Results of the inter-laboratory comparison exercise for TC and EC measurements (OCEC-2020-1)

Summary

The European Centre for Aerosol Calibration (ECAC) under ACTRIS-2 completed in June 2020 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 Ispra, Italy. A solution of phthalic acid prepared at EC JRC ERLAP (the inter-laboratory comparison exercise coordinator) was also distributed.
Twenty-four laboratories participated in this exercise, all - except one - running the EUSAAR_2 protocol as their usual thermal-optical protocol with their usual analytical instrument. Amongst those, nineteen are responsible for the aerosol chemical speciation at the EMEP or ACTRIS stations located in their countries (i.e. in The Netherlands, Czech Republic, Germany, Spain, France, Norway, Poland, Greece, Italy, Sweden, Cyprus, and Finland, plus the EC JRC). The North-Rhine Westphalia State Office for Nature, Environment and Consumer Protection, the Estonian Environmental Research Centre, the University of California-Davis and the Air Quality Agency of Paris, and the Slovenian Environmental Agency also participated.

Measurement method performance: for TC determination, repeatability and reproducibility relative standard deviations ranged from **2 %** to **6 %** and from **7 %** to **13 %** (as one relative standard deviation), respectively. For the determination of the EC/TC ratio, repeatability and reproducibility relative standard deviations ranged from **3 %** to **7 %** and from **8 %** to **16 %**, respectively.

Based on previous inter-laboratory comparisons, repeatability and reproducibility standard deviations show an inverse dependence on TC loadings becoming exponentially poorer toward lower TC contents i.e. <10 µgC / cm²; repeatability and reproducibility standard deviations slightly become poorer towards lower EC/TC ratios and exceptionally poor for EC/TC ratios <0.07.

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 filter loadings, seventeen outliers –mainly from three participants– and sixteen stragglers were identified; 80% of all entries were within 10% from the assigned TC concentration value.

Regarding EC/TC ratios, two outliers and twenty stragglers were identified. 70% of all entries were within 10% of the assigned value and 97% 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 participants most probably indicates an unsatisfactory laboratory performance as compared to the other

participants. Participants 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, quality control measures, 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 is the European standard thermal protocol (EN16909:2017).

The *European center for aerosol calibration* within the European project ACTRIS-Implementation has organized in February-June 2020 an inter-laboratory comparison exercise (ILCE) (OCEC-2020-1). Twenty-four laboratories participated including, among others, nineteen ones in charge of OC and EC measurements at EMEP/ACTRIS stations in The Netherlands, Czech Republic, Germany, Spain, France, Norway, Poland, Greece, Italy, Sweden, Cyprus, and Finland, plus the EC JRC. The North-Rhine Westphalia State Office for Nature, Environment and Consumer Protection, the Estonian Environmental Research Centre, the University of California-Davis and the Air Quality Agency of Paris, and the Slovenian Environmental Agency 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 a high-volume sampler on quartz fiber filters at the regional background site of Ispra, Italy. Filters (Pallflex, 2500 QAT) were stored in a refrigerator after exposure.

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

The homogeneity of the filter samples was investigated by ERLAP on a separate filter sample. Eleven subsamples of 3.6 cm x 1.8 cm were randomly taken across an area corresponding to the punched one in the test filter samples; three replicates of TC, OC and EC measurements were performed on each subsample. The filter homogeneity was assessed as estimate of the between-sample standard deviation calculated using analysis of variance, according to ISO 13528:2015 (E) Annex B. The homogeneity resulted better than 2% for TC and OC and 1% for EC. If sampling occurred under repeatable conditions, it can be assumed that the test filter 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 a first place laboratories which submit TC, OC and EC data to the EBAS database (ebas.nilu.no), and then laboratories which could most benefit from the outcome of this exercise in term of measurement capacity development.

The list of the twenty-four 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 2020-1, and contact persons

Code	Participant	Acronym	Contact
1	Sunset Laboratory BV	Sunset Lab	pavlos@sunlab.com
3	Global Change Research Institute AS CR v. v. i.	Czechglobe	mbengue.s@czechglobe.cz
4	Umweltbundesamt (German Environment Agency)	UBA-DE	elke.bieber@uba.de
5	Czech Hydrometeorological Institute	CHMI	milan.vana@chmi.cz
6	Instituto de Salud Carlos III	ISCIII	pmorillo@isciii.es,
7	NRW State Office for Nature, Environment and Consumer Protection	LANUV	jutta.geiger@lanuv.nrw.de
8	Estonian Environmental Research Centre	Klab	arkadi.ebber@klab.ee
9	LSCE	LSCE	jean-eudes.petit@cea.fr
10	Laboratoire d'Aérologie UMR 5560	AERO	veronique.pont@aero.obs-mip.fr
11	University of California, Davis	UCDavis	xluzhang@ucdavis.edu, ktrzepla@ucdavis.edu
12	AIRPARIF	AIRPARIF	chadia.kebbi@airparif.fr
13	IDAEA-CSIC	IDAEA CSIC	andres.alastuey@idaea.csic.es
14	NILU-Norwegian Institute for Air Research	NILU	Key@nilu.no
15	Leibniz Institute of Tropospheric Research	TROPOS	spindler@tropos.de; roedger@tropos.de
16	Institute of Environmental Engineering Polish Academy of Sciences	IPIS	barbara.mathews@ipis.zabrze.pl
17	Chief Inspectorate of Environmental Protection, Central Research Laboratory	PIOS	izabela.kaluzinska@jgora.pios.gov.pl, i.kaluzinska@gios.gov.pl
18	University of Crete, Chemistry Department	ECPL_UOC	nmihalo@noa.gr
19	Slovenian Environment Agency	SEA	judita.burger@gov.si
20	Institute of Atmospheric Sciences and Climate, ISAC-CNR Division of Lecce	CNR	d.contini@isac.cnr.it
21	Lund University, Nuclear physics	Uni-Lund	adam.kristensson@design.lth.se
22	The Cyprus Institute	CYI	j.sciare@cyi.ac.cy
23	Finnish Meteorological Institute	FMI_Matorova	Minna.aurela@fmi.fi
24	Finnish Meteorological Institute	FMI_Uto	Minna.aurela@fmi.fi
25	European Commission, DG-JRC	JRC	fabrizia.cavalli@ec.europa.eu

1.3 Sample shipment and reporting of results

Test samples were shipped to all participants (except the "local" participant, 25) on 19th and 20thFebruary 2020 via courier at ambient temperature, in closed petri dishes. A USB temperature-data logger was included to monitor the temperature experienced by the test samples from shipping to analysis.

Participants were asked to report - by the end of June 2020: i) TC, OC and EC concentrations, in µg C cm^{-2} units with three decimal digits, from three replicates of the eight test ambient $PM_{2.5}$ samples; ii) OC content of 10 µl of a phthalic acid solution (µgC in 10 µl); and iii) the record of temperatures for the period from shipping to the analysis. The recorded temperature was in all cases below 25°C with the exception of two where T exceeded 25°C for ca 1 hour.

1.4 Thermal-optical analysis

The thermal protocol EUSAAR_2 [Cavalli et al., 2010] with a transmittance optical correction for pyrolysis is the European standard thermal protocol for the measurements of TC and EC in PM samples (EN16909:2017). In this exercise, all participants, except participant 6, applied it.
All participants operated a Sunset carbon analyser, except participant 21 operating a DRI. Participants 3, 23 and 24 used the semi-continuous model with 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 4.0 to 18.6 µg cm^{-2}, corresponding to atmospheric concentrations ranging from ca. 0.7 to 3.4 µg m^{-3} collected for 24h at a face velocity of 54 cm s^{-1}. EC/TC ranged on average from 0.15 to 0.25. All submitted results (in µg cm^{-2}) for TC, EC, OC and EC/TC ratio are presented in tables in Annex 1.

As ambient PM collected on filters was used as test samples, the true values for *TC loading and EC/TC ratio* 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).

In addition, based on the 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 (ebas.nilu.no), quality control measures, i.e. percentage bias and variability, were calculated for TC, OC and EC determination for each participant (see Annex 2).

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

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 replicate measurements. In this comparison exercise, all participants provided three replicates for every sample except participants 5 (for IPRB sample), 9 (for IPRF), 12 (for IPRG), 14 (for IPRH), 21 (for IPRC), and 25 (for IPRE). However, Cochran's critical values for three replicates were used for all test samples, i.e. 0.287 (outlier) and 0.235 (straggler).

For each test filter separately, Cochran's criterion is applied to test the consistency of the highest standard deviation value (repeatability) among those reported by all participants. After the removal of the outlier, 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-four participants, the critical values for Grubb's test are 3.112 and 0.4234 - outliers for G_1 and G_2, respectively- and 2.802 and 0.4994 - stragglers for G_1 and G_2, respectively.

Based on the outcomes of above statistical analyses, 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 participant for each test samples are presented grouped by participant. Cochran's test identifies as outliers 3/IPRA; 24/IPRA; 3/IPRB; 14/IPRB; 3/IPRD; 14/IPRD; 3/IPRE; 7/IPRE; 21/IPRF; 23/IPRH (participant/sample) and 3/IPRF; 3/IPRG; and 3/IPRH as stragglers (participant/sample).

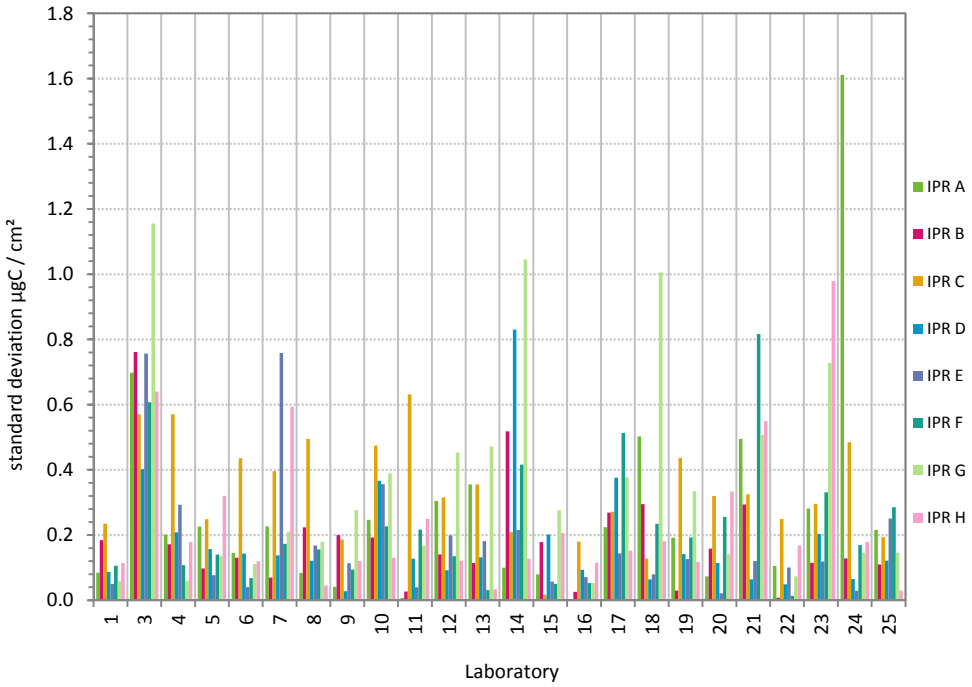

Figure 1. Standard deviation on the three replicates reported for each test filters, grouped by participant.

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

The G_1 and G_2 Grubbs' tests identifies as outliers 3/IPRA; 3/IPRB and 3/IPRG (participant/sample), and as stragglers 3/IPRE and 3/IPRF (participant/sample).

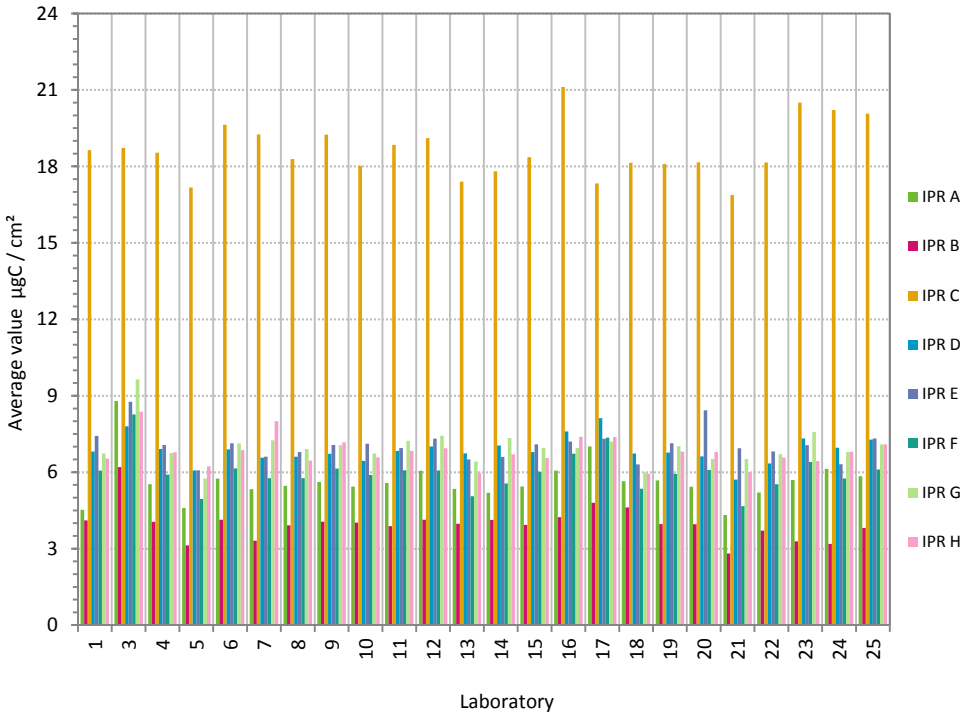

Figure 2. TC average values from three replicates reported by participants for each test sample, grouped by participant.

Localized sample heterogeneities or contaminations cannot be rigorously excluded, but the occurrence of several outliers and/or stragglers from a single participant (case of participant 3) most probably suggests unsatisfactory laboratory precision for the determination of the TC loadings as compared to the other participants.

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.

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 A	5.47	0.24	4.3	0.60	11.0
IPR B	3.88	0.17	4.4	0.50	12.8
IPR C	18.62	0.38	2.0	1.09	5.9
IPR D	6.79	0.17	2.5	0.52	7.6
IPR E	6.98	0.15	2.2	0.51	7.3
IPR F	6.04	0.25	4.2	0.75	12.4
IPR G	6.85	0.43	6.3	0.56	8.2
IPR H	6.81	0.28	4.1	0.64	9.4

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).

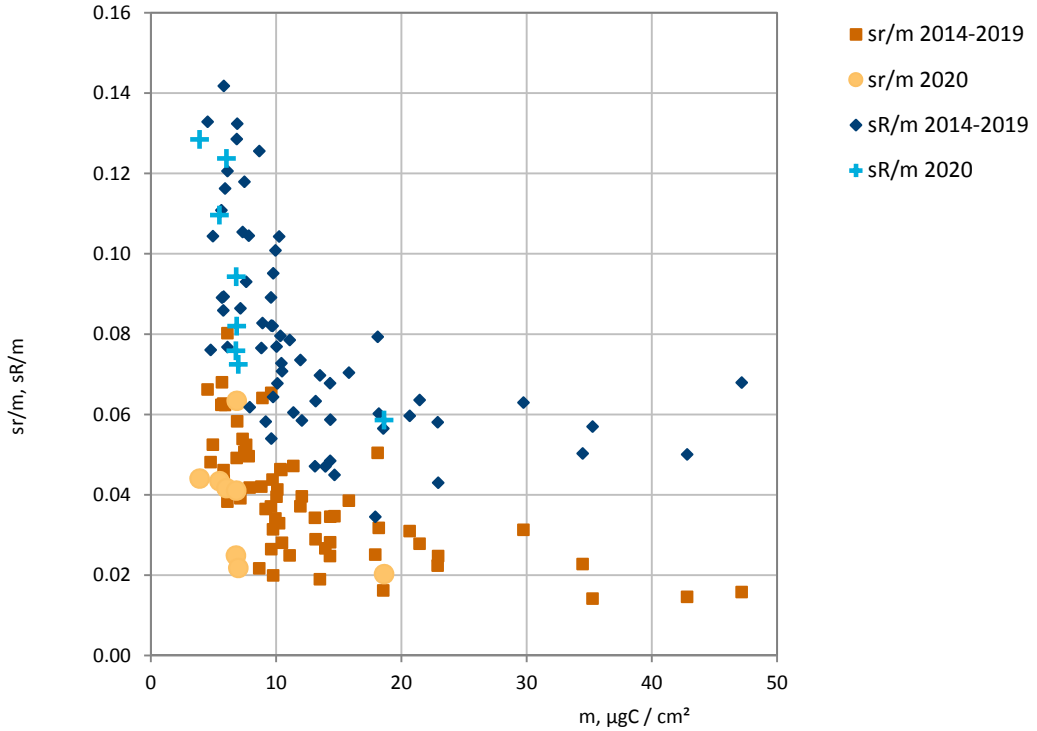

Figure 3. Repeatability and reproducibility relative standard deviation for the EUSAAR_2 protocol for TC measurement obtained during the previous inter-laboratory comparisons and the present one.

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 participant. Cochran's test identifies entries 21/IPRD; 6/IPRD; 3/IPRF; 3/IPRG; and 5/IPRG as outliers and 4/IPRC as straggler (participant/sample).

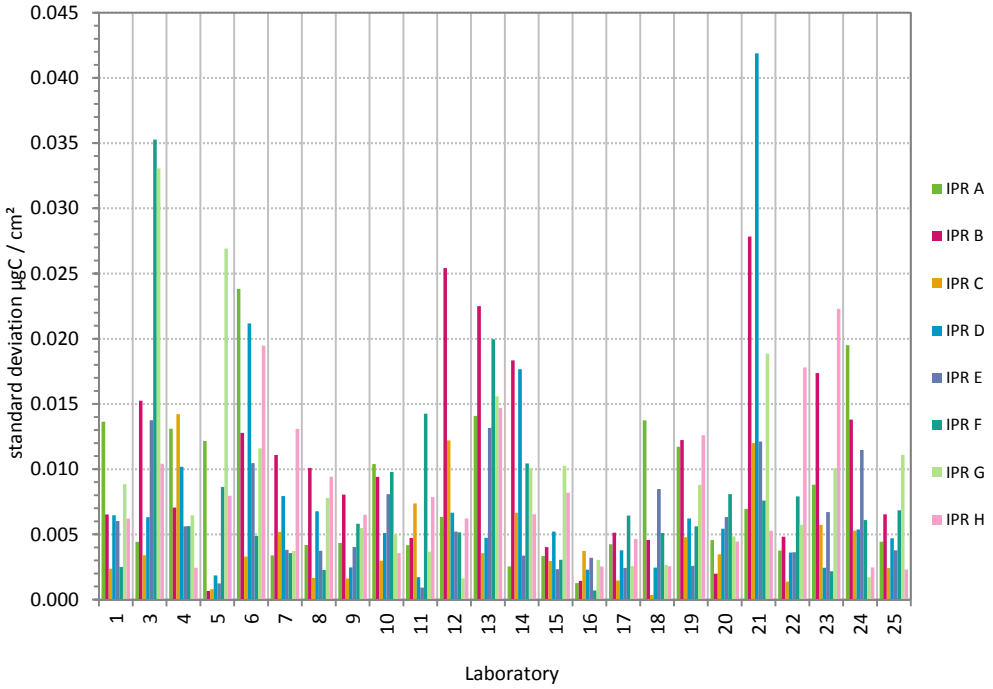

Figure 4. Standard deviation on the replicates reported for each test filters, grouped by participant.

Between-laboratory consistency. In Figure 5 the EC/TC ratio average values from the replicates reported by all participants for each test sample are presented grouped by participant. Grubbs' test identifies no outliers and the entry 20/IPRE as straggler (participant/sample).

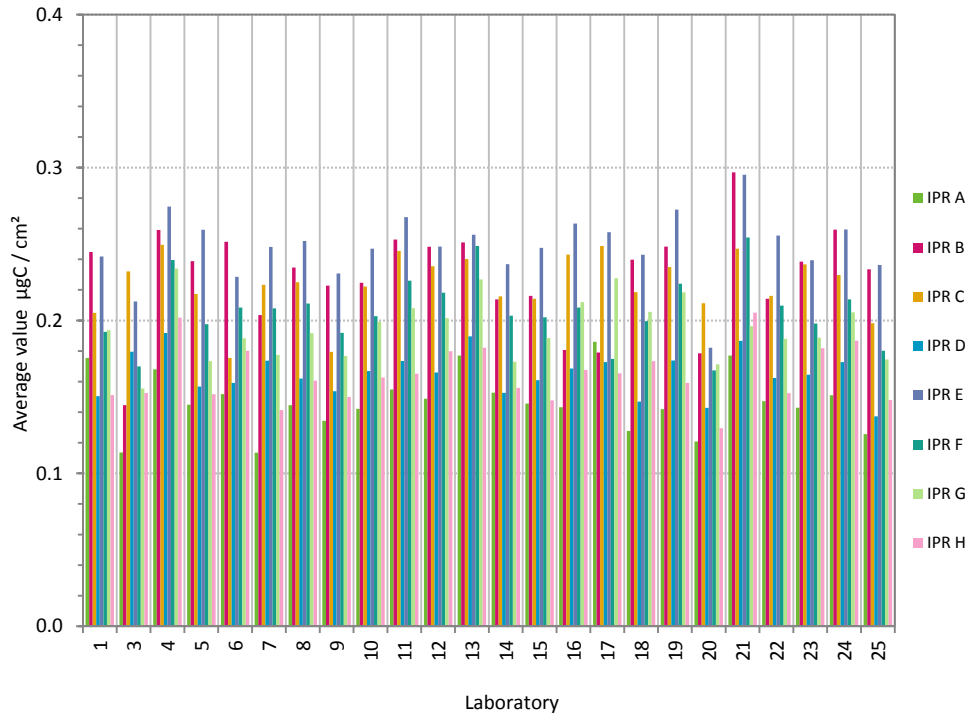

Figure 5. EC/TC average ratios from the replicates reported by participants for each test sample, grouped by participant.

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).

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

test sample	general mean	sr		sR	
	µgC / cm²	µgC / cm²	%	µgC / cm²	%
IPR A	0.15	0.01	7.0	0.02	14.2
IPR B	0.23	0.01	5.8	0.04	15.7
IPR C	0.22	0.01	2.6	0.02	9.0
IPR D	0.17	0.01	4.0	0.01	8.4
IPR E	0.25	0.01	2.9	0.02	9.4
IPR F	0.21	0.01	3.8	0.02	10.4
IPR G	0.20	0.01	4.3	0.02	9.8
IPR H	0.17	0.01	6.3	0.02	12.4

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 (*sR* and less evident for *sr*) for EC/TC ratio measurement can become poorer at lower EC/TC ratios and exceptionally poor only for EC/TC ratios <0.07.

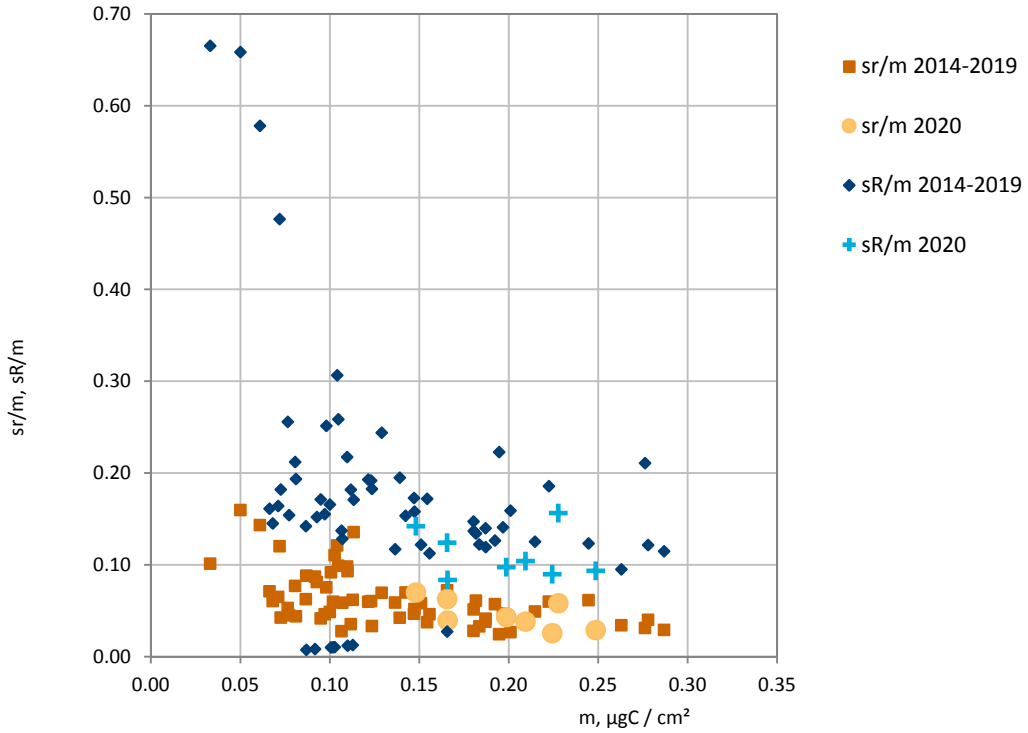

Figure 6. Repeatability and reproducibility relative standard deviation for the EUSAAR_2 protocol for EC/TC measurement obtained during the previous inter-laboratory comparisons and the present one.

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.

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 A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
assigned value	µg/cm2	5.56	3.96	18.56	6.82	7.01	5.94	6.94	6.76
standard	µg/cm2	0.37	0.27	1.01	0.33	0.39	0.36	0.39	0.45
deviation	%	6.6	6.8	5.5	4.9	5.5	6.1	5.7	6.7
2σ*	%	13.2	13.7	10.9	9.7	11.0	12.1	11.3	13.4
3σ*	%	19.8	20.5	16.4	14.6	16.5	18.2	17.0	20.1

Figure 7 shows z-scores calculated from σ*. Seventeen outliers, 3/IPRA; 17/IPRA; 21/IPRA; 3/IPRB; 5/IPRB; 17/IPRB; 21/IPRB; 17/IPRD; 21/IPRD; 3/IPRE; 20/IPRE; 3/IPRF; 17/IPRF; 21/IPRF; 3/IPRG; 5/IPRG; and 3/IPRH (participant/sample) –mainly from participant 3, 17 and 21– and sixteen stragglers, 1/IPRA, 5/IPRA, 7/IPRB, 18/IPRB, 23/IPRB; 24/IPRB; 16/IPRC; 3/IPRD; 5/IPRD; 16/IPRD; 5/ IPRE; 5/IPRF; 13/IPRF; 16/IPRF; 18/IPRG; and 7/IPRH are identified.

For each sample, fourteen to sixteen out of twenty-four participants show deviations from the assigned values within +/- 1 σ* as listed in Table 4 (i.e. within 1 z-score). 80% 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. participants 3 and 16 - or underestimating –i.e. participants 5 and 21 - 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.

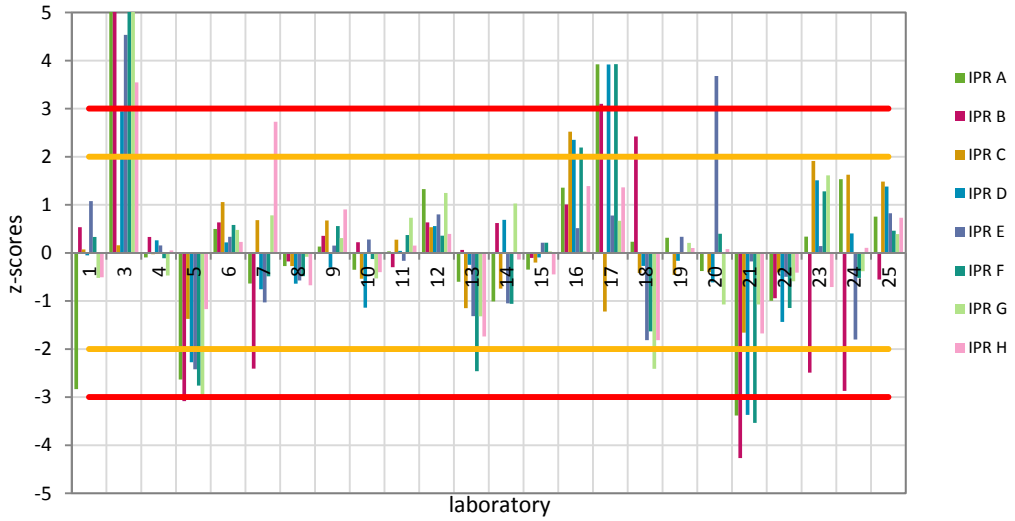

Figure 7. z-scores for TC calculated using σ* *from data obtained in a round of a proficiency testing scheme*. The scale is set from -5 to +5.

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 A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
assigned value	ratio	0.15	0.23	0.23	0.17	0.25	0.21	0.19	0.16
standard	ratio	0.01	0.02	0.02	0.01	0.02	0.02	0.02	0.02
deviation	%	10.1	10.4	8.3	8.3	6.8	8.4	10.9	10.8
2σ*	%	20.3	20.8	16.6	16.5	13.7	16.8	21.9	21.5
3σ*	%	30.4	31.1	24.9	24.8	20.5	25.3	32.8	32.3

Two outliers – 3/IPRB and 20/IPRE (participant/sample) - and twenty stragglers - 3/IPRA; 7/IPRA;13/IPRA; 17/IPRA; 21/IPRA; 16/IPRB; 17/IPRB; 20/IPRB; 21/IPRB; 6/IPRC; 9/IPRC; 25/IPRD; 3/IPRE; 21/IPRE; 3/IPRF; 13/IPRF; 20/IPRF; 21/IPRF; 5/IPRH and 21/IPRH (participant /sample) - are identified. For each sample, fourteen to seventeen out of twenty-four participants show deviations from the assigned values within +/- 1 σ* as listed in Table 5 (i.e. within 1 z-score).
70% of all entries are within 10% of the assigned value and 97% are within 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. participants 3, 11, 13, 21 and 24- or underestimating – i.e. participants 9 and 20 - 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.

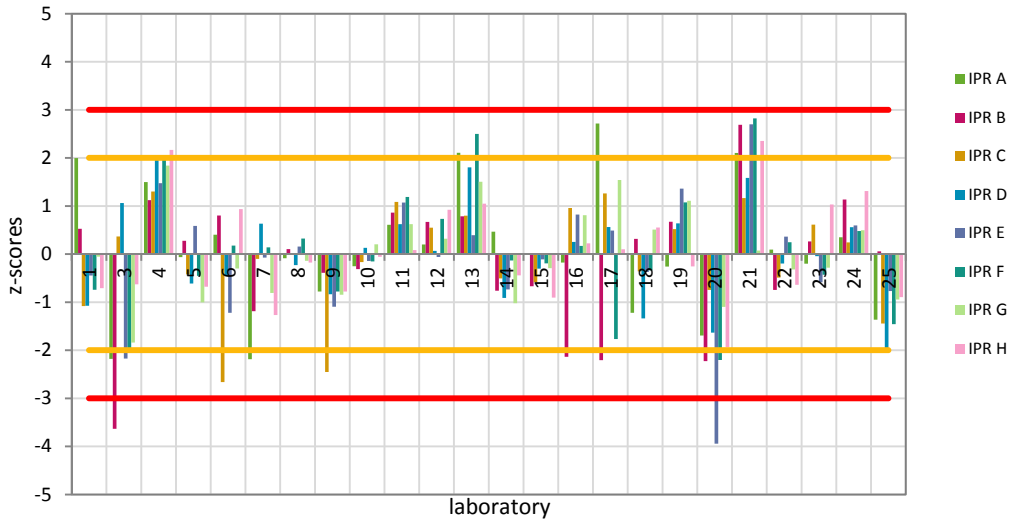

Figure 8. z-scores for EC/TC ratio calculated using σ* *from data obtained in a round of a proficiency testing scheme*.

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. Four participants out of twenty-four reported OC deviating from the assigned value by more 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 analyzed 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.).

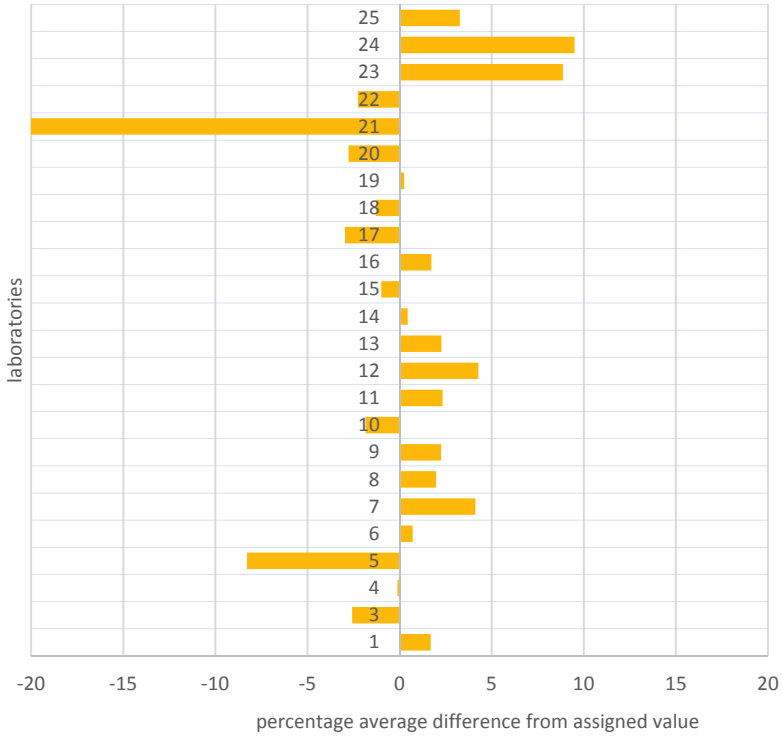

Figure 9. Phthalic acid solution –percentage differences from the assigned value, i.e. the C concentration of the test solution calculated from the mass of phthalic acid and the volume of ultra-pure water used to make the solution.

Conclusions

This inter-laboratory comparison involved twenty-four participants all applying thermal-optical analyses and the EUSAAR_2 protocol, except one.
The measurement method ***repeatability and reproducibility for TC*** ranged from 2**% to 6%** and from **7% to 13%** (as one relative standard deviation), respectively.
For the ***EC/TC ratio, repeatability and reproducibility*** ranged from **3%** to **7%** and from **8%** to **16%**, 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 observe that the method precision (both sr and sR) for TC determination becomes exponentially poorer toward lower TC contents i.e. <10 µgC / cm². For EC/TC determination, the method precision (*sR* and less evident for *sr*) becomes poorer toward lower EC/TC ratios and exceptionally poor only for EC/TC ratios <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, seventeen outliers –mainly from three participants– and sixteen stragglers were identified; 80% 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. two participants) or underestimating (i.e. two participants) 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, two outliers and twenty stragglers were identified. 70% of all entries were within 10% of the assigned value and 97% 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. five participants) or underestimating (i.e. two participants) the assigned EC/TC ratio. The participant using another thermal protocol than EUSAAR_2 did not show any significant systematic bias.
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, based on the 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, quality control measures, i.e. percentage bias and variability, were calculated for TC, OC and EC determination for each participant (Annex 2).

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Annex 1. Numerical results reported by participants

Grey cells correspond to a "no entry".

Table 1: Total carbon (µg/cm^2)

Participant	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	4.612	4.316	18.835	6.878	7.442	6.066	6.741	6.485
	4.512	3.969	18.695	6.830	7.367	5.953	6.673	6.448
	4.444	4.034	18.377	6.709	7.461	6.164	6.789	6.662
3	9.355	5.714	18.386	8.222	9.360	7.901	9.660	9.087
	9.006	5.803	19.381	7.421	9.007	8.963	8.474	7.857
	8.011	7.075	18.399	7.754	7.910	7.923	10.784	8.165
4	5.637	4.131	18.256	7.108	7.093	5.986	6.720	6.601
	5.655	4.168	18.156	6.927	7.347	5.938	6.823	6.957
	5.297	3.854	19.190	6.692	6.763	5.780	6.720	6.798
5	4.357	3.059	16.958	5.891	6.038	4.797	5.834	6.549
	4.807	3.197	17.112	6.188	6.020	4.973	5.813	5.909
	4.623		17.444	6.128	6.161	5.074	5.588	6.237
6	5.664	4.074	19.912	6.829	7.179	6.185	7.255	6.988
	5.663	4.283	19.857	6.797	7.135	6.194	7.079	6.749
	5.915	4.043	19.132	7.059	7.098	6.072	7.049	6.860
7	5.087	3.237	19.244	6.683	5.827	5.600	7.481	8.260
	5.370	3.375	18.859	6.615	6.663	5.945	7.185	7.320
	5.535	3.320	19.651	6.418	7.341	5.754	7.074	8.417
8	5.560	4.170	17.790	6.720	6.970	5.930	7.110	6.460
	5.420	3.810	18.780	6.630	6.750	5.750	6.770	6.500
	5.410	3.760	18.280	6.480	6.640	5.620	6.840	6.410
9	5.567	4.268	19.290	6.691	7.156	6.075	7.337	7.310
	5.644	3.870	19.404	6.728	6.938		7.060	7.092
	5.629	4.034	19.040	6.746	7.104	6.208	6.784	7.112
10	5.289	4.182	18.273	6.303	6.713	6.137	6.663	6.530
	5.721	4.075	17.472	6.861	7.391	5.859	6.379	6.729
	5.298	3.809	18.313	6.171	7.241	5.688	7.149	6.484
11	5.584	3.901	19.564	6.699	6.982	6.252	7.223	6.957
	5.578	3.851	18.552	6.952	6.902	6.138	7.395	6.992
	5.569	3.892	18.404	6.857	6.949	5.833	7.060	6.543
12	5.734	4.287	18.879	6.901	7.172	6.191	7.109	7.050
	6.341	4.103	19.465	7.056	7.236	5.924	7.750	6.810
	6.082	4.011	18.971	7.065	7.544	6.094		6.961
13	4.990	3.854	17.758	6.631	6.293	5.056	6.097	5.983
	5.340	4.004	17.388	6.887	6.628	5.026	6.962	6.001
	5.700	4.078	17.048	6.705	6.581	5.088	6.204	5.937
14	5.290	4.720	17.710	7.030	6.510	5.330	6.730	
	5.200	3.920	18.050	7.890	6.850	5.310	6.750	6.610
	5.090	3.750	17.670	6.230	6.450	6.040	8.550	6.790
15	5.515	3.815	18.361	6.774	7.076	6.072	6.690	6.793
	5.439	3.847	18.343	6.599	7.152	5.973	6.923	6.487
	5.356	4.139	18.376	7.001	7.040	6.006	7.241	6.400
16	6.064	4.220	21.194	7.704	7.276	6.790	6.899	7.289
	6.060	4.264	21.246	7.578	7.209	6.690	6.947	7.369
	6.066	4.219	20.912	7.522	7.134	6.709	7.005	7.516
17	6.933	4.835	17.612	7.938	7.327	7.309	6.787	7.254
	6.831	5.050	17.298	7.870	7.441	6.864	7.293	7.337
	7.260	4.516	17.071	8.552	7.156	7.887	7.524	7.550
18	5.313	4.916	18.038	6.774	6.245	5.116	5.418	5.938

	5.409	4.326	18.098	6.765	6.280	5.360	5.403	5.759
	6.227	4.608	18.284	6.659	6.396	5.585	7.152	6.121
19	5.902	3.999	18.602	6.756	7.038	6.088	7.359	6.909
	5.571	3.945	17.871	6.632	7.280	5.719	6.691	6.679
	5.569	3.950	17.823	6.915	7.095	6.000	7.013	6.836
20	5.405	4.115	18.497	6.705	8.404	5.825	6.480	6.766
	5.507	3.962	17.863	6.490	8.445	6.336	6.398	7.145
	5.364	3.798	18.108	6.664	8.435	6.091	6.674	6.480
21	4.810	2.490	17.110	5.680	6.820	5.080	5.970	6.290
	3.820	2.860	16.650	5.780	7.060	5.200	6.610	6.350
	4.330	3.070		5.660	6.940	3.730	6.970	5.370
22	5.300	3.701	18.413	6.314	6.830	5.516	6.697	6.477
	5.206	3.716	18.127	6.323	6.709	5.543	6.638	6.771
	5.090	3.704	17.917	6.403	6.908	5.529	6.784	6.482
23	5.481	3.282	20.786	7.252	7.146	6.450	8.406	7.371
	6.009	3.176	20.196	7.551	6.926	6.705	7.256	6.529
	5.578	3.406	20.517	7.164	7.115	6.049	7.058	5.419
24	7.115	3.075	20.103	6.943	6.287	5.908	6.745	6.996
	7.001	3.154	19.786	7.027	6.344	5.780	6.670	6.639
	4.269	3.326	20.738	6.899	6.305	5.573	6.952	6.794
25	6.032	3.707	19.876	7.232	7.503	5.787	7.174	7.127
	5.885	3.804	20.056	7.189	7.149	6.200	7.181	7.069
	5.607	3.926	20.262	7.418		6.335	6.925	7.086

Table 2: Elemental carbon / total carbon (ratios)

Participant	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	0.160	0.237	0.202	0.153	0.235	0.195	0.190	0.158
	0.182	0.249	0.207	0.143	0.244	0.190	0.187	0.146
	0.185	0.248	0.206	0.155	0.247	0.193	0.204	0.150
3	0.117	0.146	0.235	0.173	0.202	0.132	0.174	0.141
	0.109	0.159	0.228	0.179	0.207	0.202	0.175	0.162
	0.116	0.129	0.233	0.186	0.228	0.175	0.117	0.155
4	0.153	0.251	0.238	0.203	0.274	0.241	0.229	0.200
	0.172	0.265	0.245	0.183	0.269	0.233	0.231	0.205
	0.179	0.261	0.265	0.189	0.280	0.244	0.241	0.201
5	0.158	0.239	0.217	0.156	0.258	0.203	0.189	0.161
	0.134	0.238	0.217	0.155	0.261	0.202	0.189	0.148
	0.143		0.218	0.159	0.259	0.188	0.142	0.146
6	0.125	0.258	0.173	0.147	0.226	0.214	0.175	0.180
	0.160	0.237	0.174	0.147	0.219	0.206	0.193	0.161
	0.170	0.260	0.179	0.184	0.240	0.205	0.197	0.200
7	0.114	0.194	0.218	0.177	0.244	0.204	0.175	0.131
	0.110	0.216	0.225	0.180	0.248	0.210	0.182	0.137
	0.117	0.201	0.228	0.165	0.252	0.210	0.176	0.156
8	0.142	0.223	0.224	0.155	0.250	0.209	0.183	0.150
	0.149	0.241	0.227	0.163	0.256	0.210	0.195	0.163
	0.142	0.239	0.224	0.168	0.250	0.214	0.197	0.168
9	0.138	0.217	0.180	0.154	0.231	0.196	0.171	0.147
	0.130	0.232	0.180	0.151	0.227		0.178	0.157
	0.136	0.219	0.178	0.156	0.235	0.188	0.181	0.145
10	0.154	0.219	0.223	0.161	0.245	0.200	0.200	0.167
	0.137	0.219	0.224	0.171	0.256	0.195	0.204	0.159
	0.135	0.235	0.219	0.169	0.240	0.214	0.194	0.162
11	0.158	0.253	0.252	0.175	0.267	0.225	0.207	0.168
	0.150	0.248	0.237	0.172	0.269	0.241	0.205	0.156
	0.156	0.258	0.247	0.174	0.267	0.212	0.212	0.171
12	0.151	0.222	0.237	0.170	0.246	0.224	0.203	0.185
	0.142	0.272	0.247	0.158	0.254	0.215	0.200	0.173
	0.154	0.251	0.223	0.170	0.245	0.216		0.182
13	0.193	0.266	0.242	0.184	0.249	0.253	0.231	0.180
	0.171	0.262	0.236	0.194	0.248	0.227	0.210	0.198
	0.167	0.225	0.242	0.191	0.271	0.266	0.240	0.168
14	0.155	0.193	0.211	0.149	0.237	0.205	0.180	
	0.150	0.222	0.223	0.137	0.234	0.213	0.178	0.151
	0.153	0.227	0.213	0.172	0.240	0.192	0.161	0.161
15	0.142	0.214	0.217	0.163	0.248	0.203	0.198	0.139
	0.146	0.221	0.214	0.165	0.249	0.204	0.189	0.149
	0.149	0.214	0.211	0.155	0.245	0.199	0.178	0.155
16	0.142	0.179	0.247	0.166	0.260	0.208	0.209	0.169
	0.144	0.182	0.240	0.169	0.265	0.209	0.212	0.169
	0.144	0.181	0.242	0.170	0.265	0.209	0.215	0.165
17	0.186	0.176	0.248	0.175	0.258	0.176	0.230	0.167
	0.190	0.176	0.250	0.175	0.255	0.181	0.228	0.160
	0.182	0.185	0.248	0.168	0.260	0.168	0.225	0.169
18	0.133	0.243	0.218	0.150	0.235	0.205	0.203	0.171
	0.138	0.241	0.219	0.145	0.252	0.195	0.205	0.175
	0.112	0.235	0.218	0.145	0.241	0.199	0.208	0.174
19	0.150	0.262	0.236	0.177	0.275	0.226	0.211	0.148

	0.148	0.246	0.230	0.167	0.270	0.228	0.216	0.173
	0.129	0.237	0.239	0.178	0.273	0.218	0.228	0.156
20	0.117	0.177	0.212	0.137	0.175	0.174	0.174	0.135
	0.119	0.178	0.214	0.148	0.188	0.158	0.174	0.128
	0.126	0.181	0.207	0.143	0.183	0.170	0.166	0.126
21	0.185	0.285	0.255	0.201	0.292	0.252	0.211	0.207
	0.173	0.329	0.238	0.220	0.309	0.248	0.203	0.209
	0.173	0.277		0.140	0.285	0.263	0.175	0.199
22	0.151	0.209	0.216	0.166	0.253	0.213	0.194	0.143
	0.143	0.218	0.217	0.159	0.254	0.201	0.183	0.173
	0.148	0.215	0.215	0.163	0.260	0.215	0.187	0.141
23	0.133	0.246	0.239	0.163	0.232	0.200	0.177	0.207
	0.144	0.251	0.230	0.163	0.240	0.196	0.196	0.171
	0.151	0.219	0.241	0.167	0.246	0.198	0.194	0.167
24	0.147	0.265	0.230	0.171	0.272	0.212	0.206	0.186
	0.134	0.270	0.235	0.169	0.249	0.209	0.207	0.184
	0.172	0.244	0.224	0.179	0.257	0.221	0.203	0.189
25	0.121	0.237	0.201	0.141	0.239	0.188	0.162	0.148
	0.129	0.226	0.196	0.132	0.234	0.174	0.178	0.150
	0.128	0.237	0.198	0.139		0.178	0.184	0.146

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

Participant	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	0.737	1.024	3.811	1.054	1.749	1.181	1.281	1.024
	0.819	0.988	3.866	0.977	1.795	1.130	1.249	0.939
	0.822	1.001	3.785	1.040	1.840	1.191	1.383	1.000
3	1.091	0.834	4.319	1.424	1.891	1.045	1.684	1.283
	0.978	0.923	4.425	1.332	1.865	1.812	1.481	1.270
	0.927	0.910	4.286	1.441	1.803	1.389	1.265	1.265
4	0.865	1.038	4.348	1.443	1.946	1.444	1.541	1.319
	0.972	1.104	4.446	1.268	1.975	1.385	1.578	1.423
	0.947	1.007	5.094	1.268	1.894	1.411	1.622	1.367
5	0.689	0.732	3.680	0.921	1.559	0.974	1.101	1.053
	0.645	0.762	3.709	0.960	1.569	1.005	1.099	0.877
	0.659		3.807	0.973	1.596	0.952	0.795	0.910
6	0.708	1.051	3.451	1.003	1.625	1.324	1.271	1.260
	0.907	1.014	3.452	0.999	1.565	1.278	1.365	1.084
	1.008	1.050	3.430	1.296	1.703	1.245	1.389	1.369
7	0.581	0.628	4.186	1.182	1.424	1.141	1.309	1.083
	0.590	0.728	4.240	1.188	1.652	1.247	1.306	1.002
	0.645	0.667	4.472	1.057	1.850	1.209	1.243	1.314
8	0.790	0.930	3.990	1.040	1.740	1.240	1.300	0.970
	0.810	0.920	4.260	1.080	1.730	1.210	1.320	1.060
	0.770	0.900	4.090	1.090	1.660	1.200	1.350	1.080
9	0.768	0.928	3.477	1.028	1.650	1.191	1.252	1.078
	0.731	0.898	3.502	1.018	1.573		1.258	1.116
	0.763	0.883	3.381	1.054	1.668	1.166	1.230	1.032
10	0.815	0.916	4.083	1.015	1.648	1.225	1.332	1.087
	0.785	0.894	3.917	1.170	1.889	1.143	1.299	1.073
	0.716	0.897	4.005	1.043	1.735	1.216	1.385	1.050
11	0.883	0.986	4.930	1.171	1.865	1.409	1.495	1.167
	0.838	0.955	4.406	1.193	1.854	1.476	1.516	1.093
	0.870	1.002	4.545	1.194	1.856	1.237	1.497	1.122
12	0.864	0.950	4.475	1.170	1.764	1.387	1.441	1.301
	0.899	1.117	4.804	1.117	1.840	1.271	1.553	1.177
	0.937	1.006	4.222	1.202	1.846	1.315		1.269
13	0.964	1.024	4.294	1.223	1.566	1.278	1.406	1.079
	0.912	1.050	4.104	1.334	1.644	1.141	1.460	1.186
	0.953	0.918	4.134	1.279	1.785	1.355	1.490	1.000
14	0.820	0.910	3.730	1.050	1.540	1.090	1.210	
	0.780	0.870	4.030	1.080	1.600	1.130	1.200	1.000
	0.780	0.850	3.770	1.070	1.550	1.160	1.380	1.090
15	0.784	0.816	3.990	1.101	1.755	1.234	1.327	0.945
	0.794	0.849	3.925	1.090	1.784	1.221	1.310	0.964
	0.797	0.884	3.885	1.086	1.724	1.193	1.288	0.995
16	0.860	0.757	5.239	1.278	1.889	1.410	1.441	1.234
	0.871	0.777	5.096	1.284	1.912	1.398	1.473	1.245
	0.875	0.762	5.068	1.280	1.892	1.400	1.506	1.238
17	1.290	0.850	4.360	1.386	1.887	1.283	1.562	1.210
	1.300	0.890	4.331	1.379	1.900	1.242	1.660	1.176
	1.320	0.835	4.239	1.440	1.862	1.326	1.693	1.278
18	0.708	1.197	3.936	1.014	1.471	1.048	1.100	1.013
	0.747	1.043	3.961	0.984	1.584	1.043	1.109	1.010
	0.699	1.081	3.992	0.968	1.544	1.112	1.491	1.067
19	0.885	1.046	4.383	1.197	1.935	1.376	1.551	1.024

	0.822	0.970	4.107	1.105	1.964	1.306	1.448	1.155
	0.716	0.938	4.265	1.228	1.935	1.306	1.599	1.069
20	0.635	0.727	3.921	0.921	1.474	1.013	1.126	0.911
	0.655	0.706	3.828	0.962	1.587	1.003	1.116	0.912
	0.676	0.686	3.757	0.952	1.546	1.034	1.106	0.819
21	0.890	0.710	4.370	1.140	1.990	1.280	1.260	1.300
	0.660	0.940	3.970	1.270	2.180	1.290	1.340	1.330
	0.750	0.850		0.790	1.980	0.980	1.220	1.070
22	0.799	0.773	3.978	1.047	1.729	1.176	1.299	0.925
	0.746	0.811	3.942	1.003	1.702	1.112	1.212	1.171
	0.752	0.798	3.847	1.042	1.794	1.190	1.270	0.917
23	0.731	0.806	4.965	1.181	1.661	1.291	1.489	1.529
	0.868	0.797	4.648	1.234	1.661	1.313	1.419	1.119
	0.841	0.745	4.943	1.198	1.749	1.198	1.366	0.903
24	1.044	0.815	4.622	1.185	1.709	1.251	1.388	1.304
	0.938	0.850	4.648	1.185	1.582	1.207	1.379	1.225
	0.736	0.811	4.652	1.234	1.621	1.229	1.414	1.286
25	0.727	0.880	3.990	1.018	1.793	1.087	1.164	1.057
	0.757	0.859	3.930	0.948	1.670	1.081	1.277	1.061
	0.717	0.931	4.011	1.032		1.130	1.272	1.031

Table 4: Organic carbon (μg/cm^2)

Participant	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	3.875	3.292	15.024	5.824	5.693	4.885	5.460	5.461
	3.693	2.981	14.829	5.853	5.572	4.823	5.424	5.509
	3.622	3.033	14.592	5.669	5.621	4.973	5.406	5.662
3	8.264	4.876	14.062	6.802	7.469	6.851	7.971	7.804
	8.028	4.880	14.960	6.094	7.147	7.151	6.992	6.587
	7.084	6.165	14.113	6.313	6.106	6.534	9.519	6.895
4	4.771	3.092	13.908	5.665	5.147	4.541	5.179	5.283
	4.683	3.064	13.710	5.659	5.372	4.553	5.245	5.534
	4.350	2.847	14.096	5.424	4.869	4.368	5.098	5.431
5	3.667	2.327	13.278	4.970	4.479	3.823	4.733	5.497
	4.163	2.435	13.403	5.228	4.451	3.968	4.713	5.032
	3.964		13.637	5.155	4.565	4.122	4.793	5.327
6	4.956	3.023	16.461	5.827	5.554	4.861	5.984	5.728
	4.756	3.268	16.405	5.798	5.570	4.916	5.714	5.665
	4.906	2.993	15.702	5.763	5.395	4.826	5.661	5.491
7	4.506	2.609	15.058	5.500	4.404	4.459	6.172	7.177
	4.779	2.647	14.619	5.427	5.011	4.698	5.879	6.318
	4.890	2.653	15.179	5.361	5.491	4.544	5.830	7.103
8	4.760	3.240	13.800	5.680	5.230	4.680	5.820	5.490
	4.620	2.910	14.530	5.550	5.020	4.550	5.450	5.440
	4.630	2.860	14.200	5.390	4.980	4.420	5.490	5.330
9	4.798	3.339	15.812	5.662	5.505	4.883	6.084	6.230
	4.913	2.970	15.902	5.710	5.364		5.801	5.975
	4.866	3.151	15.658	5.691	5.434	5.041	5.554	6.078
10	4.474	3.265	14.190	5.287	5.065	4.912	5.332	5.443
	4.936	3.181	13.555	5.692	5.502	4.716	5.080	5.656
	4.582	2.912	14.308	5.128	5.506	4.472	5.764	5.433
11	4.700	2.914	14.634	5.528	5.117	4.843	5.728	5.790
	4.740	2.895	14.146	5.759	5.048	4.662	5.880	5.899
	4.699	2.890	13.860	5.663	5.094	4.596	5.563	5.421
12	4.869	3.336	14.404	5.731	5.407	4.804	5.668	5.749
	5.442	2.986	14.660	5.938	5.396	4.652	6.198	5.633
	5.145	3.005	14.749	5.862	5.697	4.779		5.693
13	4.027	2.830	13.463	5.407	4.727	3.778	4.691	4.903
	4.427	2.954	13.285	5.553	4.985	3.884	5.502	4.815
	4.747	3.160	12.914	5.425	4.796	3.734	4.714	4.938
14	4.470	3.810	13.970	5.980	4.970	4.240	5.520	
	4.420	3.050	14.010	6.810	5.260	4.190	5.550	5.610
	4.320	2.900	13.900	5.160	4.900	4.880	7.180	5.700
15	4.731	2.999	14.371	5.673	5.320	4.838	5.362	5.848
	4.644	2.998	14.418	5.509	5.369	4.752	5.613	5.523
	4.559	3.255	14.491	5.914	5.316	4.813	5.952	5.405
16	5.204	3.463	15.956	6.426	5.387	5.380	5.458	6.055
	5.190	3.487	16.150	6.294	5.297	5.293	5.473	6.124
	5.191	3.457	15.844	6.241	5.242	5.309	5.499	6.278
17	5.643	3.985	13.252	6.552	5.440	6.026	5.225	6.044
	5.531	4.160	12.968	6.491	5.541	5.622	5.633	6.161
	5.940	3.681	12.832	7.112	5.294	6.561	5.831	6.272
18	4.605	3.719	14.102	5.760	4.775	4.068	4.317	4.925
	4.663	3.284	14.137	5.781	4.697	4.317	4.293	4.749
	5.529	3.527	14.292	5.690	4.853	4.473	5.662	5.054
19	5.017	2.953	14.219	5.559	5.103	4.712	5.808	5.885

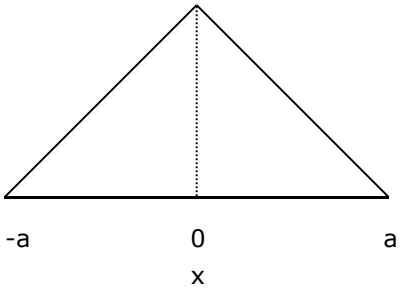
	4.749	2.975	13.764	5.527	5.316	4.413	5.243	5.524
	4.853	3.012	13.558	5.687	5.160	4.694	5.414	5.767
20	4.770	3.388	14.577	5.784	6.930	4.811	5.343	5.855
	4.842	3.255	14.034	5.528	6.869	5.323	5.282	6.244
	4.688	3.102	14.352	5.712	6.889	5.057	5.569	5.651
21	3.920	1.780	12.740	4.540	4.830	3.810	4.710	4.990
	3.170	1.920	12.680	4.510	4.880	3.900	5.260	5.020
	3.570	2.220		4.860	4.950	2.630	5.750	4.300
22	4.501	2.928	14.435	5.267	5.101	4.340	5.397	5.552
	4.460	2.905	14.185	5.320	5.007	4.432	5.426	5.600
	4.338	2.907	14.070	5.361	5.115	4.338	5.514	5.565
23	4.754	2.472	15.816	6.067	5.481	5.159	6.917	5.842
	5.146	2.383	15.548	6.318	5.265	5.397	5.838	5.415
	4.736	2.661	15.574	5.965	5.371	4.855	5.692	4.516
24	6.071	2.260	15.486	5.758	4.577	4.657	5.362	5.692
	6.062	2.304	15.138	5.842	4.763	4.573	5.291	5.415
	3.533	2.516	16.085	5.661	4.683	4.344	5.538	5.503
25	5.305	2.827	15.886	6.214	5.710	4.700	6.010	6.070
	5.129	2.944	16.126	6.241	5.479	5.119	5.904	6.008
	4.890	2.995	16.251	6.385		5.204	5.653	6.055

Annex 2. QA measures

Based on the 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, quality control measures, i.e. percentage bias and variability, were calculated for TC, OC and EC determination for each participant.

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 relative difference:

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

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.

$$\text{QA bias} = \text{RB} = \text{median}\left[\frac{D_i}{T_i}\%\right] \qquad (5)$$

In Table 1 are reported the assigned values for TC, OC and EC calculated as described in par. 2.2.1. In Tables 2, 3, 4 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. Assigned values for TC, OC and EC

	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
TC	5.56	3.96	18.56	6.82	7.01	5.94	6.94	6.76
OC	4.76	3.04	14.38	5.71	5.23	4.70	5.56	5.64
EC	0.81	0.89	4.15	1.12	1.74	1.22	1.36	1.12

Table 2. QA bias and QA variability for TC

TC QA measure	QA_bias	QA_variability	Systematic
Sunset Lab	0.1%	10.1%	no
Czechglobe	32.0%	23.3%	high
UBA-DE	0.1%	2.0%	no
CHMI	-15.0%	5.5%	low
ISCIII	3.0%	1.9%	high
LANUV	-3.3%	14.2%	no
Klab	-2.4%	1.7%	low
LSCE	2.1%	3.1%	high
AERO	-2.5%	2.9%	no
UCDavis	0.6%	2.5%	no
AIRPARIF	3.6%	2.7%	high
IDAEA CSIC	-6.8%	6.3%	low
NILU	-2.5%	5.1%	no
TROPOS	-0.6%	1.7%	no
IPIS	9.1%	5.6%	high
PIOS	14.1%	13.3%	high
ECPL_UOC	-6.1%	12.3%	no
SEA	0.4%	1.9%	no
CNR	-1.1%	10.8%	no
Uni-Lund	-13.8%	11.5%	low
CYI	-4.9%	1.9%	low
FMI_Matorova	4.8%	11.2%	no
FMI_Uto	-0.7%	12.1%	no
JRC	4.7%	4.8%	high

Table 3. QA bias and QA variability for OC

OC QA measure	QA_bias	QA_variability	Systematic
Sunset Lab	1.7%	12.0%	no
Czechglobe	38.8%	30.5%	high
UBA-DE	-3.3%	2.3%	low
CHMI	-14.3%	6.3%	low
ISCIII	2.9%	5.2%	high
LANUV	-1.8%	14.3%	no
Klab	-2.4%	1.8%	low
LSCE	4.2%	4.2%	high
AERO	-2.2%	3.5%	no
UCDavis	-1.0%	3.1%	no
AIRPARIF	2.3%	3.0%	high
IDAEA CSIC	-7.8%	7.1%	low
NILU	-1.4%	6.9%	no
TROPOS	0.9%	1.8%	no
IPIS	9.9%	6.4%	high
PIOS	13.4%	16.0%	no
ECPL_UOC	-5.1%	12.2%	no
SEA	-1.7%	2.5%	no
CNR	2.5%	14.2%	no
Uni-Lund	-17.1%	12.0%	low
CYI	-3.6%	2.5%	low
FMI_Matorova	4.9%	11.5%	no
FMI_Uto	-2.4%	13.1%	no
JRC	7.1%	6.4%	high

Table 4. QA bias and QA variability for EC

EC QA measure	QA_bias	QA_variability	Systematic
Sunset Lab	-4.2%	9.8%	no
Czechglobe	11.5%	10.2%	high
UBA-DE	16.0%	4.6%	high
CHMI	-15.7%	6.9%	low
ISCIII	1.9%	13.7%	no
LANUV	-3.6%	11.8%	no
Klab	-2.0%	4.0%	low
LSCE	-6.7%	7.4%	low
AERO	-3.0%	2.4%	no
UCDavis	8.4%	4.6%	high
AIRPARIF	9.4%	4.6%	high
IDAEA CSIC	5.0%	8.4%	no
NILU	-6.5%	3.4%	low
TROPOS	-3.1%	5.7%	low
IPIS	10.1%	15.4%	high
PIOS	8.9%	26.3%	high
ECPL_UOC	-10.3%	15.1%	low
SEA	6.7%	6.5%	no
CNR	-17.3%	5.5%	low
Uni-Lund	-4.1%	10.0%	no
CYI	-6.3%	4.5%	low
FMI_Matorova	4.3%	11.9%	no
FMI_Uto	4.9%	8.8%	no
JRC	-7.3%	4.4%	low