\% = \frac{n \cdot (D_{\max} - D_{\min})}{\sqrt{6} \cdot \sum_{i=1}^{n} T_i}\% \qquad (4)$$

Calculating the QA bias = systematic error (RB%)

An estimation of bias in single measurements requires a long data series, and only a few samples in a inter-laboratory comparison will only give a very coarse estimate or indication of the bias. However looking at the bias in inter-laboratory comparison over years will give a good indication of the performance of the laboratory.

The absolute bias may be dependent upon the concentrations, though the relative bias are considered approximate constant for the concentrations range used in the comparisons. The differences D_i, as defined above are calculated as relative difference, and a median of these relative difference are defined as the QA bias. Median is chosen instead of average to avoid that one outlier get too high influence on the results.

$$\text{QA bias} \quad = \quad \text{RB} = \text{median} \left[\frac{D_i}{T_i} \% \right] \tag{5}$$

In Tables 1, 2, 3 are reported QA measures for TC, OC and EC from the present inter-laboratory comparison. If the tendency is observed for more than 75% of the test samples, the bias is considered systematic.

Table 1. QA bias and QA variability for TC

laboratory	instrument	Bias	variability	
TROPOS	429-201	5.5%	3.9%	systematic
Empa	201-18	1.7%	2.1%	systematic
ERL	343-135	0.6%	1.8%	
SMEARII	RT-3126	4.7%	9.9%	systematic
SenUVK	336-130	-3.8%	3.8%	
nilu	9635	3.5%	5.3%	
ucdavis	418-191	0.1%	2.9%	
ipis	254-54	5.0%	5.3%	systematic
czechglobe	RT3197	37.2%	10.9%	systematic
AIRPARIF	400-178	-1.8%	3.8%	
bham	DRI2015	0.3%	4.3%	
cyi	380	-5.5%	3.5%	systematic
ECPL_UOC	4L-170	-28.8%	19.1%	
IDAEA - CSIC	202	-4.0%	2.6%	systematic
LUND-uni	DRI 005306	-1.9%	5.2%	
GDD Amsterdam	114C	-4.6%	6.2%	systematic
UBA_DE	267-65	-3.5%	3.6%	
SEA	236-41	1.5%	4.7%	
chmi	190-12	-4.3%	4.3%	systematic
jgora-pios	5- 268-67	3.8%	6.7%	systematic
Erlap	173-5	-3.5%	6.9%	systematic

Table 2. QA bias and QA variability for OC

laboratory	instrument	Bias	variability	
TROPOS	429-201	10.4%	2.3%	systematic
Empa	201-18	2.5%	3.2%	systematic
ERL	343-135	3.0%	4.0%	systematic
SMEARII	RT-3126	9.2%	10.9%	systematic
SenUVK	336-130	-1.6%	4.2%	
nilu	9635	7.1%	6.4%	systematic
ucdavis	418-191	1.3%	5.8%	
ipis	254-54	4.5%	6.4%	systematic
czechglobe	RT3197	46.1%	13.3%	systematic
AIRPARIF	400-178	-3.9%	5.7%	
bham	DRI2015	1.2%	4.1%	
cyi	380	-3.9%	4.3%	
ECPL_UOC	4L-170	-22.7%	19.5%	systematic
IDAEA - CSIC	202	-6.1%	6.2%	systematic
LUND-uni	DRI 005306	-1.6%	10.7%	
GDD Amsterdam	114C	-1.5%	5.7%	
UBA_DE	267-65	-0.3%	6.8%	
SEA	236-41	7.5%	4.8%	systematic
chmi	190-12	-1.9%	7.9%	
jgora-pios	5- 268-67	9.2%	6.7%	systematic
Erlap	173-5	0.4%	8.8%	

Table 3. QA bias and QA variability for EC

laboratory	instrument	Bias	variability	
TROPOS	429-201	-6.0%	10.8%	systematic
Empa	201-18	8.4%	9.5%	
ERL	343-135	-4.6%	11.7%	
SMEARII	RT-3126	-7.4%	19.0%	
SenUVK	336-130	-1.4%	9.8%	
nilu	9635	-5.8%	11.5%	
ucdavis	418-191	2.5%	8.4%	
ipis	254-54	17.1%	18.8%	systematic
czechglobe	RT3197	16.2%	18.5%	systematic
AIRPARIF	400-178	21.2%	12.2%	systematic
bham	DRI2015	12.0%	11.6%	systematic
cyi	380	-9.8%	12.9%	systematic
ECPL_UOC	4L-170	-42.3%	60.2%	
IDAEA - CSIC	202	15.1%	10.8%	systematic
LUND-uni	DRI 005306	22.5%	28.9%	systematic
GDD Amsterdam	114C	-2.7%	11.8%	
UBA_DE	267-65	2.3%	16.8%	
SEA	236-41	-7.9%	8.7%	systematic
chmi	190-12	0.6%	10.0%	
jgora-pios	5- 268-67	9.3%	12.7%	
Erlap	173-5	-7.1%	12.8%	systematic