



JRC Technical Report

Results of the inter-laboratory comparison exercise for TC and EC measurements

(OCEC-2023-1)

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(OCEC-2023-1)**

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Summary

The ACTRIS Centre for Aerosol In-Situ measurements ECAC (European Centre for Aerosol Calibration) completed, in February 2023, the annual 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.

Thirty-seven laboratories, with forty-one analyzers in total, 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, thirty-one are responsible for the aerosol chemical speciation at the EMEP/ACTRIS facilities located in their countries and /or National Reference Laboratories (namely in Finland, Norway, Sweden, Denmark, United Kingdom, The Netherlands, Belgium, Czech Republic, Poland, Hungary, Germany, Austria, Spain, France, Switzerland, Italy, Cyprus, Greece, plus the EC JRC). The University of California Air Quality Research Center, the Air Quality Agency of Paris, the LLC "Latvian Environment, Geology and Meteorology Centre", the Estonian Environmental Research Centre, Sunset Laboratory BV and Aerosol d.o.o. also participated.

Measurement method performance: for TC determination, repeatability and reproducibility relative standard deviations ranged from **2%** to **13%** and from **7%** to **25%** (as one relative standard deviation), respectively. For the determination of the EC/TC ratio, repeatability and reproducibility relative standard deviations ranged from **3%** to **15%** and from **8%** to **42%** (as one relative standard deviation), respectively.

Based on previous inter-laboratory comparisons and the present one, 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.

For TC filter loadings, twenty-two outliers –mainly from four participants– and twelve stragglers were identified; 77% of all entries were within 10% of the assigned TC concentration value.

Regarding EC/TC ratios, eight outliers –of which five from a single participant (that one using the QUARTZ thermal protocol) – and sixteen stragglers were identified. 55% of all entries were within 10% of the assigned value and 82% were within the 25% of the assigned EC/TC 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 documenting 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 Centre for Aerosol Calibration* under the European project ACTRIS-Implementation has organized in February 2023 an inter-laboratory comparison exercise (ILCE) (OCEC-2023-1). Thirty-seven laboratories, with forty-one analyzers in total, 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, thirty-one are responsible for the aerosol chemical speciation at the EMEP/ACTRIS facilities located in their countries and /or National Reference Laboratories (namely in Finland, Norway, Sweden, Denmark, United Kingdom, The Netherlands, Belgium, Czech Republic, Poland, Hungary, Germany, Austria, Spain, France, Switzerland Italy, Cyprus, Greece, plus the EC JRC). The University of California Air Quality Research Center, the Air Quality Agency of Paris, the LLC "Latvian Environment, the Geology and Meteorology Centre", the Estonian Environmental Research Centre, Sunset Laboratory BV and Aerosol d.o.o. 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, Tissuquartz 2500 QAT UP) 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 (IPRA, IPRB, ..., IPRH) 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. Ten 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 5% for TC, OC, and EC. If sampling occurred under repeatable conditions, it can be assumed that the test filter samples had similar homogeneities.

1.2 Participants

All applications were accepted. The list of participants is reported in Table 1. For brevity, the number assigned to each participant/analyzer will be used in the remainder of the document.

Table 1: List of participants in the inter-laboratory comparison 2023-1, and contact persons

Code	Participant	Acronym	Contact
1	Stockholm University	SU-ACES	radovan.krejci@aces.su.se
2	University of California, Davis	UCD_AQRC	nmhyslop@ucdavis.edu
3	Institute of Environmental Engineering Polish Academy of Sciences	IPIS PAN	barbara.mathews@ipis.zabrze.pl
4	Institute of Environmental Engineering Polish Academy of Sciences	IPIS PAN	barbara.mathews@ipis.zabrze.pl
5	EMPA	EMPA	christoph.hueglin@empa.ch
6	Hungarian Meteorological Service (HMS), Air Quality Reference Centre	HMS	machon.a@met.hu
7	Lund University, Department of Physics	ULUND	Adam.kristensson@nuclear.lu.se
8	IDAEA-CSIC	IDAEA-CSIC	angeliki.karanasiou@idaea.csic.es
9	IDAEA-CSIC	IDAEA-CSIC	angeliki.karanasiou@idaea.csic.es
10	Aarhus University, Section of Atmospheric Environment, Department of Environmental Science, DCE - Danish Centre for Environment and Energy	AU	mabp@envs.au.dk
11	Finnish Meteorological Institute (FMI)	FMI	meri.ruppel@fmi.fi
12	Finnish Meteorological Institute	FMI	Minna.aurela@fmi.fi
13	ISSeP	ISSeP	p.fays@issep.be
14	LAERO	LAERO	veronique.pont@aero.obs-mip.fr
15	State Limited Liability Company "Latvian Environment, Geology and Meteorology Centre"	SLLC	maiija.matroze@lvgmc.lv
16	Finnish Meteorological Institute	FMI	Minna.aurela@fmi.fi
17	TU-Wien	TU-Wien	anneliese.kasper-giebl@tuwien.ac.at
18	NILU-Norwegian Institute for Air Research	NILU	Key@nilu.no
19	Czech Hydrometeorological Institute	CHMI	Adela.holubova@chmi.cz
20	Leibniz Institute of Tropospheric Research	TROPOS	poulain@tropos.de
21	University of Vienna	UNIVIE	bernadett.weinzierl@univie.ac.at
22	INERIS	INERIS	Arnaud.papin@ineris.fr
23	NRW State Agency for Nature, Environment and Consumer Protection	LANUV	jutta.geiger@lanuv.nrw.de
24	Global Change Research Institute AS CR v. v. i.	CZECHGLOBE	mbengue.s@czechglobe.cz
25	LSCE	LSCE	nicolas.bonnaire@lsce.ipsl.fr
26	Sunset Laboratory BV	SUNLAB	luis@sunlab.com
27	UBA DE; Umweltbundesamt (German Environment Agency)	UBA	Bryan.hellack@uba.de
28	GGD Amsterdam	GGD	ppanteliadis@ggd.amsterdam.nl

29	Instituto de Salud Carlos III	ISCI	jaime.meseguer@isciii.es; sgarcia@isciii.es
30	National Physical Laboratory (NPL)	NPL	elizabeth.mcghee@npl.co.uk
31	European Commission - Joint Research Centre	JRC	Fabrizia.cavalli@ec.europa.eu
32	UNI Grenoble	IGE	jaffrezo@univ-grenoble-alpes.fr
33	ARPA Umbria	ARPA	m.galletti@arpa.umbria.it
34	EERC	KLAB	arkadi.ebber@klab.ee
35	University of Crete, Chemistry Department	ECPL_UOC	nmihalo@noa.gr; mihalo@uoc.gr
36	Chief Inspectorate of Environmental Protection, Central Research Laboratory	GIOS	i.kaluzinska@gios.gov.pl
37	Aerosol d.o.o.	Aerosol d.o.o.	martin.rigler@aerosol.eu
38	National Centre for Scientific Research "Demokritos"	ENRAC	Idiapoulis@ipta.demokritos.gr
39	National Centre for Scientific Research "Demokritos"	ENRAC	Idiapoulis@ipta.demokritos.gr
40	AIRPARIF	AIRPARIF	chadia.kebbi@airparif.fr
41	Slovenian Environment Agency	SEA	judita.burger@gov.si

1.3 Sample shipment and reporting of results

Test samples were shipped to all participants (except the "local" participant, 31) on 7th February 2023 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 shipment to analysis.

Participants reported by the deadline of 31st March 2023: i) TC, OC and EC concentrations, in $\mu\text{g C cm}^{-2}$ units with three decimal digits, from three replicates of the eight test ambient PM_{2.5} samples and ii) 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 four cases where temperature exceeded 25°C for less than 6 hours. Three USB temperature-data loggers (from participants 16, 25 and 41) failed recording.

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_{2.5} samples deposited on filters (EN16909:2017). In this exercise, all participants, except participant 29, applied it.

All participants operated a Sunset carbon analyser, except participants 7, 11 and 39 operating a DRI instrument. Participants 16, 24 and 38 used the semi-continuous Sunset carbon analyser 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 $\mu\text{g cm}^{-2}$) and *EC/TC ratios* reported by each participant 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 2.4 to 13.9 $\mu\text{g cm}^{-2}$, corresponding to atmospheric concentrations ranging from ca. 0.5 to 2.9 $\mu\text{g m}^{-3}$ collected for 24h at a face velocity of 54 cm s^{-1} . EC/TC ranged on average from 0.08 to 0.25.

All submitted results for TC, EC, OC (in $\mu\text{g cm}^{-2}$) and EC/TC ratios 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 and its robust standard deviation (see Par 2.2).

In addition, based on the results from the present inter-laboratory comparison and for the purpose of documenting TC, OC and EC air mass concentrations reported to 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).

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 35 (two replicates for IPRA sample) and 38 (two replicates for IPRB sample). However, Cochran's critical values for three replicates were used for all test samples, i.e. 0.188 (outlier) and 0.155 (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 forty-one participants, the critical values for Grubb's test are 3.394 and 0.593 -outliers for G_1 and G_2 , respectively- and 3.036 and 0.651 - 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 11/IPRA, 24/IPRA, 11/IPRB; 24/IPRC; 14/IPRD, 24/IPRD, 19/IPRG, 24/IPRG, 24/IPRH, 38/IPRH (participant/sample) and 36/IPRB; 11/IPRE and 7/IPRF as stragglers (participant/sample).

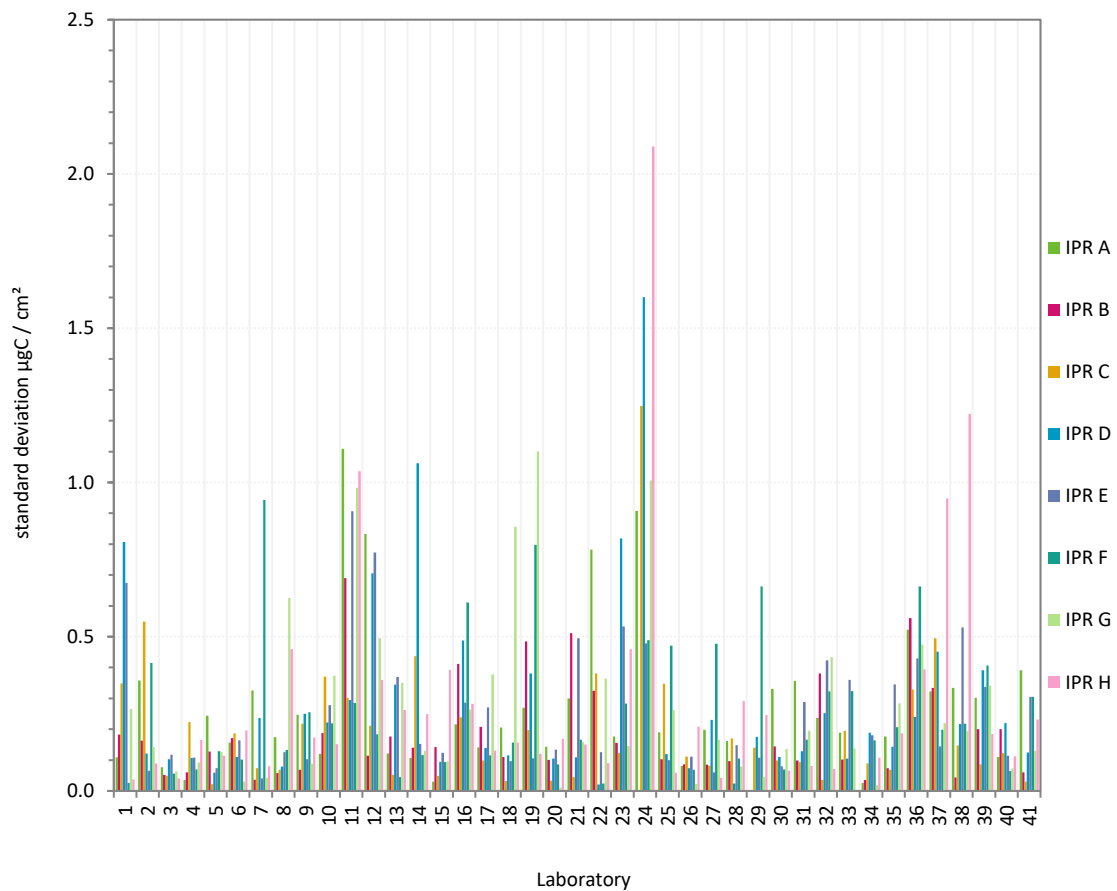


Figure 1. Standard deviation on the three replicates reported for each test filters, grouped by participant.

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 24/IPRA; 24/IPRC; 24/IPRD; 24/IPRF; 24/IPRG and 24//IPRH (participant/sample), and 37/IPRB as straggler.

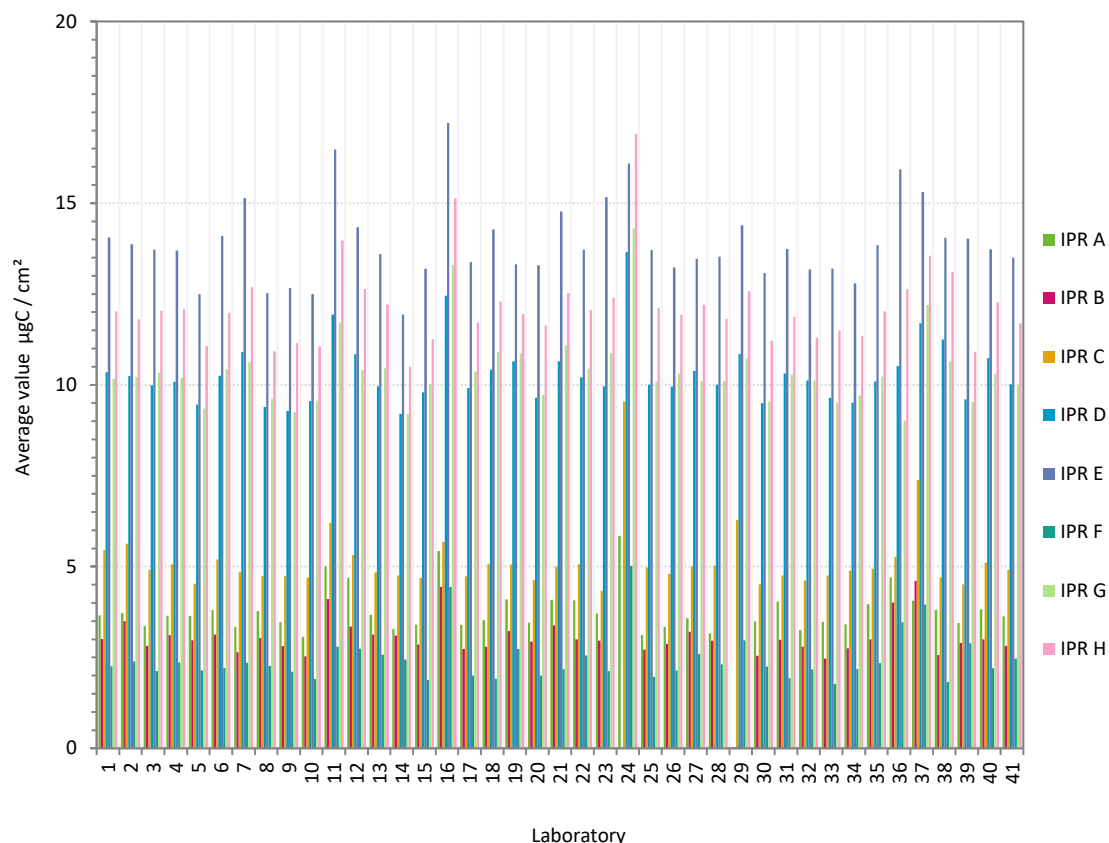


Figure 2. TC average values from three replicates reported by participants for each test sample, grouped by participant.

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 24) 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	<i>sr</i>		<i>sR</i>	
	$\mu\text{gC} / \text{cm}^2$	$\mu\text{gC} / \text{cm}^2$	%	$\mu\text{gC} / \text{cm}^2$	%
IPR A	3.699	0.297	8.0	0.53	14.3
IPR B	3.048	0.222	7.3	0.49	16.1
IPR C	5.041	0.222	4.4	0.59	11.7
IPR D	10.259	0.299	2.9	0.74	7.2
IPR E	13.907	0.331	2.4	1.15	8.3
IPR F	2.389	0.316	13.2	0.61	25.5
IPR G	10.288	0.362	3.5	0.86	8.3
IPR H	12.002	0.307	2.6	0.90	7.5

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).

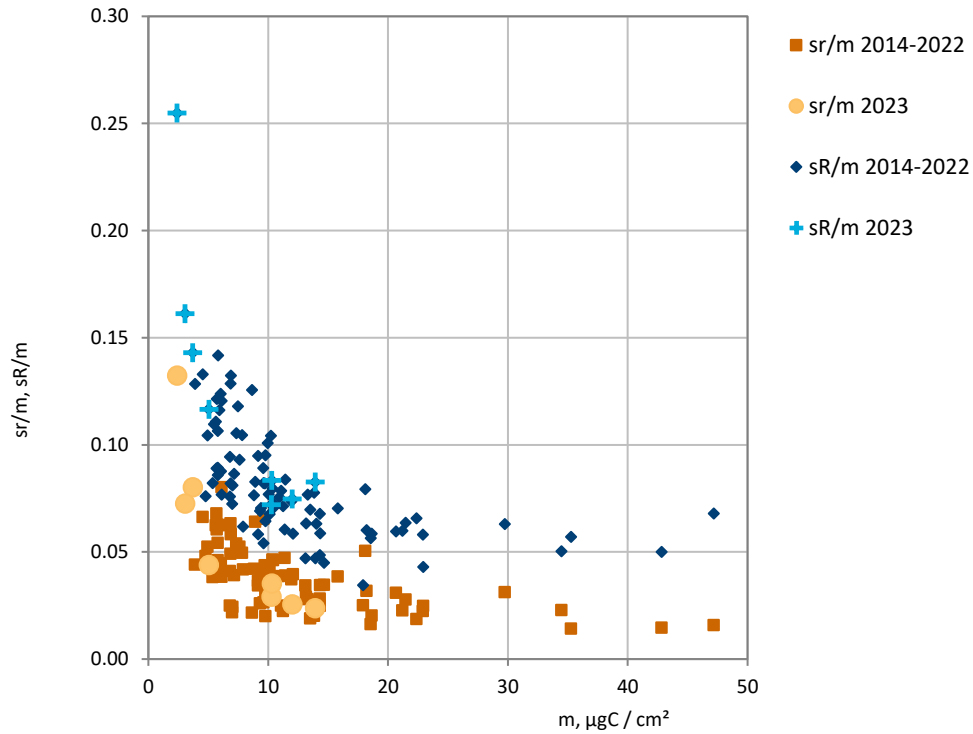


Figure 3. Repeatability and reproducibility relative standard deviation for the EUSAAR_2 protocol for TC measurement obtained during the previous inter-laboratory comparisons and the present one.

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 participant.

Cochran's test identifies entries 7/IPRA; 12/IPRA; 1/IPRD; 24/IPRD, 33/IPRF, 12/IPRG; and 12/IPRH as outliers and 17/IPRE and 19/IPRG as stragglers (participant/sample).

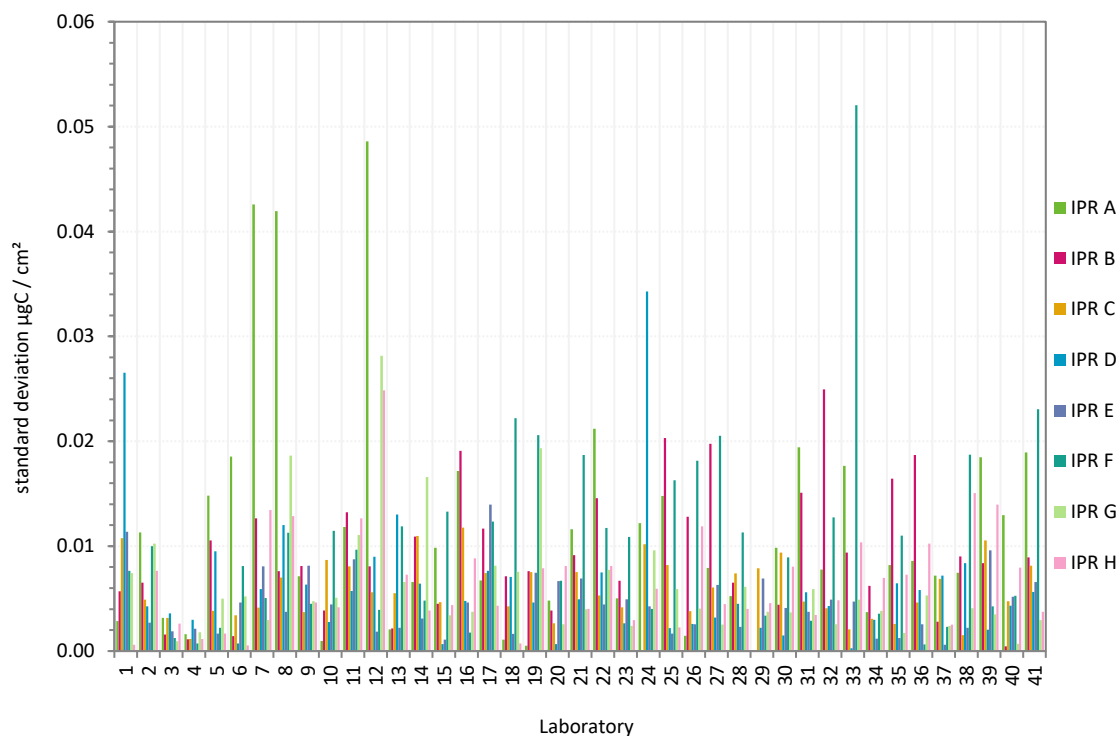


Figure 4. Standard deviation on the EC/TC ratio replicates reported for each test filters, grouped by participant.

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 entries 29/IPRD; 29/IPRE; 11/IPRG as outliers and entry 29/IPRG as stragglers. Participant 29 is the only participant not applying the EUSAAR thermal protocol but the QUARTZ thermal protocol.

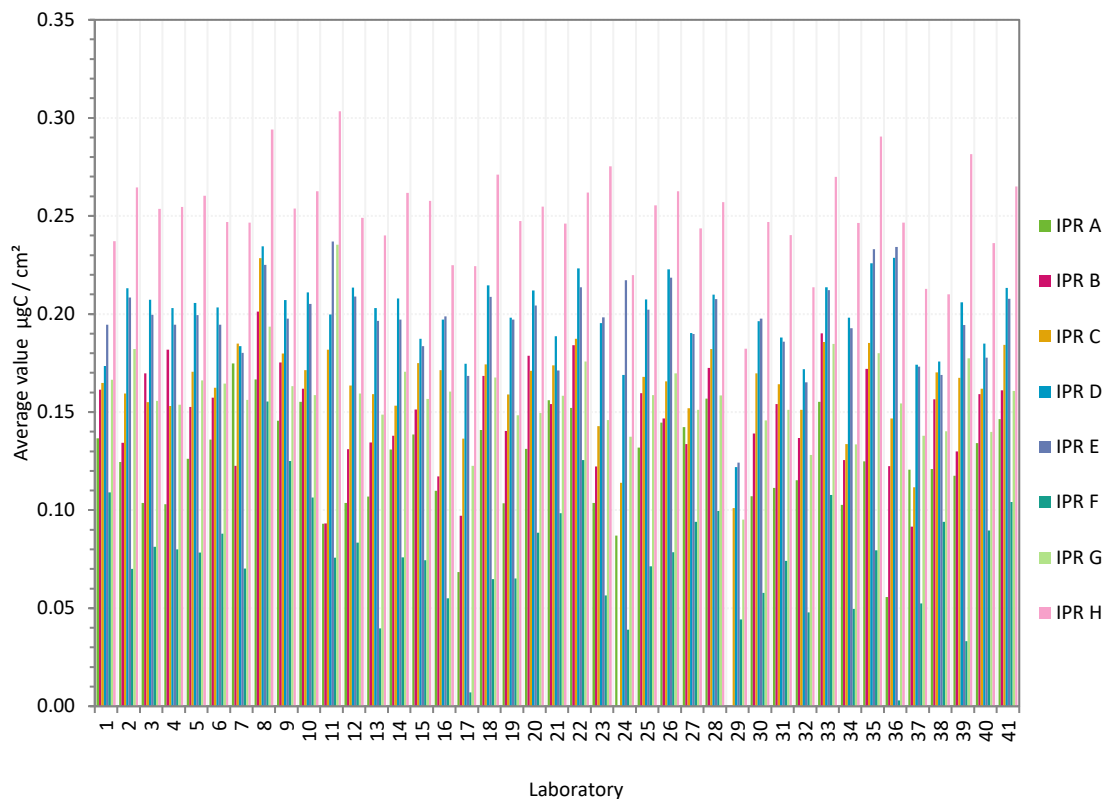


Figure 5. EC/TC average ratios from the replicates reported by participants for each test sample, grouped by participant.

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	
	M, ratio		%		%
IPR A	0.124	0.013	10.4	0.027	21.8
IPR B	0.148	0.011	7.4	0.028	18.6
IPR C	0.163	0.007	4.0	0.023	14.2
IPR D	0.202	0.006	2.9	0.016	8.0
IPR E	0.199	0.005	2.7	0.018	9.1
IPR F	0.075	0.011	15.3	0.032	42.2
IPR G	0.156	0.006	4.1	0.019	12.5
IPR H	0.251	0.007	2.9	0.024	9.8

Combining the repeatability and reproducibility relative standard deviation for the EUSAAR_2 protocol obtained during the previous four ILCs 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.

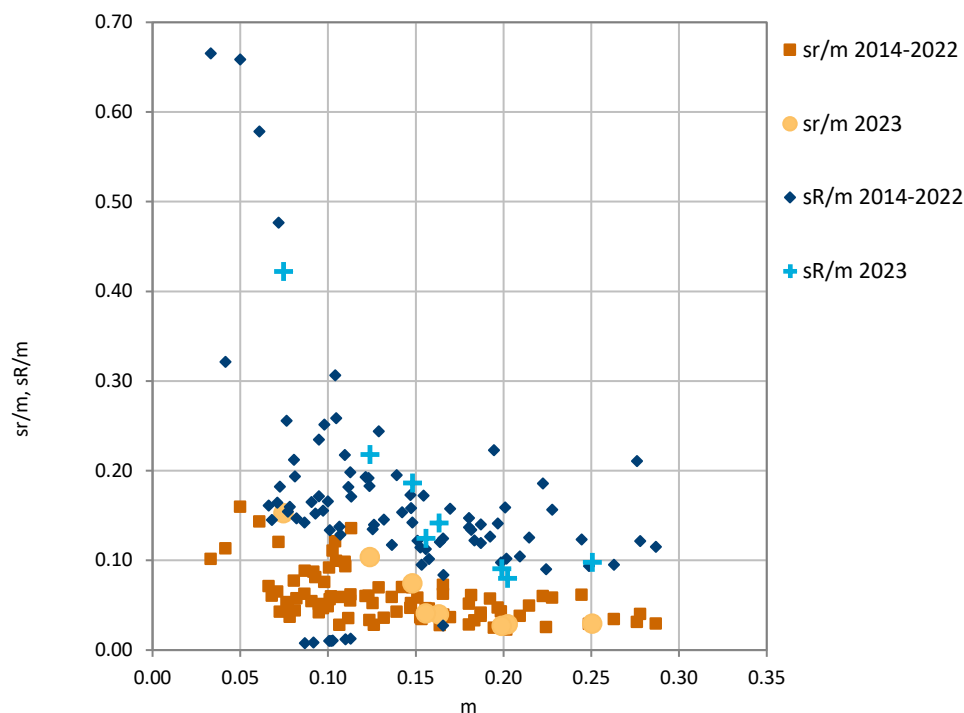


Figure 6. Repeatability and reproducibility relative standard deviation for the EUSAAR_2 protocol for EC/TC measurement obtained during the previous inter-laboratory comparisons and the present one.

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 Tables 4 and 5, 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	$\mu\text{g}/\text{cm}^2$	3.68	2.97	4.96	10.19	13.80	2.33	10.23	11.98
standard deviation	$\mu\text{g}/\text{cm}^2$	0.39	0.29	0.35	0.63	0.95	0.39	0.65	0.74
	%	10.7	9.6	7.0	6.2	6.9	16.8	6.3	6.2
2 σ^*	%	21.5	19.2	14.0	12.4	13.8	33.6	12.6	12.4
3 σ^*	%	32.2	28.8	21.0	18.7	20.7	50.4	18.9	18.7

Figure 7 shows z -scores calculated from σ^* . Twenty-two outliers, among which 16 came from 3 participants, are identified: 11/IPRA; 16/IPRA; 24/IPRA; 11/IPRB; 16/IPRB; 36/IPRB; 37/IPRB; 11/IPRC; 24/IPRC; 29/IPRC; 37/IPRC; 16/IPRD; 24/IPRD; 16/IPRE; 16/IPRF; 24/IPRF; 37/IPRF; 16/IPRG; 24/IPRG; 37/IPRG; 16/IPRH; 24/IPRH (participant/sample); in addition, twelve stragglers are identified: 12/IPRA; 36/IPRA; 16/IPRC; 11/IPRD; 37/IPRD; 11/IPRE; 24/IPRE; 36/IPRE; 36/IPRF; 11/IPRG; 11/IPRH and 37/IPRH (participant/sample).

For each sample, twenty-six to twenty-nine out of forty-one participants show deviations from the assigned values within $\pm 1 \sigma^*$ as listed in Table 4 (i.e. within 1 z -score). 77% of all entries are within 10% from the assigned value.

Several participants show the systematic tendency (i.e. for all test samples and larger than $\pm 5\%$, on average) of overestimating –i.e. participants 11, 12, 16, 21, 24, 29, 36, and 37– or

underestimating –i.e. participants 9, 10, 15, 20, 30, 32, 33, and 34- 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.

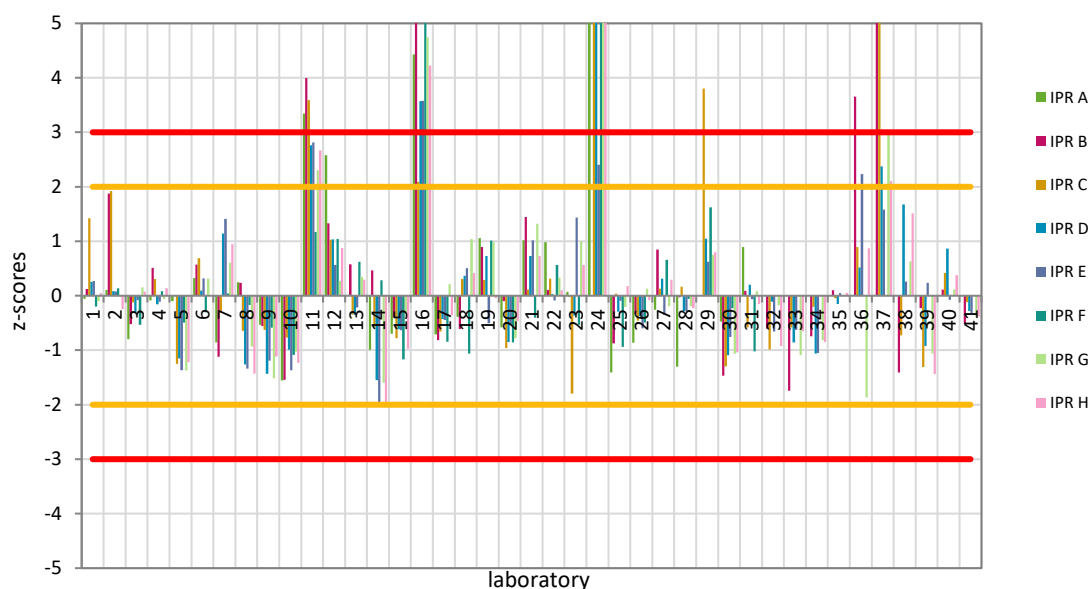


Figure 7. z-scores for TC calculated using σ^* from data obtained in a round of a proficiency testing scheme. The scale is set from -5 to +5.

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 A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
assigned value	ratio	0.13	0.15	0.16	0.20	0.20	0.08	0.16	0.25
standard deviation	ratio	0.03	0.03	0.02	0.02	0.02	0.03	0.02	0.02
	%	20%	17%	10%	9%	9%	36%	11%	8%
$2\sigma^*$	%	40%	34%	21%	19%	18%	73%	21%	16%
$3\sigma^*$	%	60%	51%	31%	28%	28%	109%	32%	23%

Eight outliers – 8/IPRC; 29/IPRC; 37/IPRC; 29/IPRD; 29/IPRE; 11/IPRG; 29/IPRG and 29/IPRH (participant/sample)- and sixteen stragglers – 17/IPRA; 36/IPRA; 11/IPRB; 17/IPRB, 37/IPRB;

24/IPRC; 11/IPRE; 8/IPRF; 17/IPRF; 36/IPRF; 8/IPRG; 17/IPRG; 8/IPRH; 11/IPRH, 35/IPRH and 38/IPRH (participant /sample)– are identified. For each sample, twenty-six to twenty-nine out of forty-one participants 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 88% are within 25% of the assigned value.

Several participants show the systematic tendency (i.e. for all test samples and larger than $\pm 5\%$, on average) of overestimating – i.e. participants 8, 10, 22, 28, 33 and 41 – or underestimating – i.e. participants 17, 19, 29, 32, 34 and 37– 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.

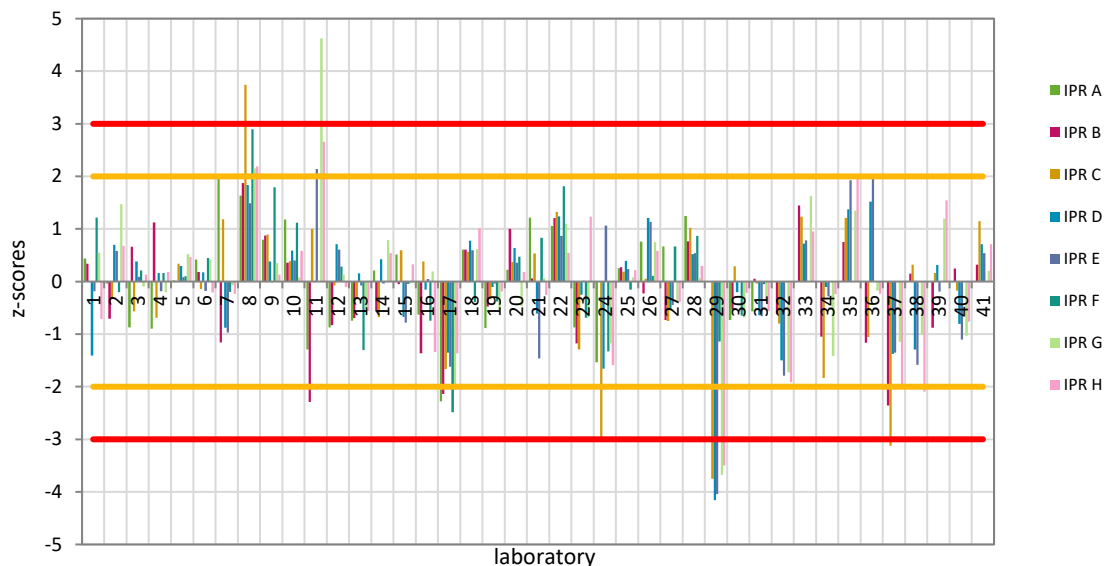


Figure 8. z-scores for EC/TC ratio calculated using σ^* from data obtained in a round of a proficiency testing scheme.

Conclusions

This inter-laboratory comparison involved 37 laboratories, with 41 analyzers in total all applying thermal-optical analyses and the EUSAAR_2 protocol, except one (participant #29).

The measurement method **repeatability and reproducibility for TC** ranged from **2% to 13%** and from **7% to 25%** (as one relative standard deviation), respectively.

For the **EC/TC ratio, repeatability and reproducibility** ranged from **3% to 15%** and from **8% to 42%**, 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. $<10 \mu\text{gC} / \text{cm}^2$. For EC/TC determination, the method precision (*sR* and less evident for *sr*) can become 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, twenty-two outliers (among which 16 came from 3 participants) and twelve stragglers were identified; 77% of all entries were within 10% from the assigned TC concentration value.

Several participants show the systematic tendency (i.e. for all test samples and larger than + or - 5% on average) of overestimating (eight participants) or underestimating (eight participants) 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 (among which half came from the participant not using the European standard thermal protocol) and sixteen stragglers were identified. 55% of all entries were within 10% of the assigned value and 88% were within the 25% of the assigned value. Several participants show the systematic tendency (i.e. for all test samples and larger than + or - 5%, on average) of overestimating (six participants) or underestimating (six participants) the assigned EC/TC ratio. Participant 29, using the QUARTZ thermal protocol showed EC/TC ratios, on average, 37% lower than the assigned values.

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, based on the results from the present inter-laboratory comparison and for the purpose of documenting 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

"-" corresponds to a "no entry".

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

Laboratory	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	3.550	3.212	5.051	9.857	13.628	2.283	9.976	11.978
	3.649	2.875	5.660	11.279	13.710	2.256	10.468	12.024
	3.768	2.921	5.651	9.906	14.835	2.230	10.049	12.052
2	3.743	3.655	5.190	10.226	13.849	2.183	10.347	11.743
	4.067	3.523	5.444	10.125	13.948	2.864	10.234	11.756
	3.352	3.330	6.241	10.366	13.824	2.112	10.063	11.903
3	3.302	2.876	4.864	9.921	13.648	2.065	10.257	12.019
	3.450	2.776	4.959	9.935	13.857	2.129	10.375	12.089
	3.339	2.802	4.931	10.105	13.658	2.177	10.355	12.018
4	3.610	3.164	5.025	10.208	13.640	2.388	10.097	12.264
	3.646	3.047	4.866	10.012	13.816	2.288	10.184	11.938
	3.682	3.128	5.307	10.037	13.619	2.421	10.282	12.054
5	3.379	2.870	4.553	9.505	12.411	2.209	9.419	11.203
	3.861	3.112	4.512	9.392	12.546	2.222	9.197	10.992
	3.682	2.919	4.519	9.480	12.531	1.994	9.413	11.024
6	3.742	3.322	5.335	10.306	14.195	2.273	10.417	11.764
	3.695	3.080	4.987	10.317	14.197	2.096	10.466	12.093
	3.987	2.991	5.275	10.121	13.911	2.272	10.413	12.113
7	3.119	2.660	4.786	11.180	15.126	3.435	10.653	12.624
	3.715	2.606	4.931	10.750	15.187	1.900	10.571	12.665
	3.187	2.675	4.833	10.793	15.111	1.717	10.635	12.779
8	3.579	2.968	4.783	9.425	12.386	2.421	9.345	10.416
	3.847	3.079	4.769	9.295	12.635	2.196	10.345	11.320
	3.905	3.055	4.658	9.438	12.544	2.187	9.193	11.016
9	3.262	2.757	4.985	9.553	12.569	2.365	9.330	11.156
	3.404	2.782	4.564	9.225	12.642	2.096	9.266	11.322
	3.743	2.887	4.680	9.061	12.772	1.854	9.156	10.975
10	3.001	2.418	4.646	9.301	12.186	2.157	9.485	11.221
	2.988	2.745	4.350	9.685	12.726	1.750	9.975	11.058
	3.203	2.419	5.086	9.687	12.570	1.814	9.243	10.917
11	4.320	3.320	5.870	12.150	16.250	3.070	11.120	13.680
	6.280	4.610	6.460	12.060	17.480	2.500	11.180	13.110
	4.400	4.390	6.280	11.600	15.710	2.810	12.850	15.120
12	4.111	3.478	5.544	11.651	13.546	2.862	10.808	12.338
	5.652	3.293	5.124	10.522	15.090	2.530	9.853	12.536
	4.335	3.268	5.285	10.353	14.370	2.832	10.554	13.036
13	3.678	2.967	4.785	9.587	13.843	2.628	10.158	12.336
	3.558	3.110	4.889	10.264	13.171	2.565	10.359	12.376
	3.800	3.318	4.845	10.039	13.771	2.542	10.841	11.902
14	3.409	3.261	4.823	8.627	12.102	2.510	9.056	10.309
	3.209	3.003	4.293	8.560	11.887	2.515	9.310	10.783
	3.242	3.035	5.160	10.432	11.808	2.311	9.228	10.416
15	3.422	2.780	4.725	9.687	13.090	1.978	10.018	11.284
	3.369	3.018	4.710	9.857	13.158	1.855	10.133	11.638
	3.420	2.764	4.634	9.843	13.329	1.795	9.943	10.854
16	5.636	4.591	5.732	11.894	17.357	4.105	13.153	15.308
	5.204	3.979	5.896	12.665	16.875	4.070	13.135	14.805
	5.444	4.762	5.426	12.796	17.385	5.145	13.600	15.276

17	3.377	2.665	4.724	10.041	13.676	2.039	10.785	11.836
	3.550	2.968	4.640	9.939	13.149	1.872	10.264	11.577
	3.271	2.570	4.836	9.766	13.303	2.094	10.051	11.733
18	3.310	2.720	5.090	10.350	14.240	1.740	10.460	12.130
	3.550	2.740	5.080	10.350	14.210	2.040	11.890	12.320
	3.720	2.920	5.030	10.550	14.390	1.970	10.360	12.440
19	4.386	2.782	4.977	10.960	13.324	2.705	9.641	12.072
	3.851	3.740	4.920	10.225	13.417	3.542	11.772	11.941
	4.053	3.142	5.286	10.766	13.205	1.947	11.186	11.831
20	3.500	2.889	4.654	9.731	13.393	2.023	9.715	11.487
	3.562	3.054	4.590	9.531	13.138	1.901	9.732	11.605
	3.289	2.872	4.637	9.684	13.338	2.068	9.735	11.820
21	3.987	2.923	5.034	10.721	14.212	2.297	11.219	12.383
	4.417	3.933	4.949	10.702	14.936	1.985	10.911	12.682
	3.840	3.285	5.014	10.524	15.158	2.241	11.126	12.510
22	3.570	2.935	4.857	10.186	13.659	2.558	10.818	12.013
	3.664	2.709	4.841	10.205	13.863	2.577	10.090	11.996
	4.970	3.350	5.508	10.228	13.633	2.529	10.420	12.160
23	3.864	3.141	4.456	9.541	15.013	2.122	10.713	12.409
	3.516	2.892	4.347	9.432	15.760	1.841	10.995	11.942
	3.742	2.856	4.209	10.901	14.726	2.408	10.916	12.862
24	5.495	-	8.756	13.546	16.369	4.860	13.196	19.140
	5.154	-	10.977	15.307	15.535	4.640	14.547	16.561
	6.868	-	8.880	12.112	16.356	5.575	15.164	15.005
25	3.304	2.808	5.369	10.013	13.822	2.507	9.795	12.135
	2.925	2.607	4.837	10.117	13.628	1.642	10.233	12.048
	3.143	2.741	4.715	9.878	13.686	1.750	10.264	12.161
26	3.432	2.773	4.901	9.996	13.336	2.163	10.288	12.135
	3.289	2.938	4.823	9.864	13.115	2.065	10.332	11.919
	3.294	2.901	4.681	9.988	13.234	2.196	10.322	11.717
27	3.715	3.195	4.968	10.440	13.445	2.263	10.242	12.159
	3.351	3.131	4.949	10.581	13.533	2.376	9.921	12.211
	3.670	3.300	5.101	10.130	13.418	3.140	10.152	12.243
28	3.281	2.861	5.184	9.986	13.404	2.431	10.196	11.512
	3.234	3.055	5.027	10.006	13.482	2.236	10.064	12.095
	2.980	2.960	4.844	10.033	13.691	2.267	10.056	11.831
29	-	-	6.410	10.720	14.270	3.710	10.760	12.520
	-	-	6.290	10.780	14.440	2.770	10.670	12.370
	-	-	6.130	11.050	14.470	2.430	10.720	12.850
30	3.369	2.388	4.559	9.619	13.031	2.249	9.557	11.265
	3.867	2.589	4.397	9.444	13.031	2.173	9.403	11.221
	3.241	2.669	4.577	9.417	13.170	2.312	9.675	11.137
31	3.728	3.062	4.652	10.442	13.548	2.104	10.068	11.806
	4.425	2.880	4.802	10.185	14.072	1.922	10.336	11.848
	3.946	3.035	4.825	10.317	13.599	1.773	10.447	11.963
32	3.502	2.627	4.602	9.892	13.661	1.883	9.831	11.265
	3.234	3.231	4.658	10.070	12.968	2.520	10.616	11.250
	3.029	2.527	4.593	10.390	12.894	2.113	9.904	11.381
33	3.270	2.360	4.960	9.540	13.100	1.910	9.420	11.500
	3.550	2.560	4.570	9.640	13.600	2.000	9.470	11.500
	3.630	2.490	4.750	9.750	12.900	1.400	9.680	11.500
34	3.380	2.790	4.790	9.730	12.910	2.050	9.724	11.410
	3.430	2.720	4.960	9.430	12.587	2.110	9.692	11.223
	3.420	2.752	4.920	9.380	12.890	2.360	9.692	11.410
35	4.088	3.044	4.925	9.965	13.446	2.252	10.277	11.968
	3.838	2.912	5.021	10.247	14.009	2.195	10.476	11.875
	-	3.035	4.888	10.060	14.074	2.578	9.916	12.234

36	5.277	4.433	5.150	10.520	16.270	3.930	9.350	12.700
	4.250	3.373	5.020	10.270	16.070	3.770	9.240	12.990
	4.590	4.220	5.643	10.750	15.447	2.710	8.480	12.210
37	4.386	4.962	6.839	11.471	15.188	3.786	11.968	14.638
	4.070	4.299	7.513	12.212	15.468	3.916	12.406	13.110
	3.740	4.557	7.804	11.395	15.264	4.176	12.223	12.901
38	3.736	2.597	4.705	11.001	14.643	1.913	10.835	14.517
	3.519	2.535	4.857	11.399	13.871	1.978	10.448	12.455
	4.174	-	4.562	11.349	13.627	1.573	10.623	12.350
39	3.784	2.739	4.553	9.970	14.410	2.638	9.542	11.124
	3.205	2.842	4.560	9.644	13.812	2.673	9.202	10.794
	3.347	3.126	4.407	9.192	13.841	3.360	9.885	10.815
40	3.785	2.958	5.026	10.962	13.614	2.271	10.356	12.310
	3.733	2.822	5.045	10.524	13.728	2.204	10.223	12.349
	3.945	3.216	5.247	10.713	13.843	2.142	10.341	12.139
41	3.950	2.760	4.940	9.920	13.700	2.220	9.870	11.900
	3.310	2.880	4.900	10.100	13.300	2.710	10.100	11.500
	3.240	2.820	4.960	9.860	13.100	2.150	9.880	11.900

Table 2: Elemental carbon / total carbon (ratio) calculated from results reported by participants

Laboratory	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	0.136	0.155	0.177	0.189	0.200	0.116	0.175	0.237
	0.139	0.163	0.159	0.143	0.202	0.101	0.164	0.237
	0.134	0.166	0.158	0.189	0.181	0.111	0.161	0.236
2	0.133	0.127	0.156	0.211	0.209	0.074	0.193	0.272
	0.112	0.139	0.165	0.211	0.206	0.059	0.179	0.257
	0.129	0.137	0.158	0.218	0.211	0.077	0.173	0.264
3	0.100	0.172	0.152	0.209	0.201	0.082	0.157	0.251
	0.106	0.169	0.158	0.203	0.197	0.082	0.156	0.254
	0.105	0.169	0.155	0.209	0.200	0.080	0.155	0.256
4	0.103	0.183	0.152	0.203	0.197	0.080	0.155	0.255
	0.105	0.181	0.153	0.206	0.193	0.081	0.154	0.253
	0.102	0.182	0.154	0.200	0.193	0.079	0.152	0.256
5	0.133	0.153	0.175	0.195	0.199	0.080	0.160	0.262
	0.109	0.142	0.169	0.210	0.198	0.076	0.170	0.261
	0.136	0.163	0.168	0.212	0.201	0.080	0.168	0.258
6	0.155	0.158	0.159	0.204	0.197	0.080	0.159	0.246
	0.135	0.158	0.166	0.204	0.197	0.096	0.165	0.247
	0.118	0.156	0.162	0.202	0.189	0.088	0.169	0.247
7	0.170	0.124	0.186	0.177	0.181	0.076	0.158	0.232
	0.220	0.134	0.189	0.189	0.172	0.069	0.157	0.258
	0.135	0.109	0.180	0.184	0.188	0.066	0.153	0.249
8	0.118	0.202	0.236	0.221	0.229	0.146	0.196	0.308
	0.192	0.208	0.224	0.242	0.222	0.153	0.174	0.293
	0.190	0.193	0.225	0.241	0.224	0.168	0.211	0.282
9	0.153	0.170	0.176	0.201	0.194	0.124	0.164	0.251
	0.144	0.171	0.180	0.207	0.207	0.130	0.158	0.251
	0.139	0.185	0.184	0.214	0.192	0.121	0.168	0.259
10	0.156	0.163	0.172	0.209	0.202	0.100	0.156	0.258
	0.155	0.158	0.180	0.214	0.210	0.120	0.155	0.264
	0.155	0.165	0.162	0.210	0.203	0.099	0.164	0.266
11	0.102	0.108	0.191	0.198	0.232	0.065	0.242	0.290
	0.080	0.085	0.180	0.195	0.232	0.084	0.242	0.304
	0.098	0.087	0.175	0.206	0.247	0.078	0.223	0.315
12	0.127	0.122	0.158	0.204	0.211	0.085	0.158	0.224
	0.048	0.134	0.169	0.216	0.207	0.079	0.188	0.273
	0.136	0.137	0.163	0.221	0.209	0.087	0.132	0.251
13	0.104	0.136	0.165	0.218	0.194	0.034	0.155	0.235
	0.108	0.132	0.155	0.193	0.197	0.032	0.149	0.248
	0.108	0.136	0.157	0.198	0.199	0.053	0.142	0.236
14	0.126	0.125	0.144	0.206	0.194	0.072	0.190	0.258
	0.138	0.146	0.165	0.203	0.198	0.074	0.161	0.266
	0.129	0.142	0.150	0.215	0.200	0.081	0.161	0.261
15	0.135	0.156	0.174	0.187	0.185	0.080	0.160	0.253
	0.131	0.147	0.170	0.188	0.183	0.059	0.157	0.262
	0.150	0.151	0.180	0.188	0.183	0.084	0.153	0.258
16	0.111	0.098	0.172	0.197	0.194	0.055	0.165	0.215
	0.126	0.136	0.159	0.202	0.202	0.057	0.158	0.231
	0.092	0.117	0.182	0.192	0.200	0.053	0.159	0.229
17	0.076	0.092	0.132	0.173	0.152	0.000	0.113	0.220
	0.065	0.111	0.145	0.183	0.174	0.021	0.126	0.229
	0.064	0.089	0.133	0.168	0.179	0.000	0.128	0.224

18	0.142	0.169	0.173	0.210	0.207	0.040	0.171	0.271
	0.141	0.175	0.179	0.212	0.210	0.083	0.159	0.270
	0.140	0.161	0.171	0.223	0.208	0.071	0.173	0.272
19	0.103	0.145	0.162	0.193	0.191	0.062	0.171	0.238
	0.104	0.132	0.165	0.202	0.195	0.046	0.136	0.253
	0.103	0.144	0.150	0.199	0.205	0.087	0.138	0.251
20	0.126	0.181	0.172	0.212	0.204	0.094	0.149	0.258
	0.131	0.174	0.168	0.213	0.211	0.090	0.147	0.260
	0.136	0.181	0.173	0.211	0.198	0.081	0.152	0.245
21	0.143	0.165	0.182	0.184	0.179	0.112	0.161	0.243
	0.158	0.147	0.168	0.194	0.166	0.106	0.154	0.251
	0.166	0.150	0.172	0.188	0.169	0.077	0.160	0.244
22	0.169	0.187	0.190	0.215	0.209	0.114	0.168	0.256
	0.159	0.197	0.191	0.227	0.214	0.125	0.184	0.258
	0.128	0.168	0.181	0.228	0.218	0.137	0.176	0.271
23	0.108	0.129	0.143	0.197	0.200	0.068	0.145	0.278
	0.098	0.121	0.139	0.196	0.202	0.054	0.149	0.272
	0.105	0.116	0.147	0.192	0.193	0.047	0.144	0.275
24	0.095	-	0.122	0.164	0.220	0.041	0.148	0.223
	0.093	-	0.103	0.137	0.219	0.041	0.135	0.223
	0.073	-	0.117	0.205	0.212	0.034	0.129	0.213
25	0.119	0.155	0.162	0.206	0.202	0.053	0.162	0.254
	0.148	0.182	0.165	0.210	0.200	0.085	0.152	0.258
	0.129	0.142	0.177	0.206	0.204	0.075	0.162	0.254
26	0.144	0.157	0.168	0.220	0.219	0.061	0.169	0.275
	0.146	0.151	0.168	0.225	0.216	0.097	0.166	0.262
	0.144	0.132	0.161	0.224	0.221	0.078	0.174	0.251
27	0.146	0.142	0.159	0.194	0.197	0.093	0.148	0.249
	0.147	0.148	0.149	0.189	0.185	0.115	0.152	0.240
	0.133	0.111	0.148	0.188	0.187	0.074	0.153	0.242
28	0.152	0.180	0.175	0.205	0.205	0.107	0.156	0.261
	0.163	0.169	0.189	0.212	0.208	0.106	0.165	0.253
	0.156	0.168	0.182	0.212	0.210	0.086	0.154	0.257
29	-	-	0.094	0.124	0.132	0.040	0.097	0.181
	-	-	0.100	0.120	0.123	0.047	0.091	0.188
	-	-	0.109	0.122	0.118	0.045	0.098	0.179
30	0.102	0.144	0.160	0.198	0.199	0.052	0.142	0.244
	0.101	0.138	0.171	0.195	0.201	0.068	0.147	0.241
	0.118	0.136	0.178	0.196	0.193	0.053	0.149	0.256
31	0.129	0.144	0.159	0.190	0.190	0.071	0.158	0.242
	0.091	0.171	0.164	0.182	0.186	0.077	0.148	0.236
	0.114	0.146	0.169	0.192	0.182	0.075	0.148	0.242
32	0.112	0.146	0.147	0.175	0.160	0.063	0.131	0.212
	0.110	0.108	0.151	0.174	0.168	0.041	0.128	0.219
	0.124	0.155	0.155	0.167	0.168	0.040	0.126	0.209
33	0.176	0.188	0.183	0.214	0.217	0.142	0.179	0.273
	0.145	0.200	0.188	0.214	0.207	0.134	0.186	0.258
	0.145	0.182	0.186	0.213	0.212	0.048	0.189	0.278
34	0.107	0.118	0.136	0.201	0.194	0.049	0.138	0.250
	0.099	0.129	0.135	0.196	0.191	0.054	0.132	0.251
	0.102	0.129	0.130	0.197	0.193	0.047	0.131	0.238
35	0.119	0.154	0.188	0.227	0.234	0.080	0.180	0.289
	0.131	0.186	0.183	0.219	0.233	0.090	0.179	0.284
	-	0.177	0.185	0.232	0.232	0.068	0.182	0.298
36	0.060	0.102	0.150	0.235	0.237	0.003	0.158	0.253
	0.061	0.128	0.141	0.228	0.235	0.003	0.148	0.235
	0.046	0.137	0.149	0.223	0.232	0.004	0.157	0.252

37	0.112	0.088	0.119	0.171	0.173	0.054	0.140	0.213
	0.124	0.094	0.106	0.169	0.173	0.053	0.138	0.210
	0.126	0.092	0.109	0.182	0.174	0.050	0.135	0.215
38	0.112	0.150	0.169	0.185	0.168	0.084	0.138	0.193
	0.126	0.163	0.172	0.175	0.171	0.082	0.145	0.221
	0.124	-	0.169	0.168	0.167	0.116	0.137	0.216
39	0.096	0.139	0.168	0.205	0.188	0.033	0.173	0.277
	0.125	0.124	0.157	0.205	0.190	0.037	0.180	0.297
	0.131	0.126	0.178	0.208	0.205	0.029	0.179	0.271
40	0.130	0.159	0.164	0.181	0.173	0.091	0.139	0.233
	0.149	0.159	0.166	0.189	0.183	0.084	0.140	0.230
	0.124	0.159	0.156	0.185	0.177	0.094	0.141	0.245
41	0.135	0.170	0.179	0.219	0.214	0.087	0.159	0.261
	0.157	0.152	0.190	0.208	0.202	0.121	0.162	0.269
	0.173	0.162	0.174	0.216	0.204	0.078	0.165	0.264

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	0.484	0.498	0.895	1.865	2.722	0.264	1.744	2.844
	0.509	0.469	0.901	1.612	2.774	0.227	1.715	2.855
	0.504	0.485	0.893	1.868	2.692	0.247	1.614	2.849
2	0.498	0.464	0.808	2.157	2.895	0.161	2.001	3.196
	0.454	0.489	0.898	2.132	2.867	0.168	1.835	3.019
	0.432	0.458	0.985	2.261	2.915	0.164	1.746	3.148
3	0.330	0.493	0.739	2.075	2.740	0.170	1.605	3.017
	0.364	0.468	0.785	2.018	2.735	0.174	1.616	3.067
	0.352	0.474	0.764	2.117	2.738	0.174	1.602	3.080
4	0.371	0.579	0.765	2.068	2.686	0.191	1.568	3.125
	0.382	0.551	0.743	2.065	2.673	0.185	1.570	3.025
	0.374	0.568	0.819	2.011	2.629	0.192	1.561	3.082
5	0.449	0.438	0.796	1.851	2.473	0.176	1.511	2.931
	0.421	0.442	0.763	1.969	2.482	0.169	1.560	2.866
	0.502	0.476	0.757	2.014	2.521	0.159	1.584	2.849
6	0.581	0.525	0.850	2.098	2.797	0.182	1.655	2.898
	0.498	0.487	0.828	2.102	2.803	0.202	1.731	2.990
	0.471	0.466	0.853	2.049	2.633	0.199	1.761	2.996
7	0.530	0.330	0.889	1.982	2.735	0.260	1.686	2.928
	0.816	0.350	0.930	2.032	2.609	0.131	1.664	3.272
	0.430	0.292	0.872	1.991	2.839	0.113	1.625	3.188
8	0.423	0.601	1.131	2.080	2.840	0.353	1.831	3.203
	0.737	0.641	1.067	2.253	2.807	0.335	1.799	3.317
	0.742	0.590	1.048	2.270	2.807	0.367	1.939	3.105
9	0.500	0.470	0.879	1.920	2.443	0.294	1.530	2.798
	0.491	0.475	0.820	1.908	2.616	0.272	1.465	2.845
	0.521	0.533	0.860	1.936	2.448	0.224	1.534	2.843
10	0.469	0.394	0.800	1.945	2.466	0.216	1.484	2.893
	0.462	0.433	0.781	2.075	2.676	0.209	1.545	2.922
	0.496	0.399	0.825	2.033	2.549	0.180	1.520	2.901
11	0.440	0.360	1.120	2.410	3.770	0.200	2.690	3.970
	0.500	0.390	1.160	2.350	4.050	0.210	2.700	3.990
	0.430	0.380	1.100	2.390	3.880	0.220	2.860	4.770
12	0.521	0.424	0.876	2.371	2.856	0.243	1.703	2.758
	0.270	0.442	0.867	2.270	3.126	0.200	1.857	3.425
	0.591	0.448	0.863	2.288	3.000	0.245	1.396	3.266
13	0.384	0.403	0.791	2.087	2.688	0.088	1.574	2.903
	0.385	0.411	0.757	1.981	2.591	0.082	1.545	3.075
	0.411	0.450	0.761	1.989	2.735	0.136	1.537	2.814
14	0.429	0.409	0.695	1.775	2.345	0.181	1.718	2.661
	0.444	0.438	0.710	1.737	2.354	0.187	1.502	2.866
	0.417	0.432	0.775	2.245	2.359	0.188	1.482	2.721
15	0.461	0.434	0.824	1.808	2.420	0.158	1.601	2.855
	0.442	0.444	0.803	1.850	2.413	0.110	1.594	3.046
	0.512	0.417	0.833	1.849	2.436	0.151	1.522	2.801
16	0.627	0.450	0.989	2.349	3.359	0.228	2.168	3.286
	0.656	0.542	0.937	2.556	3.416	0.230	2.077	3.413
	0.500	0.559	0.990	2.460	3.482	0.273	2.157	3.504
17	0.257	0.246	0.622	1.739	2.085	0.000	1.222	2.605
	0.231	0.328	0.673	1.818	2.288	0.040	1.297	2.648
	0.209	0.228	0.642	1.639	2.376	0.000	1.289	2.632

18	0.470	0.460	0.880	2.170	2.950	0.070	1.790	3.290
	0.500	0.480	0.910	2.190	2.990	0.170	1.890	3.330
	0.520	0.470	0.860	2.350	3.000	0.140	1.790	3.380
19	0.452	0.404	0.805	2.118	2.544	0.169	1.644	2.877
	0.401	0.492	0.811	2.070	2.617	0.163	1.601	3.016
	0.418	0.453	0.795	2.138	2.713	0.169	1.547	2.972
20	0.442	0.523	0.799	2.065	2.726	0.191	1.451	2.965
	0.468	0.532	0.772	2.026	2.777	0.171	1.430	3.023
	0.447	0.519	0.804	2.046	2.642	0.168	1.480	2.901
21	0.572	0.481	0.917	1.971	2.542	0.258	1.808	3.014
	0.699	0.580	0.829	2.073	2.472	0.210	1.678	3.179
	0.639	0.494	0.862	1.982	2.564	0.173	1.781	3.053
22	0.602	0.548	0.923	2.187	2.853	0.291	1.819	3.081
	0.584	0.534	0.923	2.315	2.973	0.323	1.853	3.095
	0.637	0.564	0.998	2.336	2.967	0.347	1.829	3.298
23	0.417	0.406	0.636	1.883	3.002	0.145	1.552	3.452
	0.345	0.351	0.603	1.852	3.184	0.100	1.634	3.252
	0.393	0.331	0.619	2.097	2.837	0.113	1.573	3.542
24	0.520	-	1.070	2.226	3.606	0.201	1.953	4.271
	0.481	-	1.126	2.099	3.402	0.192	1.958	3.701
	0.500	-	1.039	2.486	3.474	0.192	1.963	3.196
25	0.393	0.436	0.870	2.066	2.797	0.134	1.588	3.080
	0.433	0.474	0.796	2.124	2.732	0.140	1.553	3.108
	0.405	0.389	0.836	2.035	2.789	0.132	1.662	3.094
26	0.494	0.435	0.821	2.197	2.920	0.131	1.739	3.335
	0.481	0.444	0.811	2.217	2.831	0.200	1.717	3.122
	0.473	0.384	0.755	2.233	2.924	0.172	1.798	2.942
27	0.544	0.453	0.790	2.025	2.648	0.210	1.519	3.024
	0.494	0.464	0.736	2.000	2.504	0.273	1.506	2.935
	0.489	0.367	0.756	1.904	2.514	0.232	1.555	2.961
28	0.500	0.515	0.905	2.044	2.753	0.259	1.595	3.006
	0.526	0.517	0.952	2.126	2.799	0.236	1.664	3.061
	0.464	0.498	0.884	2.132	2.875	0.196	1.545	3.037
29	-	-	0.600	1.330	1.880	0.150	1.040	2.260
	-	-	0.630	1.290	1.770	0.130	0.970	2.320
	-	-	0.670	1.350	1.710	0.110	1.050	2.300
30	0.344	0.344	0.728	1.904	2.593	0.118	1.353	2.748
	0.390	0.356	0.753	1.843	2.619	0.148	1.382	2.701
	0.384	0.362	0.816	1.843	2.543	0.122	1.438	2.851
31	0.482	0.442	0.742	1.981	2.569	0.150	1.590	2.856
	0.402	0.494	0.788	1.850	2.615	0.148	1.525	2.798
	0.449	0.444	0.815	1.985	2.477	0.132	1.545	2.899
32	0.392	0.385	0.676	1.727	2.179	0.118	1.284	2.393
	0.355	0.350	0.706	1.753	2.183	0.103	1.360	2.463
	0.376	0.392	0.712	1.734	2.162	0.085	1.244	2.384
33	0.574	0.444	0.910	2.040	2.840	0.271	1.690	3.140
	0.514	0.513	0.857	2.060	2.820	0.267	1.760	2.970
	0.527	0.453	0.884	2.080	2.740	0.067	1.830	3.200
34	0.360	0.330	0.650	1.960	2.500	0.100	1.340	2.850
	0.340	0.350	0.670	1.845	2.409	0.113	1.277	2.818
	0.350	0.356	0.640	1.850	2.490	0.110	1.267	2.720
35	0.487	0.468	0.925	2.259	3.146	0.180	1.845	3.461
	0.502	0.541	0.917	2.245	3.269	0.199	1.870	3.373
	-	0.536	0.906	2.333	3.260	0.176	1.804	3.651
36	0.317	0.450	0.770	2.470	3.850	0.010	1.477	3.210
	0.260	0.433	0.710	2.340	3.770	0.010	1.370	3.050
	0.210	0.580	0.843	2.400	3.577	0.010	1.330	3.080

37	0.493	0.439	0.817	1.965	2.628	0.205	1.676	3.123
	0.504	0.404	0.800	2.062	2.672	0.209	1.717	2.754
	0.470	0.420	0.851	2.078	2.654	0.208	1.654	2.774
38	0.420	0.390	0.796	2.031	2.467	0.161	1.500	2.799
	0.445	0.413	0.835	1.993	2.377	0.163	1.513	2.751
	0.517	0.426	0.773	1.906	2.276	0.182	1.458	2.671
39	0.365	0.382	0.764	2.040	2.705	0.088	1.655	3.078
	0.400	0.352	0.715	1.977	2.626	0.100	1.657	3.208
	0.439	0.395	0.784	1.915	2.843	0.097	1.767	2.926
40	0.493	0.471	0.822	1.979	2.360	0.206	1.443	2.874
	0.555	0.450	0.835	1.991	2.519	0.185	1.428	2.840
	0.488	0.510	0.821	1.981	2.444	0.202	1.455	2.976
41	0.535	0.469	0.884	2.170	2.930	0.193	1.570	3.110
	0.521	0.438	0.929	2.100	2.680	0.329	1.640	3.090
	0.561	0.457	0.861	2.130	2.670	0.167	1.630	3.140

Table 4: Organic carbon ($\mu\text{g}/\text{cm}^2$)

Laboratory	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	3.066	2.714	4.156	7.992	10.906	2.019	8.232	9.133
	3.139	2.406	4.760	9.667	10.936	2.029	8.753	9.169
	3.263	2.436	4.758	8.037	12.144	1.983	8.435	9.203
2	3.244	3.191	4.382	8.069	8.069	2.022	8.346	8.548
	3.613	3.034	4.546	7.993	7.993	2.696	8.399	8.737
	2.920	2.873	5.257	8.105	8.105	1.949	8.318	8.755
3	2.972	2.383	4.125	7.846	10.908	1.895	8.652	9.001
	3.086	2.308	4.174	7.917	11.122	1.955	8.759	9.022
	2.987	2.328	4.167	7.989	10.919	2.003	8.753	8.938
4	3.239	2.585	4.260	8.140	10.954	2.197	8.529	9.139
	3.264	2.496	4.123	7.947	11.143	2.103	8.614	8.912
	3.308	2.560	4.487	8.026	10.990	2.229	8.721	8.972
5	2.930	2.432	3.757	7.654	9.938	2.033	7.909	8.272
	3.440	2.670	3.749	7.423	10.064	2.053	7.637	8.125
	3.180	2.443	3.762	7.467	10.010	1.834	7.829	8.175
6	3.161	2.796	4.486	8.208	11.397	2.091	8.762	8.866
	3.197	2.593	4.159	8.215	11.394	1.894	8.735	9.102
	3.516	2.525	4.422	8.072	11.278	2.073	8.652	9.117
7	2.669	2.327	3.897	9.198	12.391	3.175	8.967	9.696
	2.899	2.256	4.001	8.718	12.578	1.769	8.907	9.393
	2.760	2.383	3.961	8.802	12.273	1.603	9.010	9.591
8	3.155	2.367	3.652	7.345	9.545	2.068	7.514	7.213
	3.110	2.438	3.701	7.041	9.828	1.861	8.546	8.003
	3.163	2.465	3.610	7.168	9.737	1.821	7.255	7.910
9	2.762	2.287	4.106	7.632	10.127	2.071	7.800	8.358
	2.913	2.307	3.743	7.317	10.027	1.824	7.801	8.477
	3.222	2.354	3.820	7.125	10.324	1.631	7.622	8.132
10	2.532	2.024	3.845	7.356	9.719	1.941	8.001	8.327
	2.526	2.312	3.569	7.610	10.050	1.540	8.430	8.135
	2.707	2.020	4.261	7.654	10.021	1.634	7.723	8.017
11	3.890	2.960	4.750	9.730	12.490	2.870	8.430	9.710
	5.780	4.220	5.310	9.710	13.430	2.290	8.490	9.120
	3.970	4.010	5.190	9.200	11.830	2.590	9.990	10.350
12	3.590	3.054	4.668	9.280	10.689	2.619	9.105	9.580
	5.382	2.851	4.257	8.252	11.963	2.326	7.996	9.111
	3.744	2.819	4.422	8.065	11.370	2.587	9.158	9.771
13	3.294	2.564	3.994	7.500	11.155	2.539	8.584	9.433
	3.173	2.699	4.132	8.283	10.580	2.483	8.814	9.301
	3.389	2.867	4.084	8.050	11.036	2.407	9.304	9.088
14	2.979	2.853	4.128	6.852	9.757	2.329	7.338	7.648
	2.765	2.564	3.582	6.823	9.533	2.328	7.809	7.917
	2.824	2.603	4.384	8.187	9.449	2.123	7.746	7.694
15	2.962	2.346	3.901	7.879	10.670	1.830	8.417	8.429
	2.927	2.574	3.907	8.007	10.745	1.745	8.539	8.591
	2.907	2.346	3.801	7.994	10.892	1.644	8.421	8.053
16	5.008	4.141	4.743	9.545	13.998	3.877	10.985	12.022
	4.548	3.436	4.959	10.109	13.459	3.840	11.058	11.392
	4.944	4.203	4.436	10.335	13.903	4.872	11.444	11.772
17	3.120	2.419	4.102	8.302	11.591	2.039	9.563	9.231
	3.319	2.639	3.967	8.121	10.860	1.832	8.967	8.930
	3.062	2.342	4.194	8.127	10.927	2.094	8.762	9.101

18	2.830	2.260	4.210	8.180	11.280	1.680	8.680	8.840
	3.050	2.260	4.160	8.160	11.220	1.870	10.000	8.990
	3.200	2.450	4.170	8.190	11.400	1.830	8.570	9.060
19	3.934	2.378	4.172	8.842	10.780	2.536	7.996	9.195
	3.451	3.248	4.109	8.155	10.800	3.379	10.171	8.925
	3.635	2.689	4.490	8.628	10.492	1.778	9.639	8.859
20	3.058	2.366	3.855	7.666	10.666	1.831	8.263	8.523
	3.094	2.522	3.818	7.505	10.361	1.730	8.302	8.582
	2.841	2.353	3.833	7.639	10.696	1.900	8.255	8.920
21	3.415	2.442	4.117	8.750	11.670	2.039	9.411	9.369
	3.715	3.353	4.120	8.629	12.464	1.775	9.234	9.503
	3.201	2.791	4.152	8.542	12.595	2.068	9.344	9.457
22	2.966	2.387	3.934	7.999	10.807	2.067	8.999	8.932
	3.079	2.175	3.918	7.890	10.890	2.254	8.237	8.901
	4.333	2.786	4.511	7.892	10.666	2.182	8.591	8.863
23	3.447	2.736	3.820	7.657	12.011	1.977	9.161	8.957
	3.171	2.541	3.744	7.579	12.576	1.742	9.361	8.690
	3.349	2.525	3.590	8.804	11.889	2.295	9.343	9.320
24	4.975		7.687	11.320	12.763	4.659	11.243	14.869
	4.673		9.852	13.208	12.132	4.449	12.589	12.860
	6.368		7.841	9.627	12.883	5.383	13.201	11.808
25	2.911	2.372	4.499	7.947	11.024	2.372	8.207	9.055
	2.492	2.132	4.041	7.993	10.896	1.501	8.681	8.940
	2.738	2.352	3.878	7.844	10.897	1.618	8.603	9.067
26	2.938	2.338	4.080	7.841	10.416	2.032	8.549	8.799
	2.808	2.494	4.012	7.647	10.285	1.869	8.614	8.798
	2.820	2.517	3.926	7.754	10.311	2.023	8.523	8.775
27	3.171	2.742	4.178	8.416	10.797	2.053	8.723	9.134
	2.857	2.667	4.213	8.581	11.029	2.103	8.415	9.276
	3.181	2.933	4.345	8.226	10.904	2.907	8.597	9.283
28	2.781	2.346	4.279	7.942	10.651	2.173	8.601	8.507
	2.708	2.539	4.075	7.880	10.682	2.000	8.399	9.034
	2.516	2.462	3.960	7.902	10.815	2.072	8.512	8.793
29	-	-	5.810	9.400	12.400	3.560	9.710	10.300
	-	-	5.660	9.490	12.700	2.640	9.700	10.100
	-	-	5.460	9.700	12.800	2.320	9.670	10.500
30	3.026	2.045	3.831	7.716	10.439	2.132	8.205	8.517
	3.478	2.233	3.644	7.601	10.413	2.025	8.021	8.521
	2.858	2.307	3.762	7.575	10.628	2.191	8.237	8.286
31	3.246	2.620	3.911	8.461	10.980	1.954	8.478	8.949
	4.024	2.386	4.014	8.334	11.457	1.774	8.812	9.050
	3.497	2.591	4.011	8.331	11.123	1.641	8.903	9.064
32	3.110	2.243	3.926	8.165	11.482	1.766	8.547	8.872
	2.879	2.881	3.953	8.317	10.784	2.417	9.255	8.787
	2.653	2.135	3.881	8.656	10.732	2.028	8.660	8.997
33	2.690	1.910	4.050	7.500	10.300	1.640	7.740	8.370
	3.030	2.050	3.710	7.590	10.800	1.730	7.720	8.560
	3.100	2.030	3.870	7.680	10.200	1.330	7.850	8.290
34	3.020	2.460	4.140	7.770	10.410	1.950	8.384	8.560
	3.090	2.370	4.290	7.585	10.178	1.997	8.415	8.405
	3.070	2.396	4.280	7.530	10.400	2.250	8.425	8.690
35	3.601	2.575	4.000	7.706	10.300	2.073	8.432	8.507
	3.336	2.371	4.104	8.002	10.740	1.997	8.606	8.502
	-	2.499	3.982	7.727	10.815	2.402	8.112	8.583
36	4.963	3.983	4.380	8.040	12.410	3.920	7.873	9.490
	4.000	2.940	4.310	7.920	12.300	3.760	7.870	9.940
	4.370	3.640	4.800	8.350	11.867	2.700	7.150	9.130

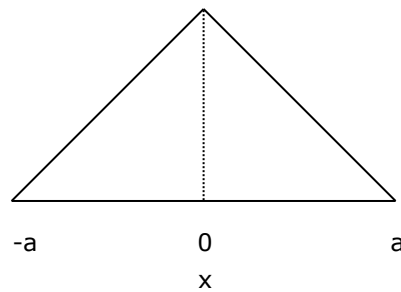
37	3.894	4.523	6.022	9.506	12.560	3.582	10.292	11.515
	3.565	3.895	6.714	10.150	12.796	3.707	10.689	10.356
	3.270	4.137	6.954	9.318	12.610	3.969	10.569	10.127
38	3.316	2.207	3.909	8.970	12.176	1.751	9.334	11.718
	3.074	2.122	4.022	9.406	11.494	1.815	8.934	9.704
	3.657	-	3.789	9.443	11.352	1.392	9.165	9.679
39	3.419	2.357	3.789	7.930	11.705	2.551	7.887	8.046
	2.805	2.490	3.845	7.668	11.186	2.573	7.545	7.585
	2.908	2.732	3.623	7.277	10.998	3.263	8.118	7.889
40	3.292	2.487	4.204	8.983	11.254	2.066	8.913	9.437
	3.177	2.372	4.210	8.533	11.209	2.019	8.795	9.509
	3.457	2.706	4.425	8.732	11.400	1.941	8.886	9.163
41	3.420	2.290	4.060	7.750	10.800	2.030	8.300	8.750
	2.790	2.440	3.970	8.000	10.700	2.380	8.480	8.420
	2.680	2.360	4.100	7.730	10.500	1.990	8.260	8.790

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

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

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:

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

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 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 in $\mu\text{g cm}^{-2}$

Assigned values	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
TC	3.68	2.97	4.96	10.19	13.80	2.33	10.23	11.98
OC	3.21	2.48	4.14	8.15	11.10	2.14	8.62	8.97
EC	0.46	0.45	0.82	2.05	2.71	0.18	1.62	3.01

Table 2. QA bias and QA variability for TC

	TC QA measure	QA_bias	QA_variability	Systematic
1	SU-ACES	0.7%	5.4%	no
2	UCD_AQRC	0.8%	8.0%	no
3	IPISPAN	-1.4%	4.1%	no
4	IPISPAN	0.2%	2.4%	no
5	EMPA	-7.9%	3.9%	low
6	HMS	2.1%	4.4%	high
7	ULUND	2.3%	8.4%	no
8	IDAEA-CSIC	-5.2%	4.9%	no
9	IDAEA-CSIC	-7.6%	2.2%	low
10	AU	-8.6%	5.3%	low
11	FMI	19.6%	9.7%	high
12	FMI	6.8%	10.6%	high
13	ISSeP	0.9%	5.3%	no
14	LAERO	-9.9%	7.5%	no
15	SLLC	-4.9%	7.2%	low
16	FMI	28.1%	30.9%	high
17	TU-Wien	-3.8%	6.4%	low
18	NILU	2.2%	10.0%	no
19	CHMI	5.4%	8.4%	no
20	TROPOS	-5.1%	5.5%	low
21	UNIVIE	5.8%	8.5%	high
22	INERIS	1.6%	4.5%	high
23	LANUV	0.3%	9.2%	no
24	CZECHGLOBE	41.1%	40.3%	high
25	LSCE	-1.5%	6.9%	no
26	SUNLAB.COM	-3.2%	4.1%	low
27	UBA	1.4%	5.7%	no
28	GGD	-1.3%	6.2%	low
29	ISCIII	5.7%	9.4%	no
30	NPL	-6.6%	4.2%	low
31	JRC	0.1%	10.9%	no
32	IGE	-5.8%	4.4%	low
33	ARPA	-5.3%	8.2%	low
34	KLAB	-6.7%	2.4%	low
35	ECPL_UOC	0.3%	3.5%	no
36	GIOS	10.9%	24.7%	high
37	Aerosol d.o.o.	17.0%	24.1%	high
38	ENRACT	2.7%	13.2%	no
39	ENRACT	-6.0%	13.5%	no
40	AIRPARIF	1.7%	4.4%	no
41	SEA	-1.9%	4.3%	low

Table 3. QA bias and QA variability for OC

	OC QA measure	QA_bias	QA_variability	Systematic
1	SU-ACES	1.8%	6.7%	no
2	UCD_AQRC	0.2%	20.2%	no
3	IPISPAN	-1.9%	4.2%	no
4	IPISPAN	0.9%	2.0%	no
5	EMPA	-8.3%	4.6%	low
6	HMS	1.7%	5.0%	high
7	ULUND	2.9%	10.4%	no
8	IDAEA-CSIC	-11.2%	4.9%	low
9	IDAEA-CSIC	-8.0%	3.3%	low
10	AU	-9.8%	5.9%	low
11	FMI	18.8%	18.9%	high
12	FMI	6.6%	12.5%	high
13	ISSeP	2.8%	7.3%	no
14	LAERO	-10.8%	8.7%	no
15	SLLC	-4.7%	6.9%	low
16	FMI	30.1%	33.4%	high
17	TU-Wien	-0.2%	5.2%	no
18	NILU	0.1%	8.9%	no
19	CHMI	6.2%	9.5%	high
20	TROPOS	-5.7%	5.1%	low
21	UNIVIE	6.6%	9.8%	no
22	INERIS	-0.6%	4.3%	no
23	LANUV	1.8%	8.1%	no
24	CZECHGLOBE	46.9%	45.6%	high
25	LSCE	-2.1%	6.5%	low
26	SUNLAB.COM	-4.1%	4.2%	low
27	UBA	2.7%	6.7%	no
28	GGD	-2.6%	6.5%	low
29	ISCIII	15.9%	9.7%	no
30	NPL	-5.7%	4.2%	low
31	JRC	1.0%	11.6%	no
32	IGE	-1.7%	5.3%	no
33	ARPA	-7.6%	8.6%	low
34	KLAB	-4.2%	3.8%	low
35	ECPL_UOC	-2.7%	5.3%	no
36	GIOS	9.2%	29.7%	no
	Aerosol			
37	d.o.o.	20.4%	25.9%	high
38	ENRACT	4.8%	15.7%	no
39	ENRACT	-5.8%	17.5%	no
40	AIRPARIF	3.0%	5.6%	high
41	SEA	-3.2%	3.1%	low

Table 4. QA bias and QA variability for EC

EC QA		QA_bias	QA_variability	Systematic
	measure			
1	SU-ACES	5.7%	21.0%	no
2	UCD_AQRC	5.2%	9.3%	no
3	IPISPAN	0.2%	12.5%	no
4	IPISPAN	-0.9%	18.0%	no
5	EMPA	-4.7%	3.2%	low
6	HMS	4.2%	5.3%	high
7	ULUND	1.6%	22.8%	no
8	IDAEA-CSIC	23.0%	38.3%	high
9	IDAEA-CSIC	-1.3%	22.8%	no
10	AU	-3.1%	9.5%	no
11	FMI	27.4%	35.5%	no
12	FMI	4.9%	13.2%	no
13	ISSeP	-5.3%	16.9%	low
14	LAERO	-6.9%	7.1%	low
15	SLLC	-4.2%	9.4%	low
16	FMI	23.0%	9.9%	high
17	TU-Wien	-21.6%	32.6%	low
18	NILU	8.1%	16.9%	high
19	CHMI	-2.2%	4.8%	low
20	TROPOS	-1.1%	10.6%	no
21	UNIVIE	7.0%	17.9%	no
22	INERIS	14.2%	30.8%	high
23	LANUV	-11.1%	18.9%	no
24	CZECHGLOBE	21.1%	9.4%	high
25	LSCE	0.1%	10.8%	no
26	SUNLAB.COM	3.9%	6.3%	no
27	UBA	-4.5%	17.2%	no
28	GGD	5.3%	12.5%	high
29	ISCIII	-30.4%	5.6%	no
30	NPL	-11.5%	9.3%	low
31	JRC	-5.3%	8.6%	low
32	IGE	-19.6%	11.2%	low
33	ARPA	5.5%	6.3%	high
34	KLAB	-20.4%	13.2%	low
35	ECPL_UOC	12.5%	6.1%	high
36	GIOS	-1.4%	54.0%	no
	Aerosol			
37	d.o.o.	-0.5%	9.7%	no
38	ENRACT	-6.5%	4.7%	low
39	ENRACT	-6.0%	20.9%	no
40	AIRPARIF	-1.5%	9.0%	no
41	SEA	3.9%	19.4%	high

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