



Results of the inter-laboratory comparison exercise for TC and EC measurements
(ref.: OCEC-2019-1)

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Summary

The European Centre for Aerosol Calibration (ECAC) under ACTRIS-2 completed in March 2019 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 JRC-ERLAP (the inter-laboratory comparison exercise coordinator) was also distributed.

Twenty-three 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, seventeen are responsible for the aerosol chemical speciation at the EMEP or ACTRIS stations located in their countries (i.e. Norway, United Kingdom, The Netherlands, Czech Republic, Spain, Cyprus, France, Finland, Sweden, Germany, Poland, Spain, plus the JRC).

Measurement method performance: for TC determination, repeatability and reproducibility relative standard deviations ranged from **3%** to **8%** and from **6%** 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 **13%** and from **12%** to **17%**, respectively.

Based on last eight 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, eleven outliers –of which seven from a single participant– and eleven stragglers were identified; 77% of all entries were within 10% from the assigned TC concentration value.

Regarding EC/TC ratios, eight outliers and seven stragglers were identified. 55% of all entries were within 10% of the assigned value and 91% 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 indicates 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,

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 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 2019 an inter-laboratory comparison exercise (ILCE) (ref. OCEC-2019-1) among twenty-three applicants including, among others, seventeen laboratories in charge of OC and EC measurements at EMEP/ACTRIS stations in Norway, United Kingdom, The Netherlands, Czech Republic, Spain, Cyprus, France, Finland, Sweden, Germany, Poland, Spain, and Italy.

The Federal Institute of Metrology METAS of Switzerland, the University of Bern, the Institute for Medical Research and Occupational Health of Zagreb, Laboratory of Climatological and Environmental Sciences in France, 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 after exposure.

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 cm² 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 ($\geq 99.5\%$) in a precisely known volume of ultra-pure water (resistivity $\geq 18.2 \text{ M}\Omega \text{ cm}$).

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-three 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 2019-1, and contact persons

Code	Participant	Acronym	Contact
1	Federal Institute of Metrology METAS	METAS	adam.kimak@metas.ch
2	NILU-Norwegian Institute for Air Research	NILU	Key@nilu.no
3	National Physical Laboratory (NPL)	NPL	elizabeth.mcghee@npl.co.uk
4	GGD Amsterdam	GDD Amsterdam	ppanteliadis@ggd.amsterdam.nl
5	Global Change Research Institute AS CR v. i.	Czechglobe	mbengue.s@czechglobe.cz
6	IDAEA - CSIC	IDAEA - CSIC	noemi.perez@idaea.csic.es
7	University of Bern	LARA	szidat@dcb.unibe.ch
8	The Cyprus Institute	CyI	k.oikonomou@cyi.ac.cy; i.hafez@cyi.ac.cy
9	Laboratoire d'Aérodynamique UMR 5560	AERO	maria.dias-alves@aero.obs-mip.fr
10	University of Helsinki	INAR_UHEL_SMEARII	liine.heikkinen@helsinki.fi
11	Lund University, Nuclear physics	Uni-Lund	adam.kristensson@nuclear.lu.se
12	Leibniz Institute of Tropospheric Research	TROPOS	spindler@tropos.de
13	IGE	IGE	jaffrezo@univ-grenoble-alpes.fr
14	University of California-Davis	UCD AQRC	xluzhang@ucdavis.edu; ktrzepla@ucdavis.edu
15	Institute of Environmental Engineering Polish Academy of Sciences	IPIS	barbara.mathews@ipis.zabrze.pl
16	INSTITUTO DE SALUD CARLOS III	ISCIII	aaguilar@isciii.es
17	Institute for Medical Research and Occupational Health	IMROH	rgodec@imi.hr
19	AIRPARIF	AIRPARIF	chadia.kebbi@airparif.fr
20	Czech Hydrometeorological Institute	CHMIi	milan.vana@chmi.cz
21	UBA	UBA_DE	elke.bieber@uba.de
22	National Centre for Scientific Research "Demokritos"	ERL	Idiapouli@ipta.demokritos.gr

23	LSCE	LSCE	nicolas.bonnaire@lsce.ipsl.fr
24	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, 24) on 30th January 2019 via courier at ambient temperature without temperature record, in closed petri dishes. Participants were asked to report TC and EC concentrations, in $\mu\text{g C cm}^{-2}$ units with three decimal digits, from three replicates of test ambient $\text{PM}_{2.5}$ samples, by the end of March 2019. In addition, participants were asked to report the OC content of 10 μl of a phthalic acid solution ($\mu\text{g} / 10 \mu\text{l}$) 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, except laboratory 16, applied it.

All laboratories operated a Sunset carbon analyser. Laboratories 5, 10, 11, 14 and 23 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 $\text{PM}_{2.5}$ collected on filters as test samples.

In this report we focus on the *TC loadings* (in $\mu\text{g cm}^{-2}$) 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 6.1 to 29.8 $\mu\text{g cm}^{-2}$, corresponding to atmospheric concentrations ranging from ca. 1.1 to 5.4 $\mu\text{g m}^{-3}$ collected for 24h at a face velocity of 54 cm s^{-1} . EC/TC ranged on average from 0.07 to 0.20. All submitted results (in $\mu\text{g cm}^{-2}$) for TC, EC, OC (calculated as $\text{OC} = \text{TC} - \text{EC}$) 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 laboratories provided three replicates for every sample except labs 10 (for IPRA, IPRB, IPRD, IPRF and IPRPG samples), and 22 (for IPRB, and IPRC). However, Cochran's critical values for three replicates were used for all test samples, i.e. 0.297 (outlier) and 0.243 (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-three participants, the critical values for Grubb's test are 3.087 and 0.4085 - outliers for G_1 and G_2 , respectively- and 2.781 and 0.4857 -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/IPRA, 22/IPRA, 11/IPRB, 22/IPRB, 5/IPRF, 17/IPRF, 5/IPRH, 10/IPRH (laboratory/sample) and 5/IPRC as straggler (laboratory/sample).

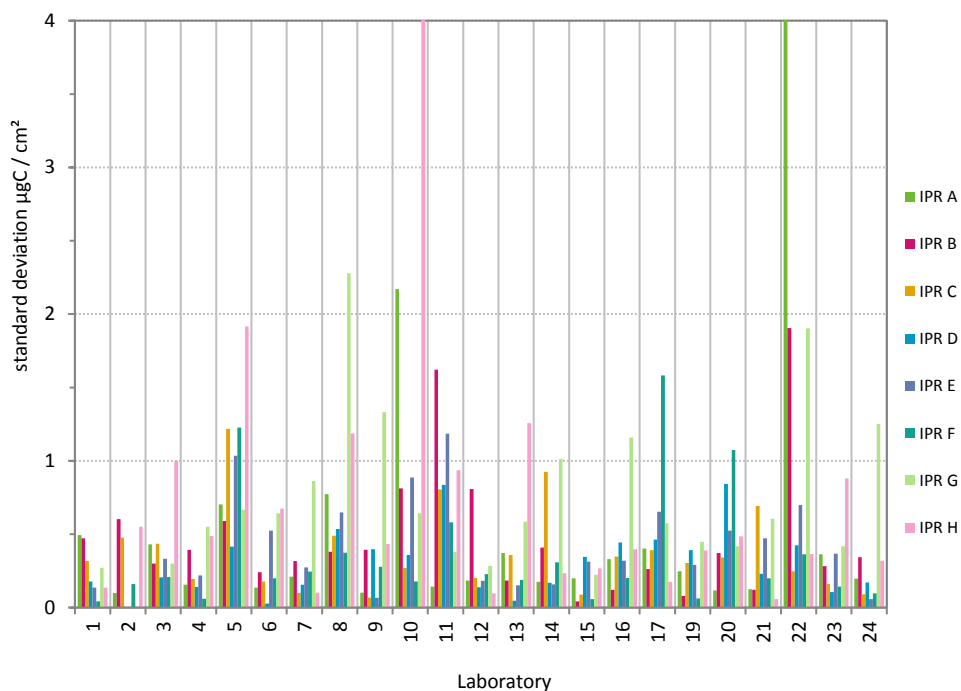


Figure 1. Standard deviation on the three replicates reported for each test filters, grouped by laboratory.

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 7/IPRC, 7/IPRD, and 7/IPRE, and as stragglers 7/IPRB, 22/IPRB, 7/IPRF and 11/IPRF.

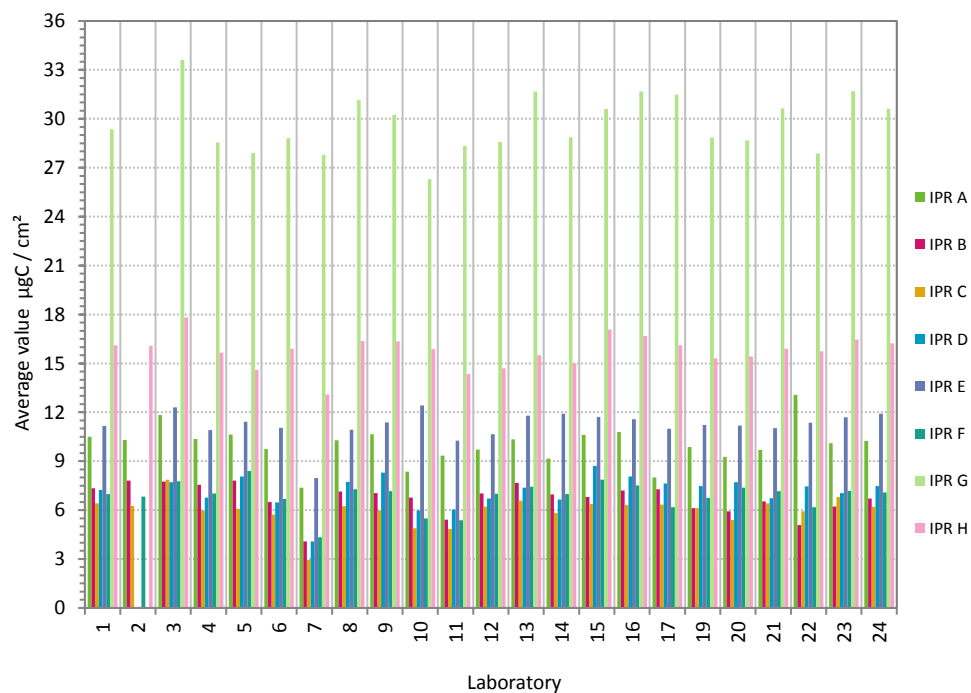


Figure 2. TC average values from three replicates reported by laboratories for each test sample, grouped by laboratory.

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 7 and 22) 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 obvious) 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	
	$\mu\text{gC} / \text{cm}^2$	$\mu\text{gC} / \text{cm}^2$	%	$\mu\text{gC} / \text{cm}^2$	%
IPR A	9.94	0.34	3.4	1.00	10.1
IPR B	6.88	0.40	5.8	0.91	13.2
IPR C	6.11	0.49	8.0	0.74	12.1
IPR D	7.32	0.39	5.4	0.77	10.5
IPR E	11.37	0.54	4.7	0.69	6.1
IPR F	6.85	0.34	4.9	0.88	12.9
IPR G	29.75	0.93	3.1	1.87	6.3
IPR H	15.80	0.61	3.9	1.11	7.0

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. $< 10 \mu\text{gC} / \text{cm}^2$ (Fig. 3).

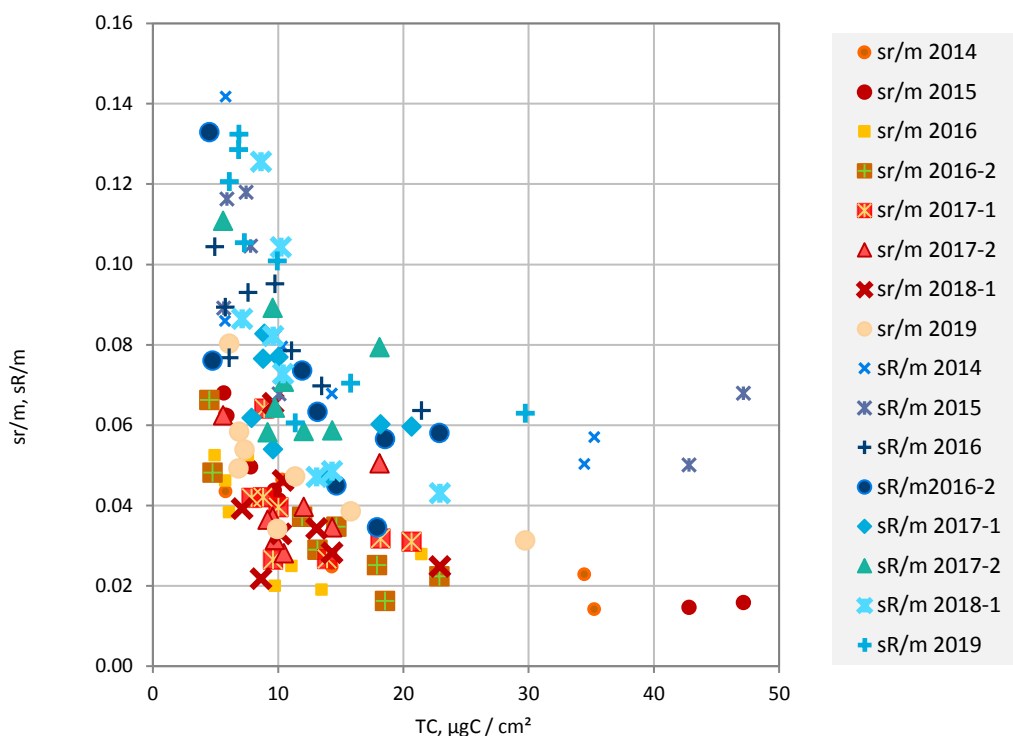


Figure 3. Repeatability and reproducibility relative standard deviation for the EUSAAR_2 protocol for TC measurement obtained during the previous inter-laboratory comparisons and the present one.

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 entries (laboratory/sample) 10/IPRA 16/IPRB, 22/IPRB, 16/IPRD, 6/IPRD, 16/IPRE, 22/IPRE, 10/ IPRG, 16/IPRG, 10/IPRH, and 16/IPRH as outliers and 16/IPRA and 17/IPRC stragglers.

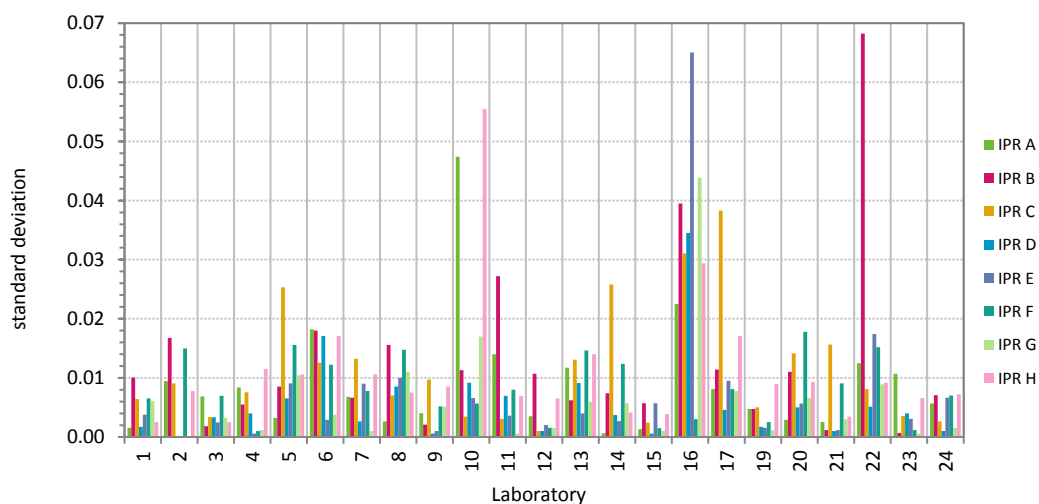


Figure 4. Standard deviation on the replicates reported for each test filters, grouped by laboratory.

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 16/IPRA, 6/IPRC, 7/IPRC and 16/IPRF as outliers and the entries 11/IPRG and 16/IPRH as stragglers

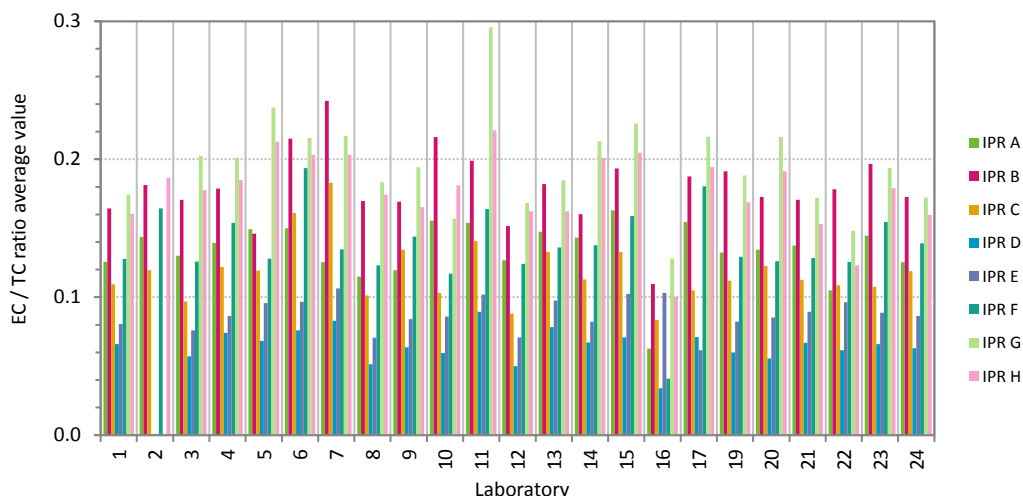


Figure 5. EC/TC average ratios from the replicates reported by laboratories for each test sample, grouped by laboratory.

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 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 A	0.14	0.01	5.9	0.02	11.7
IPR B	0.18	0.01	6.1	0.02	13.4
IPR C	0.11	0.02	13.6	0.02	17.1
IPR D	0.07	0.00	7.1	0.01	16.1
IPR E	0.09	0.01	6.3	0.01	14.2
IPR F	0.14	0.01	7.0	0.02	15.4
IPR G	0.20	0.01	2.7	0.03	15.9
IPR H	0.18	0.01	5.2	0.02	13.7

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).

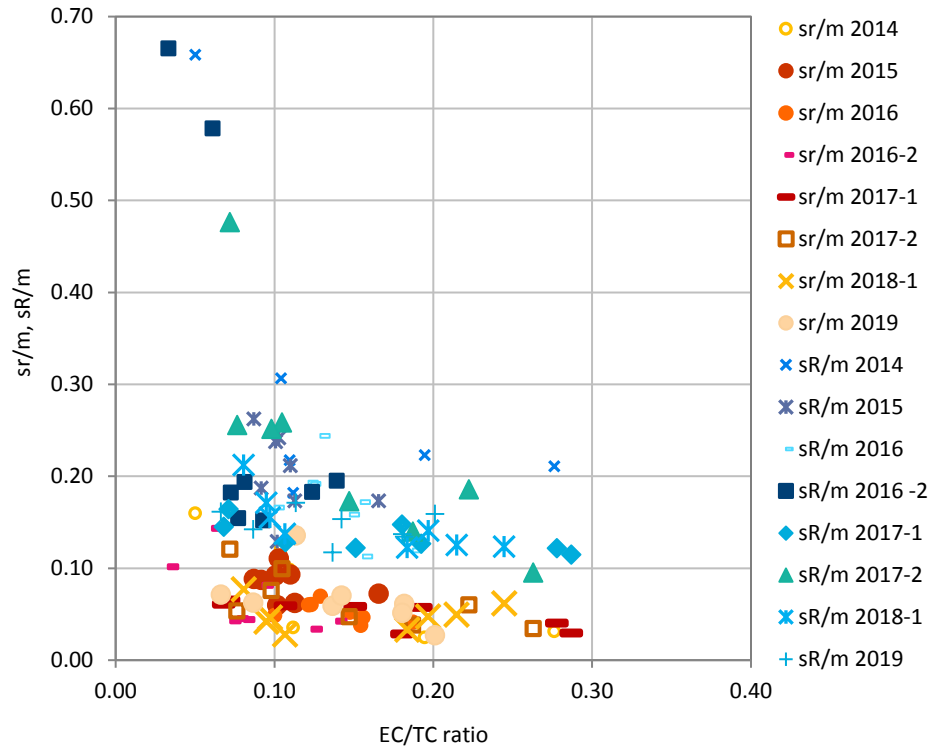


Figure 6. Repeatability and reproducibility relative standard deviation for the EUSAAR_2 protocol for EC/TC measurement obtained during the previous inter-laboratory comparisons and the present one.

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 \bar{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, quality control measures, 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 A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
assigned value	$\mu\text{g}/\text{cm}^2$	10.1	6.9	6.1	7.2	11.3	7.0	29.7	15.8
standard deviation	$\mu\text{g}/\text{cm}^2$	0.7	0.7	0.4	0.8	0.6	0.6	1.8	0.8
	%	7.4	10.6	5.9	11.5	4.9	8.1	5.9	4.8
$2\sigma^*$	%	15	21	12	23	10	16	12	10
$3\sigma^*$	%	22	32	18	35	15	24	18	14

Figure 7 shows z-scores calculated from σ^* . Eleven outliers, 7/IPRA, 22/IPRA, 7/IPRB, 3/IPRC, 7/IPRC, 10/IPRC, 11/IPRC, 7/IPRD, 7/IPRE, 7/IPRF and 7/IPRH (lab/sample) –mainly from

participant #7– and eleven stragglers, 3/IPRA, 10/IPRA, 17/IPRA, 11/IPRB, 22/IPRB, 20/IPRC, 5/IPRF, 10/IPRF, 11/IPRF, 3/IPRG and 3/IPRH are identified.

For each sample, fourteen to sixteen out of twenty-three participants show deviations from the assigned values within $\pm 1 \sigma^*$ as listed in Table 8 (i.e. within 1 z-score). 77% 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 $\pm 5\%$, on average) of overestimating –i.e. labs 3 and 16 - or underestimating –i.e. labs 7 and 11 - the assigned TC concentrations.

A contribution of filter heterogeneities to poor laboratory performances cannot be completely excluded. However, participants showing large ($|z\text{-scores}| > 2$) 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 CO₂ 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 1	IPR3	IPR5	IPR6	IPR7	IPR19	IPR27	ISP30
assigned value	ratio	0.14	0.18	0.12	0.07	0.09	0.14	0.19	0.18
standard deviation	ratio	0.02	0.02	0.02	0.01	0.01	0.02	0.03	0.02
	%	12	11	14	15	14	12	16	14
2 σ^*	%	25	23	27	30	28	23	32	27
3 σ^*	%	37	34	41	46	42	35	47	41

Eight outliers – 16/IPRA, 7/IPRB, 16/IPRB, 7/IPRC, 16/IPRD, 6/IPRF, 16/IPRF, and 16/IPRH (lab/sample) - and seven stragglers – 6/IPRC, 16/IPRC, 11/IPRD, 17/IPRE, 17/IPRF, 16/IPRG and 22/IPRH - (lab/sample) are identified. For each sample, eleven to sixteen out of twenty-three laboratories show deviations from the assigned values within $\pm 1 \sigma^*$ as listed in Table 5 (i.e. within 1 z-score).

55% of all entries are within 10% of the assigned value and 91% are within the 25% of the assigned value.

A few participants show the systematic tendency (i.e. for all test samples and larger than $\pm 5\%$, on average) of overestimating – i.e. lab 2, 6, 11 and 15 - or underestimating – i.e. lab 8 and 12 - the assigned EC/TC ratio.

A contribution of filter heterogeneities to poor laboratory performances cannot be completely excluded. However, participants showing large ($|z\text{-scores}| > 2$) 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/O₂ phases; iii) temperature calibration and iv) transit time would correct such performances and reduce the observed variability in EC/TC ratio determination.

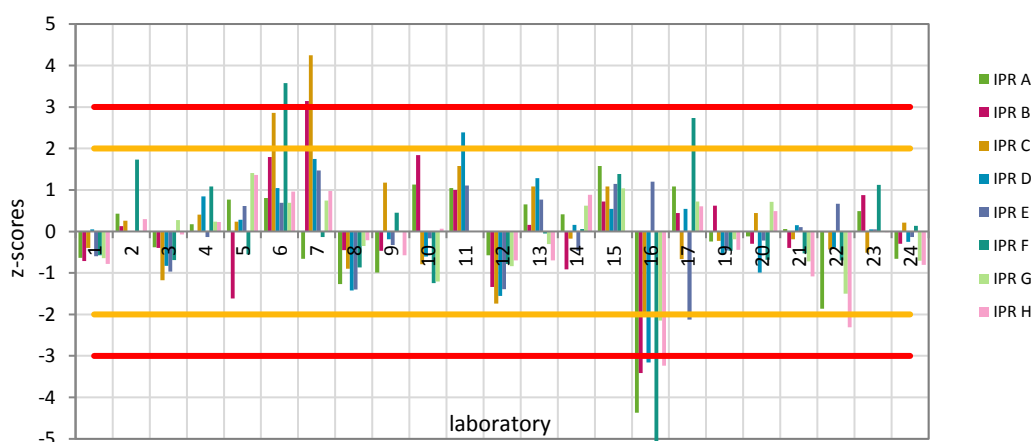


Figure 8. z-scores for EC/TC ratio calculated using σ^* from data obtained in a round of a proficiency testing scheme. The scale is set from -5 to +5.

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 ($1.57 \pm 0.02 \text{ gC l}^{-1}$, calculated from primary mass and water volume measurements) for each participant. Nineteen laboratories out of twenty-three laboratories reported OC deviating from the assigned value by less than $\pm 5\%$. 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 CO₂ 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.).

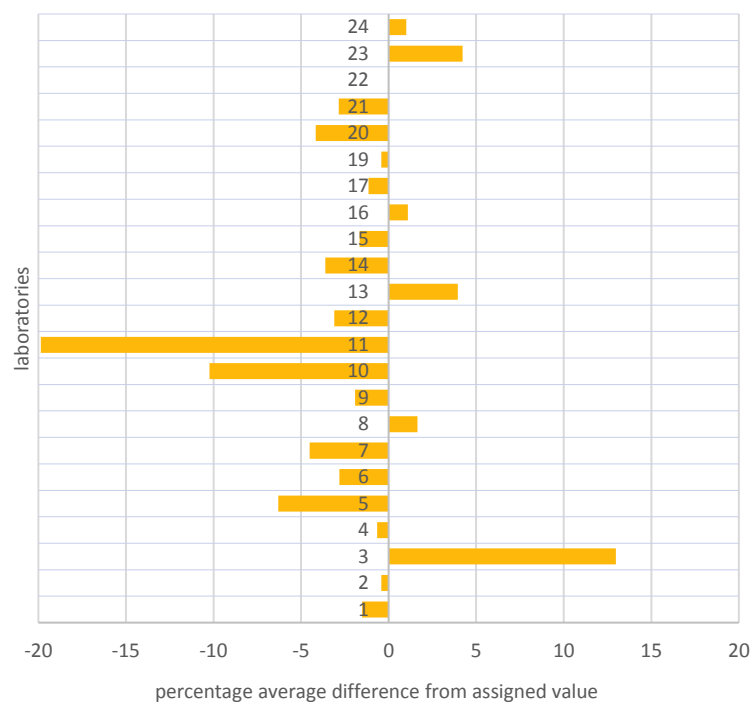


Figure 9. Phthalic acid solution –percentage differences from the assigned value, i.e. the C concentration of the test solution calculated from the mass of phthalic acid and the volume of ultra-pure water used to make the solution.

Conclusions

This inter-laboratory comparison involved twenty-three participants all applying thermal-optical analyses and the EUSAAR_2 protocol, except one.

The measurement method **repeatability and reproducibility for TC** ranged from **3% to 8%** and from **6% to 13%** (as one relative standard deviation), respectively.

For the **EC/TC ratio, repeatability and reproducibility** ranged from **3% to 13%** 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. $<10 \mu\text{gC} / \text{cm}^2$ 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, eleven outliers –of which seven from a single participant– and eleven stragglers were identified; 77% 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 labs) or underestimating (i.e. two labs) the assigned TC concentrations. Participants showing large ($|z\text{-scores}| > 2$) 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, eight outliers and seven stragglers were identified. 55% of all entries were within 10% of the assigned value and 91% 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. four labs) or underestimating (i.e. two labs) the assigned EC/TC ratio. Participants showing large ($|z\text{-scores}| > 2$) 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/O₂ 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,

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

Table 1: Total carbon loadings ($\mu\text{g}/\text{cm}^2$)

Laboratory	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	11.052	7.126	6.234	7.313	11.195	6.990	29.663	15.969
	10.291	7.866	6.219	7.359	11.286	7.011	29.134	16.238
	10.124	6.991	6.775	7.031	11.018	6.929	29.296	16.147
2	10.200	7.430	6.170	NaN	NaN	6.820	NaN	15.800
	10.400	7.480	6.780	NaN	NaN	6.670	NaN	15.700
	10.300	8.500	5.840	NaN	NaN	6.990	NaN	16.700
3	11.843	8.054	8.030	7.929	12.372	7.607	33.358	18.642
	11.384	7.749	8.187	7.528	11.940	8.007	33.940	18.100
	12.244	7.453	7.368	7.644	12.596	7.710	33.528	16.703
4	10.539	7.675	6.111	6.923	11.098	7.050	28.177	16.162
	10.233	7.114	6.064	6.737	10.666	7.079	29.194	15.636
	10.326	7.875	5.753	6.649	10.942	6.963	28.317	15.190
5	11.096	7.180	5.544	7.918	12.167	9.755	27.318	16.356
	10.964	8.346	7.468	7.742	11.873	8.026	27.789	14.891
	9.817	7.909	5.211	8.535	10.244	7.381	28.633	12.556
6	9.624	6.221	5.925	6.457	10.584	6.916	28.388	15.218
	9.893	6.598	5.709	6.505	10.945	6.589	29.556	15.879
	9.732	6.671	5.573	6.459	11.616	6.553	28.511	16.568
7	7.149	4.337	2.871	3.988	8.273	4.263	28.488	13.201
	7.448	3.728	2.915	3.972	7.792	4.603	28.059	13.077
	7.557	4.190	3.061	4.249	7.810	4.129	26.827	13.002
8	9.836	7.405	6.730	7.833	11.199	7.591	30.452	16.176
	9.848	7.292	6.221	8.196	11.396	7.386	33.687	17.646
	11.180	6.698	5.751	7.141	10.187	6.866	29.291	15.298
9	10.573	7.492	5.917	7.848	11.418	6.905	29.025	15.927
	10.761	6.917	6.053	8.448	11.307	7.097	31.662	16.313
	10.602	6.741	5.961	8.603	11.428	7.454	30.019	16.790
10	NaN	NaN	5.097	5.732	11.754	5.626	26.756	23.073
	9.891	7.344	4.970	NaN	12.080	NaN	25.848	11.922
	6.820	6.194	4.582	6.238	13.428	5.375	NaN	12.644
11	9.490	7.270	5.740	6.910	11.560	5.000	28.020	15.410
	9.300	4.630	4.640	6.000	9.980	5.070	28.760	13.910
	9.210	4.320	4.170	5.240	9.240	6.040	28.250	13.690
12	9.601	6.767	6.041	6.596	10.865	7.267	28.502	14.644
	9.921	7.929	6.201	6.668	10.531	6.879	28.335	14.657
	9.600	6.375	6.440	6.864	10.573	6.865	28.890	14.819
13	10.649	7.535	NaN	7.396	11.622	7.605	32.057	14.056
	10.444	7.614	6.319	7.408	11.910	7.479	31.003	16.186
	9.926	7.887	6.828	7.323	11.851	7.235	31.976	16.282
14	8.953	6.837	6.783	6.703	11.727	7.332	29.357	14.803
	9.233	7.411	5.758	6.773	11.949	6.748	27.697	15.257
	9.277	6.621	4.937	6.450	12.034	6.870	29.536	14.924
15	10.794	6.860	6.280	9.094	11.918	7.925	30.350	17.278
	10.662	6.778	6.376	8.604	11.860	7.855	30.780	17.181
	10.403	6.804	6.457	8.425	11.348	7.810	30.667	16.775
16	10.637	7.168	6.365	7.730	11.948	7.358	31.170	16.755
	10.549	7.089	6.640	7.894	11.412	7.744	30.863	17.021
	11.159	7.327	5.950	8.569	11.378	7.445	33.005	16.238
17	8.470	7.552	6.623	7.285	11.732	8.014	31.483	16.077
	7.723	7.253	5.890	7.441	10.503	5.296	30.895	15.967
	7.840	7.029	6.492	8.155	10.733	5.253	32.045	16.310
19	9.966	6.214	5.855	7.908	11.051	6.806	29.353	14.958
	10.038	6.057	6.064	7.336	11.052	6.732	28.520	15.209
	9.577	6.116	6.453	7.159	11.555	6.682	28.646	15.721

20	9.304	5.700	5.513	8.670	10.657	8.578	29.108	15.978
	9.334	5.731	5.654	7.113	11.182	6.503	28.661	15.165
	9.119	6.360	5.006	7.332	11.706	7.054	28.275	15.111
21	9.828	6.414	7.205	6.462	11.555	6.942	31.340	15.834
	9.623	6.554	5.939	6.861	10.838	7.341	30.275	15.949
	9.603	6.654	6.084	6.859	10.665	7.174	30.310	15.901
22	8.754	2.872	6.166	7.945	12.159	5.905	26.924	16.128
	9.421	6.213	5.670	7.212	10.873	6.062	26.627	15.407
	21.058	6.130	5.908	7.212	11.040	6.597	30.062	15.666
23	10.456	6.416	6.914	6.923	11.461	7.064	32.104	17.356
	10.137	6.018	6.688	7.112	11.517	7.150	31.269	16.452
	9.731	NaN	NaN	7.098	12.124	7.344	31.729	15.597
24	10.371	7.083	6.208	7.394	11.898	6.974	29.833	15.855
	10.014	6.409	6.091	7.360	11.866	7.165	32.053	16.396
	10.335	6.636	6.269	7.672	11.978	7.089	29.945	16.421

Table 2: Elemental carbon / total carbon (ratios)

Laboratory	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	0.127	0.163	0.114	0.065	0.079	0.121	0.181	0.158
	0.126	0.155	0.112	0.065	0.085	0.128	0.173	0.163
	0.124	0.175	0.102	0.068	0.078	0.134	0.169	0.160
2	0.133	0.190	0.121	NaN	NaN	0.152	NaN	0.189
	0.151	0.192	0.110	NaN	NaN	0.181	NaN	0.193
	0.147	0.162	0.128	NaN	NaN	0.160	NaN	0.178
3	0.138	0.170	0.097	0.060	0.075	0.134	0.203	0.176
	0.127	0.169	0.093	0.058	0.079	0.123	0.199	0.176
	0.125	0.173	0.100	0.054	0.074	0.121	0.205	0.181
4	0.135	0.176	0.121	0.070	0.086	0.155	0.200	0.176
	0.149	0.185	0.115	0.074	0.087	0.153	0.202	0.198
	0.134	0.175	0.130	0.078	0.086	0.154	0.202	0.181
5	0.153	0.138	0.124	0.075	0.089	0.117	0.234	0.203
	0.147	0.155	0.092	0.068	0.092	NaN	0.249	0.211
	0.148	0.145	0.142	0.062	0.106	0.139	0.229	0.224
6	0.161	0.200	0.148	0.074	0.095	0.183	0.218	0.189
	0.160	0.235	0.162	0.060	0.100	0.191	0.217	0.198
	0.129	0.210	0.173	0.094	0.095	0.207	0.211	0.222
7	0.120	0.238	0.173	0.080	0.115	0.137	0.218	0.213
	0.123	0.250	0.198	0.084	0.107	0.126	0.216	0.192
	0.133	0.239	0.178	0.085	0.097	0.141	0.217	0.205
8	0.117	0.155	0.094	0.048	0.067	0.114	0.178	0.174
	0.116	0.168	0.102	0.045	0.063	0.115	0.176	0.167
	0.112	0.186	0.108	0.061	0.082	0.140	0.196	0.182
9	0.115	0.167	0.132	0.064	0.085	0.138	0.190	0.159
	0.122	0.171	0.126	0.064	0.083	0.147	0.193	0.175
	0.122	0.170	0.145	0.063	0.084	0.147	0.200	0.162
10	NaN	NaN	0.105	0.066	0.079	0.121	0.145	0.245
	0.189	0.224	0.099	NaN	0.087	NaN	0.169	0.151
	0.122	0.208	0.105	0.053	0.092	0.113	NaN	0.147
11	0.144	0.169	0.138	0.097	0.100	0.164	0.296	0.229
	0.148	0.222	0.140	0.083	0.106	0.172	0.296	0.217
	0.170	0.206	0.144	0.088	0.100	0.156	0.295	0.217
12	0.130	0.154	0.088	0.051	0.069	0.126	0.170	0.156
	0.127	0.140	0.087	0.049	0.070	0.124	0.168	0.169
	0.123	0.161	0.089	0.050	0.073	0.123	0.167	0.162
13	0.142	0.179	NaN	0.080	0.102	0.120	0.184	0.152
	0.161	0.177	0.142	0.069	0.096	0.148	0.179	0.178
	0.140	0.189	0.124	0.087	0.095	0.140	0.191	0.156
14	0.143	0.169	0.085	0.064	0.079	0.135	0.218	0.205
	0.144	0.156	0.119	0.066	0.083	0.127	0.214	0.201
	0.143	0.156	0.135	0.071	0.085	0.151	0.207	0.197
15	0.162	0.187	0.131	0.071	0.100	0.159	0.225	0.200
	0.165	0.199	0.133	0.071	0.098	0.160	0.226	0.206
	0.163	0.194	0.135	0.070	0.109	0.157	0.227	0.208
16	0.068	0.067	0.049	0.069	0.167	0.044	0.118	0.087
	0.082	0.145	0.109	0.033	0.037	0.041	0.090	0.080
	0.038	0.117	0.093	0.000	0.105	0.038	0.176	0.134
17	0.150	0.191	0.061	0.075	0.071	0.171	0.210	0.183
	0.150	0.175	0.123	0.072	0.052	0.185	0.225	0.186
	0.164	0.197	0.131	0.066	0.062	0.185	0.214	0.214
19	0.136	0.195	0.117	0.061	0.081	0.129	0.189	0.164

	0.127	0.186	0.112	0.061	0.082	0.132	0.187	0.179
	0.134	0.193	0.107	0.058	0.084	0.127	0.189	0.163
20	0.136	0.180	0.114	0.061	0.090	0.106	0.215	0.187
	0.131	0.178	0.115	0.051	0.079	0.140	0.210	0.185
	0.136	0.160	0.139	0.055	0.087	0.132	0.223	0.202
21	0.137	0.170	0.096	0.068	0.090	0.118	0.172	0.155
	0.140	0.170	0.127	0.066	0.090	0.135	0.169	0.149
	0.135	0.172	0.115	0.067	0.088	0.132	0.175	0.155
22	0.115	0.257	0.104	0.056	0.116	0.123	0.145	0.131
	0.109	0.135	0.118	0.063	0.090	0.142	0.158	0.113
	0.091	0.143	0.104	0.066	0.083	0.112	0.141	0.125
23	0.154	0.197	0.105	0.070	0.086	0.154	0.193	0.178
	0.147	0.196	0.110	0.066	0.092	0.154	0.194	0.186
	0.133	NaN	NaN	0.062	0.088	0.156	0.194	0.173
24	0.119	0.165	0.117	0.064	0.094	0.139	0.174	0.155
	0.127	0.179	0.118	0.062	0.082	0.132	0.172	0.168
	0.130	0.174	0.122	0.063	0.083	0.146	0.171	0.156

Table 3: Elemental carbon loadings ($\mu\text{g}/\text{cm}^2$)

Laboratory	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	1.407	1.159	0.712	0.474	0.886	0.845	5.357	2.523
	1.299	1.221	0.694	0.476	0.960	0.898	5.040	2.652
	1.250	1.225	0.691	0.476	0.862	0.927	4.965	2.577
2	1.360	1.410	0.750	NaN	NaN	1.040	NaN	2.990
	1.560	1.430	0.740	NaN	NaN	1.210	NaN	3.020
	1.510	1.380	0.750	NaN	NaN	1.120	NaN	2.970
3	1.633	1.370	0.780	0.477	0.929	1.017	6.766	3.280
	1.445	1.312	0.764	0.437	0.941	0.984	6.753	3.193
	1.534	1.288	0.738	0.410	0.933	0.930	6.887	3.015
4	1.423	1.351	0.742	0.486	0.954	1.092	5.646	2.837
	1.520	1.314	0.696	0.495	0.927	1.085	5.908	3.092
	1.388	1.382	0.750	0.519	0.944	1.070	5.728	2.746
5	1.700	0.990	0.684	0.600	1.087	1.139	6.389	3.312
	1.615	1.290	0.684	0.527	1.092	NaN	6.922	3.135
	1.453	1.145	0.741	0.535	1.083	1.022	6.567	2.815
6	1.552	1.243	0.878	0.480	1.006	0.163	0.409	0.244
	1.579	1.552	0.926	0.393	1.097	0.163	0.420	0.257
	1.257	1.399	0.965	0.605	1.106	0.168	0.400	0.284
7	0.860	1.033	0.498	0.317	0.950	0.583	6.198	2.812
	0.919	0.930	0.579	0.333	0.830	0.581	6.064	2.507
	1.003	1.002	0.545	0.360	0.760	0.582	5.817	2.670
8	1.148	1.145	0.633	0.373	0.749	0.862	5.421	2.816
	1.141	1.228	0.636	0.372	0.718	0.853	5.916	2.943
	1.252	1.249	0.620	0.437	0.835	0.959	5.743	2.782
9	1.214	1.250	0.779	0.502	0.973	0.956	5.528	2.540
	1.313	1.183	0.763	0.538	0.941	1.046	6.124	2.854
	1.297	1.143	0.866	0.543	0.965	1.096	6.012	2.715
10	NaN	NaN	0.537	0.379	0.925	0.683	3.886	5.661
	1.864	1.648	0.493	NaN	1.044	NaN	4.362	1.802
	0.833	1.286	0.480	0.330	1.238	0.608	NaN	1.850
11	1.370	1.230	0.790	0.670	1.160	0.820	8.290	3.530
	1.380	1.030	0.650	0.500	1.060	0.870	8.520	3.020
	1.570	0.890	0.600	0.460	0.920	0.940	8.330	2.970
12	1.250	1.039	0.534	0.338	0.749	0.915	4.850	2.285
	1.263	1.110	0.541	0.326	0.737	0.856	4.769	2.480
	1.183	1.025	0.571	0.345	0.771	0.842	4.820	2.395
13	1.508	1.351	NaN	0.591	1.187	0.911	5.904	2.140
	1.680	1.351	0.898	0.508	1.142	1.108	5.551	2.886
	1.386	1.491	0.844	0.634	1.123	1.013	6.102	2.547
14	1.277	1.154	0.574	0.431	0.930	0.990	6.409	3.040
	1.329	1.154	0.686	0.445	0.989	0.856	5.925	3.064
	1.331	1.034	0.666	0.460	1.018	1.039	6.112	2.942
15	1.749	1.286	0.820	0.648	1.194	1.260	6.817	3.462
	1.755	1.347	0.846	0.614	1.163	1.258	6.967	3.537
	1.691	1.320	0.874	0.592	1.235	1.227	6.948	3.487
16	0.718	0.479	0.314	0.534	1.991	0.327	3.690	1.463
	0.866	1.031	0.724	0.262	0.418	0.314	2.782	1.361
	0.428	0.856	0.552	0.000	1.197	0.285	5.817	2.171
17	1.270	1.443	0.406	0.543	0.832	1.366	6.609	2.937
	1.160	1.272	0.724	0.538	0.545	0.977	6.941	2.978
	1.282	1.382	0.849	0.541	0.660	0.970	6.870	3.486
19	1.360	1.210	0.683	0.485	0.895	0.880	5.533	2.453

	1.275	1.129	0.681	0.450	0.905	0.890	5.324	2.728
	1.283	1.183	0.689	0.414	0.968	0.847	5.406	2.555
20	1.261	1.028	0.629	0.528	0.963	0.908	6.246	2.981
	1.227	1.021	0.650	0.362	0.885	0.911	6.019	2.808
	1.236	1.017	0.695	0.404	1.013	0.930	6.311	3.045
21	1.351	1.093	0.691	0.438	1.042	0.819	5.383	2.457
	1.348	1.117	0.753	0.456	0.974	0.991	5.105	2.384
	1.300	1.142	0.701	0.458	0.939	0.945	5.297	2.458
22	1.004	0.737	0.640	0.445	1.414	0.727	3.901	2.113
	1.028	0.837	0.668	0.455	0.981	0.859	4.208	1.745
	1.917	0.876	0.615	0.476	0.920	0.738	4.240	1.958
23	1.613	1.269	0.727	0.490	0.994	1.094	6.217	3.097
	1.494	1.182	0.737	0.476	1.065	1.108	6.082	3.061
	1.303	NaN	NaN	0.443	1.078	1.149	6.161	2.704
24	1.233	1.170	0.727	0.471	1.118	0.971	5.192	2.456
	1.267	1.148	0.722	0.457	0.973	0.946	5.503	2.750
	1.347	1.156	0.768	0.480	0.994	1.033	5.123	2.569

Table 4: Organic carbon [OC = TC-EC loadings] ($\mu\text{g}/\text{cm}^2$)

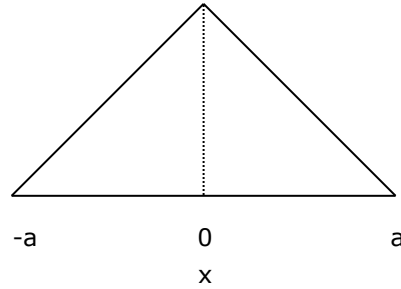
Laboratory	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	9.65	5.97	5.52	6.84	10.31	6.15	24.31	13.45
	8.99	6.65	5.53	6.88	10.33	6.11	24.09	13.59
	8.87	5.77	6.08	6.56	10.16	6.00	24.33	13.57
2	8.84	6.02	5.42	NaN	NaN	5.78	NaN	12.81
	8.84	6.05	6.04	NaN	NaN	5.46	NaN	12.68
	8.79	7.12	5.09	NaN	NaN	5.87	NaN	13.73
3	10.21	6.68	7.25	7.45	11.44	6.59	26.59	15.36
	9.94	6.44	7.42	7.09	11.00	7.02	27.19	14.91
	10.71	6.17	6.63	7.23	11.66	6.78	26.64	13.69
4	9.12	6.32	5.37	6.44	10.14	5.96	22.53	13.33
	8.71	5.80	5.37	6.24	9.74	5.99	23.29	12.54
	8.94	6.49	5.00	6.13	10.00	5.89	22.59	12.44
5	9.40	6.19	4.86	7.32	11.08	8.62	20.93	13.04
	9.35	7.06	6.78	7.22	10.78	NaN	20.87	11.76
	8.36	6.76	4.47	8.00	9.16	6.36	22.07	9.74
6	8.07	4.98	5.05	5.98	9.58	6.75	27.98	14.97
	8.31	5.05	4.78	6.11	9.85	6.43	29.14	15.62
	8.48	5.27	4.61	5.85	10.51	6.39	28.11	16.28
7	6.29	3.30	2.37	3.67	7.32	3.68	22.29	10.39
	6.53	2.80	2.34	3.64	6.96	4.02	22.00	10.57
	6.55	3.19	2.52	3.89	7.05	3.55	21.01	10.33
8	8.69	6.26	6.10	7.46	10.45	6.73	25.03	13.36
	8.71	6.06	5.59	7.82	10.68	6.53	27.77	14.70
	9.93	5.45	5.13	6.70	9.35	5.91	23.55	12.52
9	9.36	6.24	5.14	7.35	10.45	5.95	23.50	13.39
	9.45	5.73	5.29	7.91	10.37	6.05	25.54	13.46
	9.31	5.60	5.10	8.06	10.46	6.36	24.01	14.08
10	NaN	NaN	4.56	5.35	10.83	4.94	22.87	17.41
	8.03	5.70	4.48	NaN	11.04	NaN	21.49	10.12
	5.99	4.91	4.10	5.91	12.19	4.77	NaN	10.79
11	8.12	6.04	4.95	6.24	10.40	4.18	19.73	11.88
	7.92	3.60	3.99	5.50	8.92	4.20	20.24	10.89
	7.64	3.43	3.57	4.78	8.32	5.10	19.92	10.72
12	8.35	5.73	5.51	6.26	10.12	6.35	23.65	12.36
	8.66	6.82	5.66	6.34	9.79	6.02	23.57	12.18
	8.42	5.35	5.87	6.52	9.80	6.02	24.07	12.42
13	9.14	6.18	NaN	6.80	10.43	6.69	26.15	11.92
	8.76	6.26	5.42	6.90	10.77	6.37	25.45	13.30
	8.54	6.40	5.98	6.69	10.73	6.22	25.87	13.73
14	7.68	5.68	6.21	6.27	10.80	6.34	22.95	11.76
	7.90	6.26	5.07	6.33	10.96	5.89	21.77	12.19
	7.95	5.59	4.27	5.99	11.02	5.83	23.42	11.98
15	9.05	5.57	5.46	8.45	10.72	6.66	23.53	13.82
	8.91	5.43	5.53	7.99	10.70	6.60	23.81	13.64
	8.71	5.48	5.58	7.83	10.11	6.58	23.72	13.29
16	9.92	6.69	6.05	7.20	9.96	7.03	27.48	15.29
	9.68	6.06	5.92	7.63	10.99	7.43	28.08	15.66
	10.73	6.47	5.40	8.57	10.18	7.16	27.19	14.07
17	7.20	6.11	6.22	6.74	10.90	6.65	24.87	13.14
	6.56	5.98	5.17	6.90	9.96	4.32	23.95	12.99
	6.56	5.65	5.64	7.61	10.07	4.28	25.18	12.82
19	8.61	5.00	5.17	7.42	10.16	5.93	23.82	12.51

	8.76	4.93	5.38	6.89	10.15	5.84	23.20	12.48
	8.29	4.93	5.76	6.75	10.59	5.84	23.24	13.17
20	8.04	4.67	4.88	8.14	9.69	7.67	22.86	13.00
	8.11	4.71	5.00	6.75	10.30	5.59	22.64	12.36
	7.88	5.34	4.31	6.93	10.69	6.12	21.96	12.07
21	8.48	5.32	6.51	6.02	10.51	6.12	25.96	13.38
	8.28	5.44	5.19	6.41	9.86	6.35	25.17	13.57
	8.30	5.51	5.38	6.40	9.73	6.23	25.01	13.44
22	7.75	2.14	5.53	7.50	10.75	5.18	23.02	14.02
	8.39	5.38	5.00	6.76	9.89	5.20	22.42	13.66
	19.14	5.25	5.29	6.74	10.12	5.86	25.82	13.71
23	8.84	5.15	6.19	6.43	10.47	5.97	25.89	14.26
	8.64	4.84	5.95	6.64	10.45	6.04	25.19	13.39
	8.43	NaN	NaN	6.66	11.05	6.20	25.57	12.89
24	9.14	5.91	5.48	6.92	10.78	6.00	24.64	13.40
	8.75	5.26	5.37	6.90	10.89	6.22	26.55	13.65
	8.99	5.48	5.50	7.19	10.98	6.06	24.82	13.85

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

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

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:

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

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

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

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:

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

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.

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

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

	TC QA measure	QA_bias	QA_variability	Systematicity
1	METAS	1.0%	3.3%	no
2	NILU	2.1%	6.6%	no
3	NPL	12.7%	8.8%	high
4	GDD Amsterdam	-1.8%	6.7%	no
5	Czechglobe	3.3%	11.2%	no
6	IDAEA - CSIC	-3.8%	4.4%	low
7	LARA	-33.9%	18.6%	low
8	Cyl	3.7%	4.2%	high
9	AERO	2.4%	7.1%	high
10	INAR_UHEL_SMEARII	-14.1%	12.7%	no
11	Uni-Lund	-12.9%	7.7%	low
12	TROPOS	-3.6%	3.9%	no
13	IGE	5.2%	5.6%	high
14	UCD AQRC	-3.9%	5.8%	no
15	IPIS	4.7%	8.7%	high
16	ISCI	6.1%	3.8%	high
17	IMROH	2.6%	10.8%	no
19	AIRPARIF	-2.4%	5.7%	low
20	CHMI	-2.9%	8.3%	no
21	UBA_de	-1.1%	4.7%	no
22	ERL	-2.1%	22.9%	no
23	LSCE	3.0%	8.3%	no
24	ERLAP	2.2%	3.1%	high

Table 2. QA bias and QA variability for OC

OC QA measure	QA_bias	QA_variability	Systematic
METAS	1.9%	5.2%	no
NILU	1.5%	5.6%	no
NPL	11.9%	10.0%	high
GDD Amsterdam	-2.8%	8.8%	no
Czechglobe	2.0%	9.8%	no
IDAEA - CSIC	-4.1%	51.3%	no
LARA	-34.8%	17.4%	low
Cyl	4.9%	10.1%	high
AERO	2.4%	8.6%	high
INAR_UHEL_SMEARII	-12.5%	21.7%	low
Uni-Lund	-18.0%	24.0%	low
TROPOS	-2.0%	8.8%	no
IGE	4.2%	14.0%	high
UCD AQRC	-5.0%	6.6%	no
IPIS	2.1%	10.0%	no
ISCIII	14.5%	36.0%	high
IMROH	1.0%	20.6%	no
AIRPARIF	-2.3%	2.3%	no
CHMI	-5.8%	9.4%	no
UBA_de	-0.2%	6.2%	no
ERL	-1.2%	17.7%	no
LSCE	1.5%	7.9%	no
ERLAP	3.2%	5.7%	high

Table 3. QA bias and QA variability for EC

EC QA measure	QA_bias	QA_variability	Systematic
METAS	-3.2%	5.2%	no
NILU	9.2%	5.6%	no
NPL	10.0%	10.0%	no
GDD Amsterdam	5.8%	8.8%	high
Czechglobe	13.5%	9.8%	high
IDAEA - CSIC	7.2%	51.3%	no
LARA	-19.8%	17.4%	low
Cyl	-6.6%	10.1%	no
AERO	1.4%	8.6%	no
INAR_UHEL_SMEARII	-11.9%	21.7%	no
Uni-Lund	6.2%	24.0%	no
TROPOS	-14.9%	8.8%	low
IGE	14.6%	14.0%	high
UCD AQRC	-2.0%	6.6%	no
IPIS	23.8%	10.0%	high
ISCIII	-37.1%	36.0%	low
IMROH	13.5%	20.6%	no
AIRPARIF	-4.3%	2.3%	low
CHMI	-4.4%	9.4%	no
UBA_de	-2.1%	6.2%	low
ERL	-12.1%	17.7%	low
LSCE	6.0%	7.9%	high
ERLAP	-1.0%	5.7%	no