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

PT OC&EC-2024-01

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Contents

Abstract

The ACTRIS Centre for Aerosol In-Situ measurements ECAC (European Centre for Aerosol Calibration) completed, in March 2024, the annual inter-laboratory exercise for the measurement of total, elemental and organic carbon (TC; EC; OC) in particulate matter collected on filters. This exercise was provided by the European Reference Laboratory for Air Pollution of the EC-JRC.

The overall scope of this ILC is to enhance the comparability and determine the uncertainty of the TC, OC and EC atmospheric concentration data produced across Europe. This ILC scheme was based on ambient $PM_{2.5}$ aerosol samples collected on quartz fibre filters at a rural background site in Ispra, Italy.

The primary goal is to assess participants' performance in determining the TC loading and the EC/TC ratio, to evaluate the accuracy of the instrument response throughout the analysis and the optical correction for charring, respectively. 35 laboratories, with 37 analyzers in total, participated in this exercise, all - except 1 - running the EUSAAR_2 protocol as their usual thermal-optical protocol with their usual analytical instrument.

Participants' performance is determined in terms of z-scores, a measure of the participants' bias compared to an assigned value associated with its standard deviation. For TC filter loadings, 2 outliers and 14 stragglers and for the EC/TC ratios, 11 outliers and 19 stragglers were identified, respectively.

1 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 Reference Laboratory for Air Pollution (ERLAP) of the European Commission – Joint Research Centre (EC – JRC) has completed in March 2024 an OC & EC inter-laboratory comparison exercise (PT OC&EC-2024-01) as part of the support and services provided by the *European Centre for Aerosol Calibration,* the Thematic Centre for aerosol in-situ measurements of ACTRIS - ERIC (Aerosol, Clouds and Trace Gases Research Infrastructure - European Research Infrastructure Consortium).

Thirty-five laboratories, with thirty-seven analyzers in total, participated in this exercise, all - except one laboratory using the NIOSH-870 thermal protocol - 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 RI facilities located in their countries and /or National Reference Laboratories (namely in Italy, Germany, France, Croatia, Hungary, Spain, Finland, Latvia, The Netherlands, Slovenia, Austria, Greece, Belgium, United Kingdom, Cyprus, Czech Republic, Poland, Norway, Sweden, plus the EC - JRC).

The University of California Air Quality Research Center, the Institute of Public Health of Belgrade, the Polish Central Laboratory Pomiarowo-Badawcze Sp. z o.o., and the Sunset Laboratory BV in The Netherlands also participated.

2 Organization

2.1 PT provider

The European Reference Laboratory for Air Pollution of the EC - JRC (via E. Fermi 2749, I-21027 Ispra (VA)) took the legal responsibility for all activities of the proficiency testing (PT), as a result of the contract JRC N°36775 signed with TROPOS (the leading institution of the ACTRIS Thematic Centre for aerosol in-situ measurements).

Personnel:

- Fabrizia Cavalli (PT coordinator and statistician) – fabrizia.cavalli@ec.europa.eu; jrc-erlap@ec.europa.eu;
- Jean-Philippe Putaud (preparing test items –from sampling to dispatch–, stability and homogeneity determination and testing).

JRC-ERLAP did not make use of any externally provided products and/or services for any of the operations involved in the PT.

2.2 PT ITEMS: production, distribution, homogeneity and stability

The measurands of this ILC scheme were TC, OC and EC (in unit format µg cm^{-2}) in $PM_{2.5}$ deposited on quartz fibre filters, in the concentration range for applicability of the EN 16909:2017 standard (1.8-45 µg cm^{-2} and 0.2-16 µg cm^{-2} for OC and EC, respectively).

PRODUCTION: In lack of suitable certified reference material for atmospheric OC and EC, this proficiency testing scheme made use of ambient (outdoor) $PM_{2.5}$ aerosol collected with a high-volume sampler (namely a Tisch Environmental non-FRM $PM_{2.5}$ sampler) on binder-free quartz fiber filters (Pallflex, Tissuquartz 2500 QAT UP, 20.32 x 25.4 cm) at the regional background site of Ispra, Italy. Filter samples were stored in a refrigerator at temperature of 3±2 °C after exposure.

DISTRIBUTION: Aliquots (according to participants needs to triplicate measurements) were punched out from 8 filter samples (label: IPRA, IPRB, …, IPRH), all in the concentration range for the applicability of the EN 16909:2017 standard; PT items were then packaged in closed petri dishes and securely labelled.

To limit the contribution of localized heterogeneities and/or contaminations to the occurrence and recurrence of poor performance from a single participant, PT items were distributed randomly to participants.

PT items were dispatched on 05.02.2024 to all participants - except to EC – JRC, the "local" participant, i.e. nr 40 - via courier (limiting to a max of 3 days the time needed for transport) at ambient temperature.

A single use USB temperature-data logger (Mini 1 way) was included to qualitatively monitor the temperature experienced by the PT items from dispatch to analysis. Participants treated PT items in the same manner as routine samples, including handling and storage.

The recorded temperature was in all cases below 25°C with the exception of 7 cases where temperature exceeded 25°C for less than 4 hours (for a max of 8°C h). In one case only (participant 23), PT items experienced a temperature above 25°C for 8 days for a total of 220°C hour.

HOMOGENEITY: the homogeneity of the PT items was assessed by the PT provider for all measurands on the basis of the recommendations listed in ISO 13528:2022, informative Annex B.

Studies were conducted prior to the circulation of PT items to evaluate possible impacts of inhomogeneity on the measurands.

Ten (10) subsamples of 4.7 cm diameter were randomly taken from a specific filter sample across an area corresponding to the one used to punch the PT item aliquots; three replicates of TC, OC and EC measurements were performed on each subsample. The sample homogeneity was assessed as the estimate of the between-sample standard deviation, calculated using the analysis of variance, according to ISO 13528:2022 (E) Annex B, par. B.3.

The homogeneity resulted better than 3% for EC and 2% for OC and TC. In previous rounds of this PT scheme, the homogeneity resulted always better than 5% for TC, OC, and EC. Because 5% represents also the accepted repeatability value for the measurement of TC, OC and EC (EN 16909:2017 (E)), a homogeneity of 5% is considered sufficient. If sampling occurs under repeatable conditions, it is reasonable to assume that all PT items have a similar homogeneity.

STABILITY: The stability of the PT items was assessed by the PT provider on the basis of the recommendations listed in ISO 13528:2022, informative Annex B, for all measurands.

Studies were conducted prior to the circulation of the PT items to evaluate possible impacts of temperature conditions over the duration of the PT scheme round (including transport and storage) on the measurands.

Based on the time and temperature limits for sample transport and storage described in EN16909:2017 (par. 7.2), and on the temperature conditions foreseeable during transport and storage at participants' premises (as determined from previous PT scheme rounds), nine (9) subsamples from three (3) specific samples were exposed to a temperature of 25 °C ± 0.5 for a period of ca. 7 weeks (i.e. duration of the proficiency testing scheme round).

The effect of temperature conditions during transport and storage was assessed by comparing the measurement results at $t=t_f$ (i.e. after 6-7 weeks) to the initial value at $t=t_0$ (in refrigerator at T of 3±2 °C) for each measurand. Sample stability was assessed by determining if the difference of the means of the measurements performed at $t=t_0$ and $t=t_f$ were statistically different from zero according to a t-test at the 99% level of confidence. All three samples resulted stable over the prescribed period for all measurands. It is reasonable to assume that also PT items were similarly stable.

2.3 Participants

Thirty-five (35) laboratories, with thirty-seven (37) analyzers in total, participated in this exercise.

The list of participants is reported in Table 1. For brevity, and because participants agreed on disclosure of their own results, the number assigned to each participant/analyzer will be used in the remainder of the document.

Table 1. List of participants in the PT-OC&EC-2024-01, and contact persons.

Code	Participant	Acronym	Contact
1	Consiglio Nazionale delle Ricerche (CNR-ISAC)	CNR-ISAC	d.contini@isac.cnr.it
2	University of Genoa and INFN	UNIGE/INFN	federico.mazzei@ge.infn.it
3	Federal Environment Agency	UBA	julian.ruediger@uba.de
4	Laboratoire d' aérologie	LAERO	veronique.pont@aero.obs-mip.fr
6	Institute for Medical Research and Occupational Health	IMI	rgodec@imi.hr
7	Hungarian Meteorological Service	HMS	machon.a@met.hu
8	Institute of Environmental Assessment and Water Research-Spanish National Research Council	IDAEA-CSIC	angeliki.karanasiou@idaea.csic.es
9	Institute of Environmental Assessment and Water Research-Spanish National Research Council	IDAEA-CSIC	angeliki.karanasiou@idaea.csic.es
10	Leibniz Institute for Tropospheric Research	TROPOS	poulain@tropos.de
11	Finnish Metereological Institute	FMI	minna.aurela@fmi.fi
12	Latvian Environment, Geology and Meteorology Centre	LVGMC	georgijs.bakradze@lvgmc.lv
13	National Institute for Public Health and the Environment	RIVM	pecconsultingbv@gmail.com
14	Landesamt fü~~u~~r Natur, Umwelt und Verbraucherschutz	LANUV	david.czorny@lanuv.nrw.de
15	Slovenian Environment Agency	SEA	judita.burger@gov.si
16	Agenzia Regionale per la Protezione Ambientale Umbria	ARPA Umb	m.vecchiocattivi@arpa.umbria.it
17	Institut National de l’Environnement Industriel et des Risques	INERIS	arnaud.papin@ineris.fr
18	Technische Universität Wien	TU Wien	anneliese.kasper-giebl@tuwien.ac.at
19	Environmental Chemical Processes Laboratory_ University of Crete	ECPL_UOC	tsagaraki-maria@hotmail.com
21	Laboratoire Inter-Universitaire des Systèmes Atmosphériques (LISA CNRS UMR 7583)	LISA	gael.noyalet@lisa.ipsl.fr
22	Institut Scientifique de Service Public	ISSeP	p.fays@issep.be
23	Centralne Laboratorium Pomiarowo-Badawcze Sp. z o.o.	CLP-B	kagrzybek@clpb.pl
24	National Physical Laboratory	NPL	krzysztof.ciupek@npl.co.uk
25	National Centre for Scientific Research "Demokritos"	NCSR D	ldiapouli@ipta.demokritos.gr
26	The Cyprus Institute	CyI	j.sciare@cyi.ac.cy
27	Institute of Chemical Process Fundamentals of the Czech Academy of Sciences	ICPF	vodicka@icpf.cas.cz
28	Institute of Environmental Engineering Polish Academy of Sciences	IPIŚ PAN	barbara.mathews@ipis.zabrze.pl
29	Norwegian Institute for Air Research	NILU	key@nilu.no
30	Laboratoire des Sciences du Climat et de l'Environnement	LSCE	nicolas.bonnaire@lsce.ipsl.fr

31	Chief Inspectorate of Environmental Protection	GIOS	i.kaluzinska@gios.gov.pl
32	Environmental Chemical Processes Laboratory, University of Crete	ECPL_UoC	abougiat@noa.gr
33	Sunset Laboratory B.V.	SLBV	luis@sunlab.com
34	University of Vienna, Faculty of Physics, Aerosol Physics and Environmental Physics Group	UNIVIE	agnieszka.kupc@univie.ac.at
36	Lund University, Department of Physics	LU_Physics	adam.kristensson@nuclear.lu.se
37	UC Davis Air Quality Research Center	UCD AQRC	mvlangston@ucdavis.edu
38	Institute of Public Health of Belgrade	IPH Bg	andrej.sostaric@zdravlje.org.rs
39	Department of Environmental Science, Stockholm University	SU-ACES	radovan.krejci@aces.su.se
40	European Commission JRC	EC - JRC	fabrizia.cavalli@ec.europa.eu

Source: JRC 2024.

2.4 Thermal-optical analysis

The thermal protocol EUSAAR_2 [Cavalli et al., 2010] with a transmittance-based optical correction for pyrolysis is the European standard thermal protocol for the measurements of TC and EC in PM2.5 samples deposited on filters (EN16909:2017). In this ILC round, all participants applied it, with the exception of participant 23 applying the protocol NIOSH-870.

All participants operated a Sunset carbon analyser, except participant 36 operating a DRI instrument. Participants 11, 25 and 27 used the semi-continuous Sunset carbon analyser model with NDIR detector.

EC -JRC participated in this ILC according to the European standard EN16909 and the requirements of ISO/IEC 17025:2018.

3 DATA EVALUATION

Participants reported by the deadline of 24th April 2024: i) TC, OC and EC concentrations, in µg C cm^{-2} units with three significant digits, from three replicates of the eight PT items (corresponding uncertainties were not required) and ii) the record of temperature conditions over the duration of the PT scheme round.

To evaluate the accuracy of the instrument response throughout the analysis and the optical correction for charring, we focus on *TC loadings* (in µg cm^{-2}) and *EC/TC ratios,* respectively. Indeed, TC represents the most robust (and protocol-independent) output of the thermal-optical analysis, while the EC/TC ratio is free from biases in the total carbon determination calibration, and reflects, instead, possible biases or differences among participants in the OC/EC split determination.

On average, reported TC loadings ranged from 3.83 to 20.5 µg cm^{-2}, corresponding to atmospheric concentrations ranging from ca. 0.80 to 4.27 µg m^{-3} collected for 24h at a face velocity of 54 cm s^{-1}. EC/TC ranged on average from 0.083 to 0.202.

All submitted results for TC, EC, OC (in µg cm^{-2}) and EC/TC ratios are presented in Tables A1-A4 in Annex A.

3.1 LABORATORY PERFORMANCE

3.1.1 Description

The assessment of the *laboratory performance* aims at describing the laboratory bias compared to an assigned value associated with its standard deviation. As ambient PM collected on filters was used as PT item (in absence of suitable certified reference material for atmospheric TC, OC and EC deposited on filters), the *true* values for *TC loadings and EC/TC ratios* were not known. For each PT item, the TC loading and EC/TC ratio assigned value and its standard deviation was calculated as follows:

- 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 PT scheme was chosen. With this approach, the assigned value X for each PT item is the robust average calculated, with a recursive algorithm, from the results reported by all participants (ISO 13528:2005)). The results coming from different measurement methods (i.e. participants 23) were also included, because the number was not sufficient in order to produce a statistically meaningful evaluation if treated separately.

- Determining the standard deviation for PT scheme: 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 PT 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).

For the current PT scheme, this approach is considered producing reliable assigned values and associated robust standard deviations because of the participation of a large number of experienced and expert laboratories, and due to the use of a (almost) single thermal-protocol. In addition, by experience from previous rounds, the robust standard deviations from all data in a round of PT scheme are in the range of the overall method precision (repeatability and reproducibility).

In general, this approach might become statistically ineffective [ISO 13528:2015 (E)], for example, if the number of participant is lower than twelve (12). Although this condition does not apply to the current PT scheme round, the robust mean and its standard deviation were also calculated applying the Q/Hampel method to verify their reliability (https://quodata.de/content/qhampel-webtool, as in ISO 13528:2015 (E)).

The values obtained did not significantly differ (less than 2%) from those retrieved as the *consensus value from participant results*, in Tables 2 and 3, which were then used for further elaboration.

Each participant's performance is determined in terms of *z-scores,* a measure of the deviation from the assigned value taking into account its standard deviation.

For each laboratory *i* and PT item *j*, a *z-score* z_{ij} was calculated as:

$$z_{ij} = (x_{ij} - X_j) / \sigma_j^*$$

Equation 1. z-score

where x_{ij} is the result from the participant *i for item j*; X_j is the assigned value for sample *j*; and σ_j^* is the standard deviation for proficiency assessment for sample *j*.

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.

3.1.2 Results: Laboratory performance for TC

The assigned values X and the related standard deviations for proficiency assessment σ* calculated from the entire database for PT item, are reported in Table 2.

Table 2. Assigned values and standard deviations for proficiency assessment σ* from data obtained in a round of a proficiency testing scheme for TC.

		IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
assigned value	µg/cm²	14.9	20.5	5.63	17.7	12.2	12.3	7.95	3.83
standard deviation, σ*	µg/cm²	1.02	1.30	0.440	1.46	0.889	1.14	0.610	0.376
σ*		7%	6%	8%	8%	7%	9%	8%	10%
2σ*		14%	13%	16%	16%	15%	19%	15%	20%
3σ*		20%	19%	23%	25%	22%	28%	23%	29%

Source: JRC 2024.

All z-scores from all participants and for each PT item are reported in Table A5 of Annex A and shown in Figure 1.

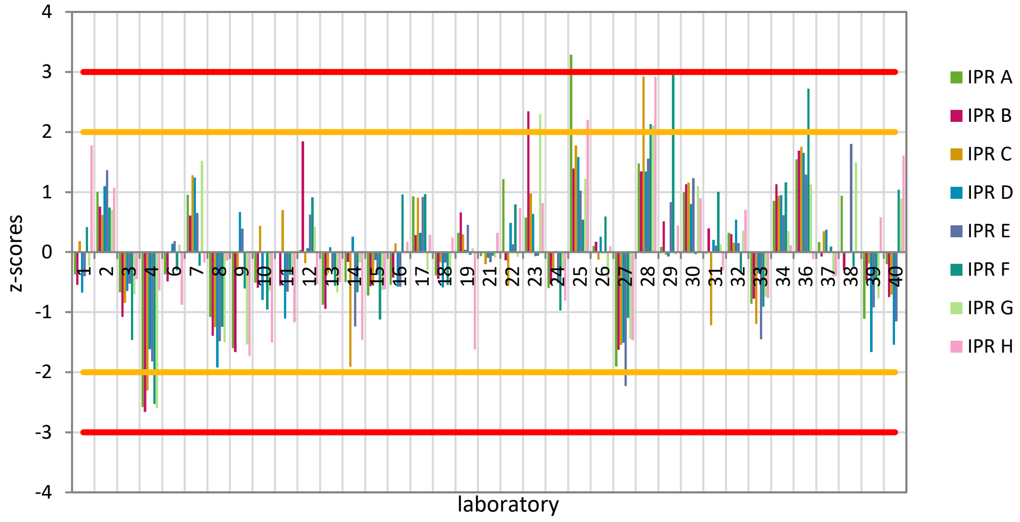
Two (2) outliers are identified: 25/IPRA and 29/IPRF (participant/sample); in addition, fourteen (14) stragglers are identified: 4/IPRA; 4/IPRB; 23/IPRB; 4/IPRC; 28/IPRC; 27/IPRE; 4/IPRF; 28/IPRF; 36/IPRF; 4/IPRG; 23/IPRG; 28/IPRG; 25/IPRH; and 28/IPRH (participant/sample).

For each sample, twenty-five (25) to twenty-seven (27) out of thirty-seven (37) entries show deviations from the assigned values within +/- 1 σ* (i.e. within 1 z-score) as listed in Table 2. Seventy-nine percent (79%) of all entries are within 10% from the assigned value.

Several participants show the systematic tendency (i.e. for all PT items and larger than ± 5%, on average) of overestimating –i.e. participants 2, 23, 25, and 28- or underestimating –i.e. participants 3, 4, 8, 14, 27 and 33- the assigned TC values (Table A7 in Annex A).

A contribution of filter heterogeneities to poor laboratory performances cannot be completely excluded. However, participants showing large (|z-scores|> 2) and/or systematic biases shall carefully examine their procedures and identify appropriate corrective actions that are likely to prevent the recurrence of such results in the future. A more accurate determination of the instrument's calibration constant (e.g. implementing CO_2 calibration, where possible) would probably reduce the observed variability in TC determination.

Figure 1. z-scores for TC calculated using σ* from data obtained in a round of a proficiency testing scheme.



Source: JRC 2024.

3.1.3 Results: Laboratory performance for EC/TC

The assigned values, X, and the related standard deviations for proficiency assessment, σ*, are reported in Table 3.

Table 3. 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	0.184	0.202	0.168	0.122	0.170	0.122	0.083	0.114
standard deviation, σ*	ratio	0.021	0.018	0.015	0.016	0.012	0.011	0.012	0.015
σ*	%	12%	9%	9%	13%	7%	9%	14%	13%
2σ*	%	23%	18%	18%	26%	14%	18%	28%	26%
3σ*	%	35%	26%	26%	39%	21%	27%	43%	39%

Source: JRC 2024..

All z-scores from all participants and for each PT item are reported in Table A6 of Annex A and shown in Figure 2.

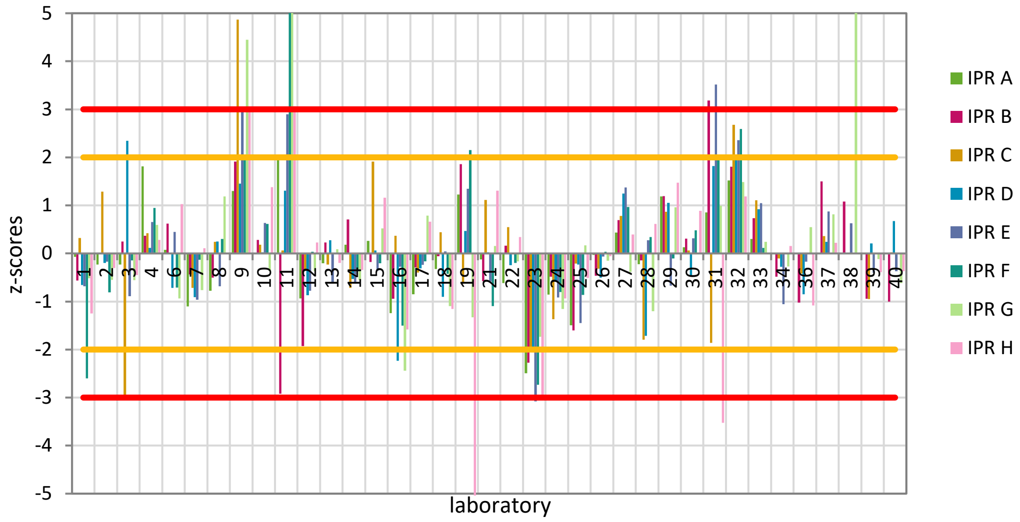
Eleven (11) outliers – 31/IPRB; 9/IPRC; 23/IPRE; 31/IPRE; 11/IPRF; 9/IPRG; 11/IPRG; 38/IPRG; 11/IPRH; 19/IPRH and 31/IPRH (participant/sample)- and nineteen (19) stragglers – 23/IPRA; 11/IPRB; 23/IPRB; 3/IPRC; 32/IPRC; 3/IPRD; 16/IPRD; 9/IPRE; 11/IPRE; 32/IPRE; 1/IPRF; 9/IPRF; 19/IPRF; 23/IPRF; 32/IPRF; 38/IPRF; 16/IPTG; 9/IPRH and 23/IPRH (participant /sample)– are identified.

For each sample, twenty-six (26) to twenty-seven (27) out of thirty-seven (37) entries show deviations from the assigned values within +/- 1 σ* (i.e. within 1 z-score) as listed in Table 3. Sixty-seven percent (67%) of all entries were within 10% of the assigned value and seventy-eight percent (78%) were within 20% of the assigned EC/TC ratio value.

Several participants show the systematic tendency (i.e. for all test samples and larger than ± 5%, on average) of overestimating - i.e. participants 4, 9, 27, 32 and 37 - or underestimating - i.e. participants 1, 16, 18, 23, 24 and 25- the assigned EC/TC ratio. Participant 23, applying the NIOSH-870 thermal protocol, underestimated EC/TC ratio by 25% ± 7, on average whereas participant 37, applying the IMPROVE_ A thermal protocol, overestimated EC/TC ratio by ±5%, on average (Table A8 in Annex A).

A contribution of filter heterogeneities to poor laboratory performances cannot be completely excluded. However, participants showing large (|z-scores|> 2) and/or systematic biases shall carefully examine their procedures and identify appropriate corrective actions that are likely to prevent the recurrence of such results in the future. A more solid and stable in time instrument set-up in terms of i) laser stability; ii) FID response in He and He/O_2 phases; iii) oven temperature calibration iv) selection of the time period (in sec) for determining the initial laser signal and v) transit time would improve such performances and reduce the observed biases in EC/TC ratio determination.

Figure 2. z-scores for EC/TC ratio calculated using σ* from data obtained in a round of a proficiency testing scheme. The z-score axis is set to ±5.



Source: JRC 2024.

4 Conclusions

The inter-laboratory exercise PT OC&EC-2024-01 for the measurement of total carbon, elemental carbon and organic carbon in $PM_{2.5}$ deposited on filters involved thirty-five (35) laboratories, with thirty-seven (37) analyzers in total, all applying thermal-optical analyses and the EUSAAR_2 protocol, except one laboratoryusing the NIOSH-870 thermal protocol (Participant 23.

In absence of a suitable certified reference material for atmospheric OC and EC, the PT items used to assess laboratories' performance consisted of atmospheric $PM_{2.5}$ deposited on filters.

The assigned values for TC loadings and EC/TC ratios in the PT items and the corresponding uncertainties were calculated as robust averages and standard deviation, respectively from all data obtained in this round of the PT scheme.

Laboratory performances were assessed for both TC loadings and EC/TC ratios based on z-scores.

For TC filter loadings, two outliers and fourteen stragglers –mainly from two participants– were identified; 79% of all entries were within 10% of the assigned TC concentration value. Several participants show the systematic tendency of overestimating (four participants) or underestimating (six participants) the assigned TC concentrations.

Participants showing large (|z-scores|> 2) and/or systematic biases shall carefully examine their procedures and identify appropriate corrective actions that are likely to prevent the recurrence of such results in the future. A more accurate determination of the instrument's calibration constant (e.g. implementing CO_2 calibration where possible) would correct this tendency.

Regarding EC/TC ratios, eleven outliers and nineteen stragglers were identified. 67% of all entries were within 10% of the assigned value and 78% were within 20% of the assigned EC/TC ratio value.

Several participants show the systematic tendency of overestimating - i.e. participants 4, 9, 27, 32 and 37 - or underestimating - i.e. participants 1, 16, 18, 23, 24 and 25 - the assigned EC/TC ratio. Participant 23, applying the NIOSH-870 thermal protocol, underestimated EC/TC ratio by 25% ± 7 on average.

A contribution of filter heterogeneities to poor laboratory performances cannot be completely excluded. However, participants showing large (|z-scores|> 2) and/or systematic biases shall carefully examine their procedures and identify appropriate corrective actions that are likely to prevent the recurrence of such results in the future. A more solid and stable in time instrument set-up in terms of i) laser stability; ii) FID response in He and He/O_2 phases; iii) oven temperature calibration iv) determination of the initial laser signal and v) transit time would improve such performances and reduce the observed variability in EC/TC ratio determination.

For informative purposes only, results from this inter-laboratory comparison round were also used to determine the repeatability and reproducibility of the standard measurement method described in EN16909:2017, according to the ISO 5725-2:2019 (ANNEX B). The measurement method repeatability and reproducibility for TC ranged from 2% to 6% and from 6% to 11% (as one relative standard deviation), respectively. For the EC/TC ratio, repeatability and reproducibility ranged from 3% to 8% and from 9% to 27%, respectively. Combining the repeatability (sr) and reproducibility (sR) relative standard deviation for the EUSAAR_2 protocol obtained during the previous ILC exercises and the present one, we observed that the method precision (both sr and sR) for TC determination becomes exponentially poorer toward lower TC contents, i.e. <10 µgC / cm². For EC/TC determination, the method precision (*sR* and less evident for *sr*) can become poorer toward lower EC/TC ratios and exceptionally poor only for EC/TC ratios <0.07.

In addition, based on the results from the present inter-laboratory comparison and for the purpose of documenting the TC, OC and EC mass concentrations reported to the EBAS database, quality control measures, i.e. percentage bias and variability, were calculated for TC, OC and EC determination for each participant (ANNEX C).

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List of abbreviations and definitions

Abbreviations	Definitions
ACTRIS	Aerosol, Cloud and Trace Gases Research InfraStructure
TC	Total Carbon
EC	Elemental Carbon
OC	Organic Carbon
EMEP	Cooperative programme for monitoring and evaluation of the long range transmission of air pollutants in Europe
ERLAP	European Reference Laboratory for Air Pollution
PT	Proficiency Testing
PM	Particulate Matter
IPR	ISPRA
ILC	Inter-Laboratory Comparison

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Annexes

Annex A. Numerical results and z-scores

("-" corresponds to a "no entry")

Table A1. Total carbon (µg/cm^2) reported by each participant.

Participant	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	14.3	19.9	5.61	17.2	11.8	13.1	7.68	4.56
1	14.7	19.6	5.48	16.4	11.5	12.4	7.86	4.61
1	14.6	19.9	6.05	16.5	12.1	12.8	7.88	4.31
2	16.8	21.2	6.06	18.9	13.7	13.0	8.19	4.16
2	15.6	21.7	5.79	18.7	13.6	13.1	8.60	4.38
2	15.3	21.6	5.87	20.3	12.8	13.2	8.36	4.15
3	14.7	18.9	5.76	16.1	12.1	10.8	7.50	3.60
3	14.2	19.3	5.49	16.9	11.8	10.5	7.59	3.81
3	13.8	19.2	4.53	17.2	11.2	10.4	7.48	3.57
4	12.7	17.2	4.75	15.3	10.2	9.1	6.65	3.34
4	11.8	16.7	4.60	15.2	10.2	9.3	6.12	3.50
4	12.4	17.29	4.52	15.5	11.3	9.8	6.33	3.92
6	14.8	19.7	5.73	18.1	12.2	11.4	7.96	3.69
6	14.6	20.2	5.47	17.8	12.5	11.9	7.93	3.43
6	14.2	19.7	5.70	17.7	12.2	12.4	8.19	3.37
7	16.1	21.3	6.23	19.2	13.0	12.2	8.83	3.75
7	16.1	21.7	6.52	19.9	12.9	11.8	8.96	3.72
7	15.4	20.9	5.84	19.4	12.3	12.0	8.84	3.81
8	13.8	18.5	5.15	15.2	11.1	10.9	6.97	3.72
8	14.1	18.9	5.09	15.1	10.6	10.8	7.03	3.88
8	13.5	18.7	5.01	14.4	10.8	10.8	7.10	3.72
9	13.5	19.0	5.80	18.4	12.7	10.9	6.86	-
9	13.4	17.7	5.59	17.8	12.4	12.0	7.02	3.27
9	12.9	-	5.15	19.8	12.4	11.8	7.16	3.08
10	14.2	19.9	5.99	16.3	11.8	11.2	7.59	3.28
10	14.4	19.5	5.54	16.4	12.3	11.1	7.67	3.23
10	14.5	19.8	5.94	16.9	12.4	11.2	7.43	3.27
11	14.9	19.9	6.73	16.0	11.8	13.3	8.18	3.37
11	14.7	20.0	5.66	16.6	11.5	10.7	7.62	3.50
11	15.1	19.4	5.44	15.6	11.5	11.5	7.34	3.30
12	14.8	21.0	5.32	18.7	12.8	13.1	7.65	3.64
12	14.9	27.2	5.83	17.6	12.4	13.4	8.20	3.58
12	15.0	20.5	5.51	17.1	12.9	13.4	8.78	3.66

13	14.1	19.3	5.54	17.3	12.0	11.3	7.32	3.64
13	13.9	19.1	5.41	18.3	11.8	11.6	7.60	3.70
13	14.0	19.5	5.49	17.8	11.9	11.9	7.70	3.57
14	14.9	20.1	4.83	18.2	11.2	11.8	7.76	3.40
14	14.1	20.1	4.86	18.0	11.2	11.0	7.80	3.21
14	14.2	20.6	4.69	18.0	10.8	11.7	7.97	3.21
15	14.5	19.7	5.32	16.8	12.1	11.0	7.47	3.68
15	14.0	20.2	5.39	18.0	11.9	11.0	7.59	3.54
15	13.9	19.4	5.49	17.7	11.5	11.0	7.64	3.56
16	14.2	19.6	5.53	17.5	12.0	13.8	8.00	4.06
16	14.4	19.9	5.79	16.8	11.5	12.8	7.88	3.66
16	14.4	20.3	5.77	16.2	11.4	13.5	8.01	3.96
17	16.3	21.3	6.01	18.7	13.6	13.3	7.93	4.10
17	16.1	20.7	6.03	19.2	12.8	13.6	7.73	3.90
17	15.1	20.6	6.06	16.5	12.6	13.2	7.63	3.81
18	14.6	20.1	5.57	16.4	12.1	11.6	7.75	3.77
18	-	20.0	5.70	17.2	11.8	11.5	8.12	3.77
18	14.4	19.7	5.41	16.9	12.1	11.8	7.44	4.21
19	15.1	21.6	5.67	17.6	12.4	12.4	7.82	3.39
19	15.3	21.2	5.87	18.3	12.4	12.0	8.21	3.04
19	15.2	21.2	5.75	17.4	12.8	12.2	7.95	-
21	14.7	20.6	5.28	17.9	12.5	12.4	7.85	3.71
21	14.8	21.0	5.92	17.5	11.7	12.5	7.97	3.56
21	14.9	19.9	5.44	17.3	11.8	11.7	7.88	4.56
22	15.4	20.6	5.54	18.4	11.8	13.4	7.84	3.86
22	17.8	20.4	5.37	18.7	12.3	13.3	7.87	4.43
22	15.2	20.0	5.25	18.1	12.7	12.8	8.00	4.01
23	15.6	27.4	6.18	19.4	11.8	12.3	11.39	4.10
23	15.3	21.6	5.95	18.4	12.1	12.4	8.42	4.36
23	15.6	21.7	6.06	18.1	12.3	11.8	8.24	3.94
24	14.5	20.1	5.59	17.1	11.8	10.7	-	3.37
24	14.5	19.8	5.36	18.3	11.6	10.8	7.70	3.61
24	13.8	19.5	5.54	17.8	11.7	11.9	7.86	3.59
25	18.8	22.3	6.45	18.4	13.3	12.8	8.55	4.94
25	18.0	22.4	6.42	21.0	13.3	12.9	8.77	4.77
25	18.0	22.2	6.37	20.7	12.6	13.0	8.77	4.24
26	14.7	20.9	5.53	18.1	12.4	13.1	7.97	3.52
26	15.4	20.5	5.67	17.9	12.0	12.9	7.48	3.98
26	14.9	20.8	5.53	18.2	12.0	12.8	7.61	4.09
27	13.3	18.7	5.03	15.4	10.2	10.9	7.17	3.50

27	12.9	18.4	5.06	15.6	10.0	11.7	7.04	3.21
27	12.7	18.0	4.78	15.5	10.3	10.5	6.99	3.12
28	16.4	22.3	6.91	19.8	13.8	15.0	9.25	4.92
28	16.4	22.0	6.98	19.7	13.4	14.5	9.22	4.90
28	16.4	22.5	6.88	19.4	13.4	14.5	9.23	4.95
29	15.1	20.1	5.55	17.3	11.5	16.0	8.01	3.99
29	14.9	22.3	5.60	17.1	12.1	17.5	7.88	3.76
29	15.0	21.2	5.69	18.5	15.1	13.8	7.88	4.23
30	15.5	22.4	6.37	18.9	13.2	11.9	8.41	3.94
30	16.2	21.1	6.00	19.0	13.4	13.0	8.68	4.54
30	16.0	22.4	6.06	18.7	13.2	11.7	8.78	4.02
31	14.3	21.1	5.28	17.2	11.7	14.1	7.94	3.61
31	15.0	21.2	5.05	18.1	12.6	13.4	7.96	4.23
31	15.3	20.7	4.96	18.6	12.5	12.8	8.19	3.30
32	14.8	20.9	5.60	18.2	12.1	11.7	8.38	4.05
32	15.4	20.3	5.83	18.5	12.6	11.7	8.15	4.13
32	15.5	21.4	5.68	18.7	12.2	12.2	7.97	4.10
33	14.1	19.8	5.11	17.1	11.0	11.3	7.47	3.57
33	13.9	19.5	5.13	17.2	10.7	11.3	7.28	3.49
33	14.1	19.2	5.09	17.3	11.0	11.2	7.75	3.56
34	15.5	22.3	5.94	19.4	12.7	14.0	8.07	3.79
34	16.0	21.9	6.28	19.1	12.8	13.7	8.27	4.01
34	15.8	21.7	5.91	18.8	12.6	13.1	8.16	3.81
36	16.6	23.4	6.84	19.9	13.3	15.3	9.05	3.71
36	16.5	22.7	6.30	20.4	13.5	15.8	8.62	3.77
36	16.3	22.0	6.07	20.0	13.1	15.0	8.25	3.87
37	14.8	20.4	5.75	18.4	12.0	12.6	7.63	3.59
37	14.9	20.6	6.06	18.1	12.5	12.5	7.62	3.61
37	15.5	20.3	5.55	18.3	12.0	12.0	7.85	3.83
38	15.9	19.9	-	-	13.7	12.3	8.76	-
38	15.3	20.1	-	-	13.8	11.8	9.08	-
38	16.4	20.3	-	-	13.7	11.9	8.75	-
39	13.9	18.9	5.25	15.1	11.2	12.3	7.28	4.35
39	13.9	21.1	5.31	15.1	11.2	11.7	6.82	3.74
39	13.5	19.7	6.09	15.6	11.6	11.3	8.34	-
40	14.8	19.4	5.23	15.0	11.3	13.7	8.53	4.59
40	14.5	20.0	5.31	15.5	10.9	13.5	8.74	4.38
40	14.8	19.2	5.43	15.8	11.2	13.2	8.21	4.33

Source: JRC 2024.

Table A2: Elemental carbon / total carbon (ratio) calculated from the results reported by each participant.

Participant	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	0.187	0.192	0.169	0.116	0.163	0.088	0.076	0.091
1	0.178	0.195	0.165	0.112	0.164	0.096	0.076	0.090
1	0.183	0.189	0.184	0.108	0.159	0.096	0.078	0.104
2	0.175	0.199	0.187	0.121	0.168	0.111	0.079	0.110
2	0.181	0.200	0.192	0.118	0.165	0.112	0.073	0.108
2	0.182	0.207	0.181	0.119	0.170	0.115	0.076	0.109
3	0.186	0.213	0.167	0.243	0.154	0.113	0.075	0.122
3	0.173	0.193	0.185	0.119	0.154	0.119	0.080	0.110
3	0.179	0.213	0.021	0.116	0.170	0.128	0.073	0.089
4	0.180	0.211	0.174	0.122	0.180	0.130	0.098	0.123
4	0.195	0.214	0.170	0.126	0.179	0.129	0.075	0.121
4	0.294	0.200	0.178	0.125	0.172	0.136	0.096	0.109
6	0.176	0.217	0.164	0.106	0.178	0.114	0.071	0.123
6	0.190	0.206	0.174	0.105	0.171	0.112	0.076	0.134
6	0.191	0.216	0.165	0.122	0.175	0.116	0.067	0.129
7	0.150	0.189	0.156	0.107	0.153	0.121	0.070	0.120
7	0.163	0.205	0.155	0.109	0.157	0.123	0.076	0.113
7	0.168	0.189	0.161	0.109	0.165	0.117	0.075	0.113
8	0.162	0.190	0.172	0.129	0.167	0.121	0.097	0.118
8	0.170	0.194	0.172	0.119	0.158	0.127	0.095	0.113
8	0.172	0.195	0.169	0.131	0.160	0.127	0.098	0.110
9	0.213	0.234	0.247	0.128	0.213	0.138	0.147	-
9	0.215	0.238	0.227	0.160	0.198	0.137	0.124	0.127
9	0.208	-	0.245	0.148	0.202	0.157	0.133	0.188
10	0.187	0.209	0.170	0.126	0.181	0.127	0.076	0.127
10	0.181	0.207	0.176	0.122	0.178	0.132	0.077	0.140
10	0.184	0.204	0.166	0.121	0.172	0.126	0.082	0.136
11	0.234	0.239	0.149	0.142	0.203	0.249	0.218	0.206
11	0.226	0.000	0.172	0.139	0.199	0.278	0.140	0.000
11	0.220	0.211	0.185	0.148	0.208	0.187	0.131	0.270
12	0.167	0.188	0.170	0.105	0.161	0.123	0.089	0.117
12	0.163	0.134	0.151	0.110	0.164	0.123	0.074	0.116
12	0.162	0.181	0.166	0.111	0.157	0.121	0.072	0.119
13	0.179	0.204	0.163	0.137	0.161	0.123	0.084	0.111
13	0.179	0.209	0.165	0.122	0.163	0.122	0.085	0.110
13	0.182	0.204	0.165	0.122	0.164	0.120	0.081	0.111
14	0.190	0.217	0.154	0.116	0.165	0.119	0.075	0.108

14	0.187	0.213	0.158	0.115	0.158	0.117	0.080	0.104
14	0.187	0.214	0.160	0.112	0.166	0.117	0.073	0.114
15	0.191	0.197	0.190	0.126	0.162	0.117	0.091	0.129
15	0.194	0.197	0.205	0.121	0.168	0.121	0.095	0.129
15	0.183	0.202	0.193	0.123	0.167	0.120	0.080	0.135
16	0.171	0.184	0.177	0.085	0.159	0.106	0.056	0.082
16	0.152	0.200	0.162	0.085	0.179	0.106	0.051	0.093
16	0.150	0.172	0.180	0.092	0.162	0.104	0.055	0.096
17	0.169	0.200	0.161	0.118	0.157	0.116	0.092	0.117
17	0.167	0.199	0.160	0.110	0.176	0.124	0.102	0.127
17	0.163	0.191	0.165	0.125	0.168	0.120	0.081	0.127
18	0.182	0.200	0.192	0.119	0.173	0.121	0.066	0.106
18	-	0.200	0.159	0.099	0.156	0.106	0.059	0.103
18	0.173	0.203	0.172	0.107	0.182	0.125	0.084	0.081
19	0.214	0.241	0.163	0.127	0.183	0.146	0.075	0.042
19	0.205	0.230	0.156	0.134	0.189	0.145	0.062	0.029
19	0.211	0.234	0.156	0.129	0.184	0.144	0.064	-
21	0.187	0.185	0.194	0.118	0.151	0.109	0.082	0.127
21	0.181	0.196	0.169	0.123	0.163	0.115	0.087	0.145
21	0.177	0.194	0.189	0.127	0.175	0.106	0.084	0.128
22	0.175	0.205	0.169	0.121	0.167	0.120	0.078	0.119
22	0.161	0.205	0.177	0.116	0.171	0.118	0.082	0.113
22	0.178	0.204	0.182	0.120	0.171	0.120	0.082	0.125
23	0.135	0.170	0.141	0.089	0.129	0.091	0.077	0.068
23	0.130	0.159	0.138	0.090	0.133	0.095	0.051	0.080
23	0.129	0.156	0.139	0.095	0.139	0.091	0.058	0.061
24	0.164	0.198	0.145	0.117	0.157	0.110	-	0.105
24	0.160	0.193	0.147	0.112	0.160	0.114	0.074	0.093
24	0.174	0.189	0.151	0.111	0.160	0.115	0.064	0.101
25	0.159	0.177	0.167	0.126	0.149	0.118	0.089	0.101
25	0.149	0.169	0.172	0.111	0.153	0.116	0.084	0.105
25	0.149	0.174	0.155	0.120	0.156	0.103	0.080	0.112
26	0.191	0.191	0.163	0.115	0.166	0.129	0.083	0.117
26	0.178	0.196	0.151	0.116	0.169	0.117	0.080	0.106
26	0.181	0.194	0.176	0.113	0.172	0.120	0.079	0.115
27	0.193	0.211	0.175	0.139	0.190	0.134	0.074	0.120
27	0.191	0.216	0.183	0.143	0.187	0.130	0.080	0.118
27	0.196	0.215	0.180	0.144	0.180	0.132	0.080	0.121
28	0.179	0.200	0.141	0.096	0.173	0.124	0.068	0.122
28	0.179	0.198	0.142	0.094	0.173	0.126	0.068	0.122

28	0.180	0.200	0.141	0.096	0.173	0.126	0.069	0.124
29	0.208	0.226	0.180	0.138	0.170	0.118	0.090	0.135
29	0.215	0.212	0.180	0.142	0.163	0.112	0.095	0.138
29	0.204	0.231	0.181	0.138	0.153	0.132	0.096	0.132
30	0.189	0.216	0.166	0.113	0.172	0.123	0.086	0.130
30	0.184	0.206	0.178	0.116	0.173	0.123	0.081	0.116
30	0.188	0.200	0.163	0.117	0.175	0.135	0.081	0.134
31	0.195	0.263	0.153	0.167	0.185	0.146	0.094	0.006
31	0.225	0.255	0.135	0.144	0.217	0.163	0.095	0.137
31	0.186	0.257	0.133	0.142	0.229	0.119	0.093	0.042
32	0.219	0.238	0.205	0.158	0.197	0.151	0.101	0.135
32	0.215	0.237	0.213	0.156	0.193	0.149	0.102	0.128
32	0.216	0.226	0.203	0.147	0.201	0.150	0.097	0.130
33	0.189	0.218	0.186	0.141	0.177	0.120	0.085	0.115
33	0.193	0.212	0.180	0.141	0.187	0.125	0.087	0.116
33	0.190	0.215	0.186	0.129	0.181	0.124	0.084	0.110
34	0.181	0.193	0.173	0.119	0.157	0.124	0.072	0.115
34	0.187	0.193	0.158	0.120	0.151	0.123	0.083	0.101
34	0.185	0.195	0.168	0.116	0.165	0.121	0.083	0.132
36	0.163	0.178	0.154	0.106	0.165	0.120	0.082	0.089
36	0.158	0.185	0.163	0.111	0.167	0.125	0.089	0.109
36	0.166	0.188	0.168	0.111	0.171	0.134	0.096	0.096
37	0.223	0.235	0.174	0.127	0.180	0.134	0.095	0.122
37	0.211	0.227	0.169	0.121	0.174	0.126	0.092	0.119
37	0.196	0.223	0.177	0.131	0.185	0.128	0.089	0.110
38	0.208	0.226	-	-	0.166	0.103	0.183	-
38	0.210	0.225	-	-	0.194	0.097	0.202	-
38	0.193	0.212	-	-	0.171	0.089	0.177	-
39	0.172	0.192	0.156	0.130	0.164	0.109	0.081	0.101
39	0.173	0.174	0.163	0.123	0.170	0.121	0.087	0.115
39	0.183	0.190	0.143	0.124	0.161	0.121	0.075	-
40	0.166	0.182	0.167	0.132	0.162	0.113	0.079	0.107
40	0.163	0.179	0.166	0.129	0.166	0.121	0.074	0.105
40	0.184	0.191	0.171	0.138	0.168	0.129	0.074	0.112

Source: JRC 2024.

Table A3: Elemental carbon loadings (µg/cm^2) reported by each participant.

Participant	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	2.67	3.82	0.947	1.99	1.93	1.15	0.580	0.417
1	2.62	3.82	0.906	1.84	1.88	1.19	0.601	0.417
1	2.67	3.76	1.11	1.79	1.91	1.23	0.611	0.448
2	2.95	4.21	1.13	2.29	2.31	1.45	0.643	0.457
2	2.83	4.34	1.11	2.21	2.24	1.47	0.630	0.475
2	2.77	4.47	1.06	2.41	2.17	1.52	0.638	0.453
3	2.74	4.03	0.960	3.92	1.86	1.23	0.562	0.438
3	2.45	3.72	1.01	2.02	1.81	1.25	0.604	0.418
3	2.46	4.08	0.097	1.99	1.90	1.33	0.549	0.319
4	2.28	3.64	0.826	1.86	1.83	1.18	0.649	0.410
4	2.29	3.57	0.781	1.92	1.83	1.20	0.459	0.425
4	3.64	3.45	0.805	1.94	1.94	1.33	0.607	0.428
6	2.60	4.27	0.939	1.93	2.18	1.30	0.569	0.454
6	2.77	4.17	0.952	1.87	2.15	1.33	0.603	0.461
6	2.72	4.24	0.940	2.17	2.13	1.44	0.550	0.434
7	2.42	4.02	0.970	2.06	1.99	1.48	0.620	0.450
7	2.63	4.44	1.01	2.16	2.03	1.45	0.680	0.420
7	2.59	3.95	0.940	2.11	2.03	1.40	0.660	0.430
8	2.23	3.52	0.888	1.96	1.85	1.32	0.673	0.440
8	2.39	3.66	0.876	1.80	1.68	1.37	0.670	0.437
8	2.32	3.64	0.849	1.89	1.73	1.37	0.693	0.409
9	2.87	4.44	1.43	2.36	2.70	1.50	1.01	-
9	2.88	4.21	1.27	2.84	2.46	1.64	0.873	0.414
9	2.68	5.33	1.26	2.94	2.51	1.85	0.951	0.580
10	2.66	4.16	1.02	2.05	2.14	1.43	0.573	0.416
10	2.60	4.05	0.975	2.00	2.18	1.46	0.591	0.451
10	2.68	4.04	0.985	2.04	2.14	1.41	0.611	0.443
11	3.48	4.76	1.00	2.28	2.40	3.32	1.78	0.694
11	3.33	-	0.972	2.32	2.28	2.98	1.06	-
11	3.33	4.10	1.01	2.31	2.38	2.15	0.960	0.891
12	2.47	3.96	0.905	1.97	2.07	1.61	0.681	0.424
12	2.44	3.64	0.882	1.93	2.03	1.65	0.605	0.414
12	2.44	3.70	0.914	1.90	2.02	1.61	0.629	0.434
13	2.52	3.93	0.903	2.37	1.93	1.39	0.618	0.404
13	2.49	3.99	0.891	2.23	1.93	1.41	0.646	0.406
13	2.55	3.99	0.907	2.17	1.95	1.43	0.626	0.398
14	2.83	4.36	0.745	2.10	1.84	1.41	0.584	0.367

14	2.64	4.29	0.768	2.06	1.77	1.29	0.625	0.334
14	2.65	4.41	0.75	2.02	1.79	1.37	0.579	0.366
15	2.78	3.90	1.01	2.12	1.96	1.29	0.680	0.473
15	2.73	3.98	1.10	2.19	1.99	1.33	0.719	0.456
15	2.55	3.91	1.06	2.18	1.91	1.32	0.613	0.480
16	2.43	3.61	0.981	1.48	1.90	1.46	0.446	0.334
16	2.20	3.99	0.938	1.44	2.06	1.35	0.402	0.340
16	2.15	3.49	1.04	1.49	1.85	1.41	0.440	0.380
17	2.75	4.27	0.969	2.21	2.13	1.54	0.728	0.480
17	2.68	4.12	0.962	2.12	2.25	1.68	0.791	0.493
17	2.46	3.94	1.00	2.06	2.11	1.59	0.620	0.482
18	2.65	4.01	1.07	1.95	2.09	1.40	0.513	0.399
18	-	4.00	0.904	1.70	1.84	1.22	0.479	0.387
18	2.49	4.00	0.931	1.81	2.20	1.47	0.624	0.343
19	3.25	5.21	0.924	2.23	2.28	1.81	0.586	0.141
19	3.14	4.88	0.915	2.46	2.34	1.74	0.510	0.088
19	3.21	4.97	0.900	2.24	2.36	1.76	0.506	-
21	2.74	3.80	1.03	2.11	1.88	1.35	0.645	0.471
21	2.68	4.12	1.00	2.16	1.91	1.44	0.691	0.515
21	2.65	3.88	1.03	2.20	2.07	1.24	0.662	0.582
22	2.69	4.23	0.934	2.22	1.97	1.61	0.609	0.459
22	2.86	4.19	0.949	2.16	2.10	1.57	0.644	0.499
22	2.70	4.07	0.957	2.17	2.17	1.54	0.658	0.500
23	2.11	4.65	0.870	1.72	1.53	1.12	0.880	0.280
23	1.98	3.42	0.820	1.66	1.62	1.18	0.430	0.350
23	2.00	3.39	0.840	1.73	1.71	1.07	0.480	0.240
24	2.38	3.98	0.810	2.00	1.86	1.17	-	0.354
24	2.32	3.83	0.786	2.04	1.86	1.24	0.567	0.337
24	2.40	3.69	0.838	1.98	1.86	1.37	0.506	0.363
25	2.99	3.95	1.08	2.32	1.98	1.51	0.763	0.501
25	2.68	3.79	1.10	2.32	2.03	1.49	0.739	0.501
25	2.67	3.87	0.989	2.48	1.97	1.34	0.702	0.476
26	2.81	4.00	0.900	2.08	2.06	1.69	0.658	0.412
26	2.74	4.02	0.855	2.08	2.03	1.51	0.602	0.422
26	2.70	4.03	0.972	2.05	2.07	1.53	0.603	0.472
27	2.56	3.96	0.879	2.14	1.94	1.45	0.532	0.419
27	2.46	3.99	0.928	2.23	1.87	1.52	0.563	0.379
27	2.49	3.87	0.858	2.23	1.86	1.39	0.559	0.376
28	2.95	4.47	0.975	1.91	2.38	1.87	0.632	0.602
28	2.94	4.36	0.989	1.86	2.31	1.83	0.629	0.596

28	2.94	4.49	0.971	1.86	2.33	1.83	0.634	0.614
29	3.15	4.53	1.00	2.38	1.96	1.88	0.720	0.540
29	3.20	4.73	1.01	2.42	1.97	1.95	0.750	0.520
29	3.06	4.89	1.03	2.54	2.30	1.82	0.760	0.560
30	2.92	4.84	1.06	2.14	2.26	1.47	0.722	0.512
30	2.98	4.35	1.07	2.21	2.32	1.59	0.705	0.526
30	3.01	4.48	0.986	2.18	2.31	1.58	0.707	0.540
31	2.79	5.54	0.810	2.88	2.16	2.06	0.750	0.020
31	3.37	5.41	0.680	2.61	2.74	2.18	0.760	0.580
31	2.86	5.34	0.660	2.65	2.86	1.52	0.760	0.140
32	3.24	4.99	1.15	2.88	2.38	1.76	0.846	0.548
32	3.30	4.83	1.24	2.89	2.44	1.74	0.835	0.530
32	3.35	4.85	1.16	2.75	2.44	1.83	0.771	0.532
33	2.67	4.31	0.951	2.41	1.94	1.35	0.637	0.410
33	2.67	4.13	0.920	2.41	2.00	1.41	0.630	0.403
33	2.67	4.13	0.949	2.24	1.99	1.38	0.653	0.393
34	2.81	4.30	1.03	2.30	1.98	1.73	0.579	0.434
34	3.00	4.22	0.993	2.29	1.93	1.69	0.686	0.405
34	2.92	4.23	0.991	2.18	2.08	1.58	0.680	0.504
36	2.70	4.17	1.05	2.11	2.20	1.83	0.740	0.330
36	2.60	4.19	1.03	2.26	2.25	1.98	0.770	0.410
36	2.70	4.14	1.02	2.21	2.24	2.01	0.790	0.370
37	3.30	4.80	1.00	2.34	2.16	1.70	0.726	0.437
37	3.15	4.68	1.02	2.18	2.18	1.57	0.702	0.429
37	3.04	4.52	0.982	2.39	2.22	1.54	0.699	0.422
38	3.30	4.50	-	-	2.28	1.27	1.61	-
38	3.20	4.53	-	-	2.69	1.14	1.84	-
38	3.17	4.31	-	-	2.34	1.06	1.55	-
39	2.39	3.62	0.819	1.97	1.84	1.34	0.593	0.440
39	2.40	3.67	0.863	1.85	1.90	1.42	0.591	0.429
39	2.47	3.74	0.871	1.94	1.87	1.37	0.629	-
40	2.45	3.53	0.873	1.99	1.83	1.55	0.670	0.492
40	2.36	3.58	0.884	2.00	1.81	1.63	0.643	0.462
40	2.73	3.67	0.928	2.18	1.88	1.70	0.605	0.484

Source: JRC 2024.

Table A4: Organic carbon (μg/cm^2) reported by each participant.

Laboratory	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	11.6	16.1	4.66	15.2	9.89	11.9	7.10	4.13
1	12.1	15.8	4.57	14.6	9.64	11.2	7.26	4.20
1	11.9	16.2	4.95	14.7	10.1	11.5	7.27	3.87
2	13.9	17.0	4.93	16.6	11.4	11.5	7.54	3.70
2	12.8	17.3	4.68	16.5	11.3	11.6	7.97	3.90
2	12.5	17.1	4.80	17.9	10.6	11.7	7.72	3.70
3	12.0	14.9	4.80	12.8	10.2	9.61	6.94	3.16
3	11.7	15.5	4.48	14.9	9.94	9.28	6.99	3.39
3	11.3	15.1	4.44	15.2	9.31	9.06	6.93	3.25
4	10.4	13.6	3.92	13.4	8.32	7.87	6.00	2.93
4	9.5	13.1	3.82	13.3	8.35	8.06	5.66	3.08
4	10.1	13.8	3.71	13.6	9.34	8.47	5.72	3.49
6	12.2	15.4	4.79	16.2	10.1	10.1	7.39	3.24
6	11.8	16.1	4.51	16.0	10.4	10.6	7.32	2.97
6	11.5	15.4	4.76	15.6	10.1	11.0	7.64	2.93
7	13.7	17.3	5.26	17.1	11.0	10.7	8.21	3.30
7	13.4	17.2	5.51	17.7	10.9	10.4	8.28	3.30
7	12.8	16.9	4.90	17.3	10.3	10.6	8.18	3.38
8	11.6	15.0	4.27	13.3	9.21	9.60	6.30	3.28
8	11.7	15.2	4.22	13.3	8.88	9.48	6.36	3.44
8	11.2	15.1	4.16	12.5	9.04	9.43	6.40	3.31
9	10.6	14.6	4.37	16.1	10.0	9.40	5.85	-
9	10.5	13.5	4.32	15.0	10.0	10.4	6.14	2.85
9	10.2	-	3.89	16.9	9.92	10.0	6.21	2.50
10	11.6	15.8	4.98	14.2	9.65	9.80	7.02	2.86
10	11.8	15.5	4.56	14.4	10.1	9.62	7.08	2.78
10	11.8	15.7	4.96	14.9	10.3	9.78	6.82	2.82
11	11.4	15.2	5.72	13.7	9.38	10.0	6.40	2.67
11	11.4	-	4.69	14.3	9.18	7.73	6.56	-
11	11.8	15.3	4.43	13.3	9.08	9.32	6.38	2.41
12	12.4	17.1	4.41	16.7	10.8	11.5	6.97	3.21
12	12.5	16.6	4.95	15.6	10.4	11.8	7.59	3.16
12	12.6	16.8	4.60	15.2	10.9	11.8	8.15	3.22
13	11.6	15.3	4.63	14.9	10.1	9.90	6.70	3.23
13	11.4	15.1	4.52	16.1	9.91	10.2	6.96	3.29
13	11.5	15.5	4.58	15.6	9.95	10.5	7.08	3.17
14	12.1	15.8	4.09	16.1	9.33	10.4	7.17	3.03

14	11.5	15.8	4.09	15.9	9.42	9.70	7.17	2.88
14	11.5	16.2	3.94	16.0	9.01	10.3	7.40	2.85
15	11.8	15.9	4.31	14.7	10.1	9.69	6.79	3.21
15	11.3	16.2	4.29	15.8	9.89	9.64	6.87	3.08
15	11.4	15.4	4.43	15.6	9.57	9.66	7.03	3.08
16	11.8	16.0	4.55	16.1	10.1	12.3	7.55	3.72
16	12.2	16.0	4.85	15.4	9.47	11.4	7.48	3.62
16	12.3	16.8	4.73	14.7	9.57	12.1	7.59	3.58
17	13.6	17.1	5.04	16.6	11.4	11.7	7.20	3.62
17	13.4	16.6	5.07	17.1	10.5	11.9	6.94	3.40
17	12.7	16.7	5.06	14.4	10.4	11.7	7.01	3.33
18	11.9	16.1	4.49	14.4	10.0	10.2	7.24	3.37
18	-	16.0	4.80	15.5	10.0	10.3	7.64	3.38
18	11.9	15.7	4.48	15.1	9.94	10.4	6.81	3.87
19	11.9	16.4	4.74	15.4	10.2	10.6	7.24	3.25
19	12.2	16.3	4.95	15.8	10.0	10.3	7.69	2.96
19	12.0	16.3	4.85	15.1	10.5	10.4	7.44	
21	12.0	16.8	4.25	15.8	10.7	11.0	7.20	3.24
21	12.1	16.9	4.92	15.4	9.77	11.1	7.28	3.05
21	12.3	16.1	4.41	15.1	9.76	10.4	7.21	3.98
22	12.7	16.4	4.60	16.2	9.82	11.8	7.23	3.41
22	14.9	16.2	4.43	16.6	10.2	11.7	7.22	3.93
22	12.5	15.9	4.30	16.0	10.5	11.3	7.34	3.51
23	13.5	22.7	5.31	17.7	10.3	11.2	10.52	3.82
23	13.3	18.1	5.14	16.7	10.5	11.3	7.98	4.00
23	13.5	18.3	5.23	16.4	10.6	10.7	7.76	3.70
24	12.1	16.2	4.78	15.1	10.0	9.55		3.02
24	12.2	16.0	4.57	16.2	9.77	9.60	7.14	3.27
24	11.4	15.8	4.70	15.8	9.79	10.5	7.36	3.23
25	15.8	18.4	5.38	16.0	11.3	11.2	7.79	4.44
25	15.3	18.6	5.32	18.6	11.3	11.4	8.03	4.27
25	15.3	18.4	5.38	18.2	10.6	11.6	8.07	3.77
26	11.9	16.9	4.63	16.0	10.3	11.4	7.32	3.11
26	12.7	16.4	4.82	15.8	10.0	11.3	6.88	3.55
26	12.2	16.8	4.56	16.1	10.0	11.3	7.01	3.62
27	10.7	14.8	4.15	13.3	8.25	9.43	6.64	3.08
27	10.4	14.4	4.14	13.3	8.13	10.1	6.48	2.83
27	10.2	14.1	3.92	13.3	8.46	9.10	6.43	2.74
28	13.5	17.9	5.93	17.9	11.4	13.2	8.62	4.32
28	13.4	17.6	5.99	17.8	11.1	12.6	8.59	4.31

28	13.4	18.0	5.91	17.6	11.1	12.7	8.60	4.33
29	12.0	15.6	4.55	14.9	9.55	14.1	7.29	3.45
29	11.7	17.6	4.59	14.7	10.1	15.5	7.13	3.24
29	11.9	16.3	4.67	15.9	12.8	11.9	7.13	3.67
30	12.6	17.6	5.31	16.7	10.9	10.5	7.68	3.43
30	13.2	16.8	4.93	16.8	11.0	11.4	7.98	4.01
30	13.0	17.9	5.08	16.5	10.9	10.2	8.07	3.48
31	11.5	15.6	4.47	14.3	9.49	12.0	7.19	3.59
31	11.6	15.8	4.37	15.5	9.87	11.2	7.20	3.65
31	12.5	15.4	4.30	16.0	9.63	11.2	7.43	3.16
32	11.5	15.9	4.45	15.3	9.69	9.91	7.54	3.50
32	12.1	15.5	4.58	15.7	10.2	10.0	7.32	3.60
32	12.2	16.6	4.52	15.9	9.73	10.4	7.20	3.56
33	11.5	15.5	4.15	14.7	9.03	9.91	6.83	3.16
33	11.2	15.3	4.21	14.7	8.66	9.84	6.65	3.08
33	11.4	15.1	4.14	15.0	8.98	9.77	7.09	3.17
34	12.7	18.0	4.91	17.1	10.7	12.2	7.49	3.36
34	13.0	17.7	5.29	16.8	10.9	12.0	7.58	3.60
34	12.9	17.5	4.92	16.6	10.5	11.5	7.48	3.31
36	13.9	19.2	5.79	17.8	11.1	13.4	8.31	3.38
36	13.9	18.5	5.27	18.1	11.3	13.8	7.85	3.36
36	13.6	17.9	5.05	17.8	10.8	12.9	7.46	3.50
37	11.5	15.6	4.75	16.0	9.83	11.0	6.90	3.15
37	11.8	15.9	5.04	15.9	10.3	10.9	6.92	3.18
37	12.4	15.8	4.57	15.9	9.78	10.4	7.15	3.41
38	12.6	15.4	-	-	11.4	11.0	7.51	-
38	12.1	15.6	-	-	11.2	10.6	7.24	-
38	13.2	16.0	-	-	11.4	10.9	7.20	-
39	11.5	15.3	4.43	13.1	9.35	10.9	6.68	3.91
39	11.5	17.5	4.45	13.3	9.31	10.3	6.23	3.31
39	11.1	16.0	5.22	13.7	9.74	10.0	7.71	-
40	12.3	15.9	4.35	13.1	9.42	12.1	7.86	4.10
40	12.1	16.4	4.43	13.5	9.13	11.8	8.10	3.92
40	12.1	15.6	4.50	13.6	9.31	11.5	7.61	3.84

Source: JRC 2024.

Table A5: z-scores for TC.

		IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	CNR-ISAC	-0.37	-0.54	0.18	-0.68	-0.40	0.42	-0.23	1.8
2	UNIGE/INFN	1.0	0.76	0.62	1.1	1.37	0.74	0.71	1.1
3	UBA	-0.67	-1.1	-0.84	-0.65	-0.53	-1.5	-0.70	-0.45
4	LAERO	-2.6	-2.7	-2.3	-1.6	-1.82	-2.5	-2.60	-0.64
6	IMI	-0.37	-0.49	0.00	0.14	0.18	-0.30	0.12	-0.88
7	HMS	0.96	0.61	1.3	1.2	0.65	-0.22	1.5	-0.17
8	IDAEA-CSIC	-1.1	-1.4	-1.2	-1.9	-1.48	-1.2	-1.5	-0.14
9	IDAEA-CSIC	-1.6	-1.7	-0.27	0.67	0.39	-0.60	-1.5	-1.7
10	TROPOS	-0.51	-0.59	0.44	-0.80	-0.01	-0.96	-0.63	-1.5
11	FMI	0.02	-0.56	0.70	-1.1	-0.66	-0.38	-0.39	-1.2
12	LVGMC	0.04	1.8	-0.18	0.07	0.63	0.91	0.42	-0.54
13	RIVM	-0.88	-0.95	-0.35	0.08	-0.28	-0.56	-0.67	-0.51
14	LANUV	-0.50	-0.16	-1.9	0.26	-1.24	-0.67	-0.17	-1.5
15	SEA	-0.72	-0.57	-0.53	-0.13	-0.38	-1.1	-0.63	-0.62
16	ARPA Umb	-0.55	-0.42	0.14	-0.58	-0.58	0.96	0.02	0.17
17	INERIS	0.93	0.28	0.91	0.32	0.92	0.97	-0.31	0.29
18	TU Wien	-0.39	-0.44	-0.17	-0.59	-0.17	-0.54	-0.29	0.24
19	ECPL_UOC	0.32	0.66	0.29	0.04	0.46	-0.05	0.07	-1.6
21	LISA	-0.07	0.01	-0.20	-0.09	-0.17	-0.06	-0.09	0.32
22	ISSeP	1.2	-0.13	-0.56	0.49	0.13	0.80	-0.08	0.73
23	CLP-B	0.58	2.3	0.98	0.64	-0.07	-0.06	2.3	0.82
24	NPL	-0.60	-0.53	-0.31	0.02	-0.51	-0.97	-0.27	-0.81
25	NCSR D	3.3	1.4	1.8	1.6	1.02	0.54	1.2	2.2
26	CyI	0.10	0.17	-0.13	0.26	-0.02	0.59	-0.43	0.10
27	ICPF	-1.9	-1.6	-1.5	-1.5	-2.23	-1.09	-1.4	-1.5
28	IPIŚ PAN	1.5	1.3	2.9	1.3	1.56	2.1	2.1	2.9
29	NILU	0.09	0.52	-0.04	-0.07	0.83	3.0	-0.04	0.45
30	LSCE	1.0	1.1	1.2	0.80	1.23	-0.04	1.1	0.90
31	GIOS	-0.02	0.40	-1.2	0.21	0.11	1.0	0.13	-0.30
32	ECPL_UoC	0.32	0.30	0.16	0.54	0.15	-0.33	0.36	0.71
33	SLBV	-0.86	-0.77	-1.2	-0.35	-1.45	-0.91	-0.74	-0.76
34	UNIVIE	0.85	1.1	0.94	0.95	0.61	1.2	0.35	0.12
36	LU_Physics	1.5	1.7	1.8	1.7	1.29	2.7	1.1	-0.11
37	UCD AQRC	0.16	-0.07	0.35	0.37	0.02	0.10	-0.41	-0.40
38	IPH Bg	0.94	-0.29	-	-	1.80	-0.24	1.5	-
39	SU-ACES	-1.1	-0.47	-0.19	-1.7	-0.92	-0.43	-0.77	0.58
40	EC - JRC	-0.20	-0.75	-0.70	-1.5	-1.15	1.0	0.89	1.6

Source: JRC 2024.

Table A6: z-scores for EC/TC ratio.

		IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	CNR-ISAC	-0.07	-0.56	0.32	-0.66	-0.68	-2.6	-0.51	-1.25
2	UNIGE/INFN	-0.23	0.00	1.3	-0.20	-0.17	-0.81	-0.55	-0.31
3	UBA	-0.23	0.25	-2.96	2.3	-0.89	-0.14	-0.56	-0.45
4	LAERO	1.81	0.37	0.42	0.12	0.66	0.95	0.59	0.28
6	IMI	0.07	0.62	-0.01	-0.71	0.45	-0.71	-0.93	1.0
7	HMS	-1.1	-0.44	-0.72	-0.91	-0.96	-0.13	-0.76	0.11
8	IDAEA-CSIC	-0.77	-0.51	0.24	0.25	-0.68	0.30	1.2	0.00
9	IDAEA-CSIC	1.3	1.9	4.9	1.5	3.0	2.0	4.4	3.0
10	TROPOS	0.00	0.28	0.18	0.02	0.63	0.61	-0.36	1.4
11	FMI	2.0	-2.9	0.06	1.3	2.9	11	6.8	3.1
12	LVGMC	-0.94	-1.9	-0.36	-0.87	-0.78	0.03	-0.37	0.23
13	RIVM	-0.20	0.23	-0.23	0.28	-0.61	0.00	0.09	-0.20
14	LANUV	0.18	0.71	-0.71	-0.53	-0.60	-0.37	-0.56	-0.35
15	SEA	0.26	-0.17	1.9	0.06	-0.36	-0.20	0.52	1.2
16	ARPA Umb	-1.2	-0.94	0.37	-2.2	-0.28	-1.5	-2.4	-1.6
17	INERIS	-0.85	-0.29	-0.40	-0.31	-0.24	-0.17	0.79	0.66
18	TU Wien	-0.32	-0.06	0.44	-0.90	0.04	-0.42	-1.1	-1.16
19	ECPL_UOC	1.2	1.9	-0.63	0.47	1.3	2.2	-1.3	-5.3
21	LISA	-0.13	-0.57	1.1	0.02	-0.58	-1.10	0.15	1.3
22	ISSeP	-0.62	0.16	0.55	-0.24	-0.02	-0.20	-0.17	0.34
23	CLP-B	-2.5	-2.3	-1.9	-2.0	-3.1	-2.7	-1.7	-3.0
24	NPL	-0.86	-0.48	-1.4	-0.59	-0.91	-0.80	-1.2	-0.94
25	NCSR D	-1.5	-1.60	-0.21	-0.23	-1.4	-0.86	0.17	-0.51
26	CyI	-0.03	-0.46	-0.32	-0.51	-0.06	0.04	-0.15	-0.06
27	ICPF	0.43	0.70	0.78	1.25	1.4	0.97	-0.38	0.40
28	IPIŚ PAN	-0.22	-0.14	-1.8	-1.7	0.28	0.34	-1.2	0.61
29	NILU	1.2	1.2	0.86	1.1	-0.67	-0.10	0.96	1.5
30	LSCE	0.13	0.31	0.06	-0.45	0.31	0.48	0.00	0.89
31	GIOS	0.85	3.2	-1.9	1.8	3.5	2.0	1.0	-3.5
32	ECPL_UoC	1.5	1.80	2.7	2.0	2.4	2.6	1.5	1.2
33	SLBV	0.30	0.74	1.1	0.92	1.0	0.12	0.24	0.00
34	UNIVIE	0.01	-0.48	-0.11	-0.28	-1.1	0.10	-0.27	0.16
36	LU_Physics	-1.0	-1.0	-0.41	-0.85	-0.17	0.43	0.55	-1.1
37	UCD AQRC	1.2	1.5	0.36	0.24	0.88	0.72	0.81	0.22
38	IPH Bg	0.92	1.1	-	-	0.63	-2.4	8.9	-
39	SU-ACES	-0.39	-0.94	-0.95	0.21	-0.40	-0.42	-0.12	-0.39
40	EC DG JRC	-0.63	-1.0	0.02	0.67	-0.37	-0.06	-0.62	-0.37

Source: JRC 2024.

Table A7: percentage deviation (%) from assigned value for TC.

		IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	CNR-ISAC	-3	-3	1	-6	-3	4	-2	18
2	UNIGE/INFN	7	5	5	9	10	7	5	11
3	UBA	-5	-7	-7	-5	-4	-14	-5	-4
4	LAERO	-18	-17	-18	-13	-13	-24	-20	-6
6	IMI	-3	-3	0	1	1	-3	1	-9
7	HMS	7	4	10	10	5	-2	12	-2
8	IDAEA-CSIC	-7	-9	-10	-16	-11	-12	-12	-1
9	IDAEA-CSIC	-11	-11	-2	6	3	-6	-12	-17
10	TROPOS	-3	-4	3	-7	0	-9	-5	-15
11	FMI	0	-4	5	-9	-5	-4	-3	-12
12	LVGMC	0	12	-1	1	5	9	3	-5
13	RIVM	-6	-6	-3	1	-2	-5	-5	-5
14	LANUV	-3	-1	-15	2	-9	-6	-1	-14
15	SEA	-5	-4	-4	-1	-3	-10	-5	-6
16	ARPA Umb	-4	-3	1	-5	-4	9	0	2
17	INERIS	6	2	7	3	7	9	-2	3
18	TU Wien	-3	-3	-1	-5	-1	-5	-2	2
19	ECPL_UOC	2	4	2	0	3	0	1	-16
21	LISA	0	0	-2	-1	-1	-1	-1	3
22	ISSeP	8	-1	-4	4	1	7	-1	7
23	CLP-B	4	15	8	5	0	-1	18	8
24	NPL	-4	-3	-2	0	-4	-9	-2	-8
25	NCSR D	22	9	14	13	7	5	9	22
26	CyI	1	1	-1	2	0	6	-3	1
27	ICPF	-13	-10	-12	-12	-16	-10	-11	-15
28	IPIŚ PAN	10	9	23	11	11	20	16	29
29	NILU	1	3	0	-1	6	28	0	4
30	LSCE	7	7	9	7	9	0	8	9
31	GIOS	0	3	-10	2	1	9	1	-3
32	ECPL_UoC	2	2	1	4	1	-3	3	7
33	SLBV	-6	-5	-9	-3	-11	-8	-6	-8
34	UNIVIE	6	7	7	8	4	11	3	1
36	LU_Physics	11	11	14	14	9	25	9	-1
37	UCD AQRC	1	0	3	3	0	1	-3	-4
38	IPH Bg	6	-2	-	-	13	-2	11	-
39	SU-ACES	-8	-3	-1	-14	-7	-4	-6	6
40	EC DG JRC	-1	-5	-6	-13	-8	10	7	16

Source: JRC 2024.

Table A8: percentage deviation (%) form assigned value for EC/ TC ratio.

		IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
1	CNR-ISAC	-1	-5	3	-8	-5	-23	-7	-16
2	UNIGE/INFN	-3	0	11	-3	-1	-7	-8	-4
3	UBA	-3	2	-26	30	-6	-1	-8	-6
4	LAERO	21	3	4	1	5	8	8	4
6	IMI	1	5	0	-9	3	-6	-13	13
7	HMS	-13	-4	-6	-12	-7	-1	-11	1
8	IDAEA-CSIC	-9	-4	2	3	-5	3	17	0
9	IDAEA-CSIC	15	17	43	19	21	18	64	38
10	TROPOS	0	2	2	0	4	5	-5	18
11	FMI	23	-26	1	17	20	96	98	39
12	LVGMC	-11	-17	-3	-11	-5	0	-5	3
13	RIVM	-2	2	-2	4	-4	0	1	-3
14	LANUV	2	6	-6	-7	-4	-3	-8	-4
15	SEA	3	-2	17	1	-2	-2	7	15
16	ARPA Umb	-14	-8	3	-29	-2	-13	-35	-20
17	INERIS	-10	-3	-3	-4	-2	-1	11	8
18	TU Wien	-4	0	4	-12	0	-4	-16	-15
19	ECPL_UOC	14	16	-6	6	9	19	-19	-69
21	LISA	-1	-5	10	0	-4	-10	2	17
22	ISSeP	-7	1	5	-3	0	-2	-2	4
23	CLP-B	-29	-20	-17	-25	-21	-24	-25	-38
24	NPL	-10	-4	-12	-8	-6	-7	-17	-12
25	NCSR D	-17	-14	-2	-3	-10	-8	2	-7
26	CyI	0	-4	-3	-7	0	0	-2	-1
27	ICPF	5	6	7	16	9	9	-5	5
28	IPIŚ PAN	-3	-1	-16	-22	2	3	-17	8
29	NILU	14	11	8	14	-5	-1	14	19
30	LSCE	1	3	1	-6	2	4	0	11
31	GIOS	10	28	-16	23	24	17	14	-45
32	ECPL_UoC	18	16	23	26	16	23	21	15
33	SLBV	4	7	10	12	7	1	3	0
34	UNIVIE	0	-4	-1	-4	-7	1	-4	2
36	LU_Physics	-12	-9	-4	-11	-1	4	8	-14
37	UCD AQRC	14	13	3	3	6	6	12	3
38	IPH Bg	11	10	-	-	4	-21	128	-
39	SU-ACES	-4	-8	-8	3	-3	-4	-2	-5
40	EC DG JRC	-7	-9	0	9	-2	-1	-9	-5

Source: JRC 2024.

Annex B. METHOD PERFORMANCE

The assessment of the *method performance* aims at deriving, from the results of the present exercise, the precisions of the standard measurement method described in EN16909:2017, 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 test item except participants 9 (two replicates for IPRB and IPRH), 18 (two replicates for IPRA), 19 (two replicates for IPRH), 24 (two replicates for IPRG), 38 (no replicates for IPRC, IPRD and IPRH) and 39 (two replicates for IPRH). However, Cochran's critical values for three replicates were used for all test samples, i.e. 0.204 (outlier) and 0.168 (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.

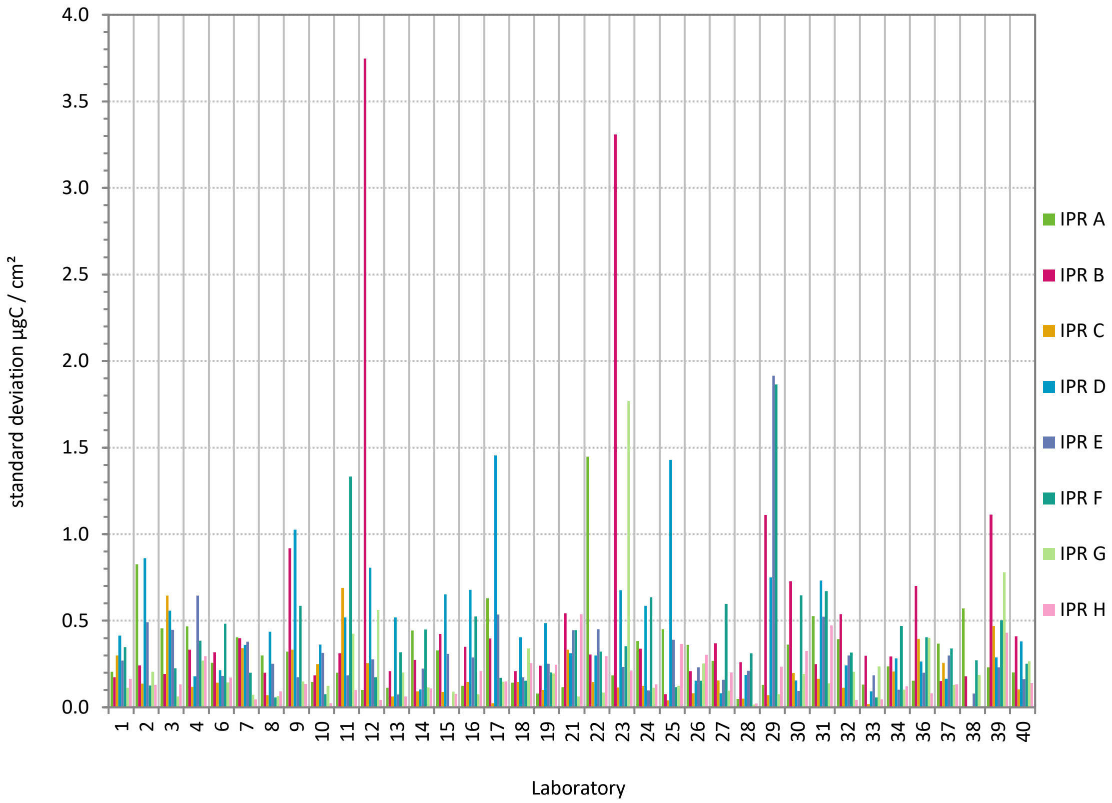
Grubb's test verifies the between-laboratory consistency (reproducibility) and is applied to test, at the first place, the significance of the largest observation (or two as for G_2), and then the significance of the smallest observation (or two as for G_2). For an inter-laboratory comparison among thirty-seven participants, the critical values for Grubb's test are 3.3434 and 0.564 -outliers for G_1 and G_2, respectively- and 3.003 and 0.625 - stragglers for G_1 and G_2, respectively.

Based on the outcomes of above statistical analyses, outliers are discarded. From the retained values and for each sample separately, the mean values and the method repeatability (*sr*) and reproducibility (*sR*) standard deviations are calculated. Subsequently, the dependence of precision (i.e. repeatability and reproducibility) upon the mean values is investigated [ISO5725-2].

B.1 Method performance for TC

Within-laboratory consistency. In Figure B1, 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 22/IPRA. 12/IPRB, 23/IPRB, 3/IPRC, 11/IPRC, 29/IPRE, 11/IPRF, 29/IPRF, 23/IPRG and 21/IPRH (participant/sample); 22/IPRA as straggler (participant/sample).

Figure B1. Standard deviation on the three replicates reported for each test filters, grouped by participant.

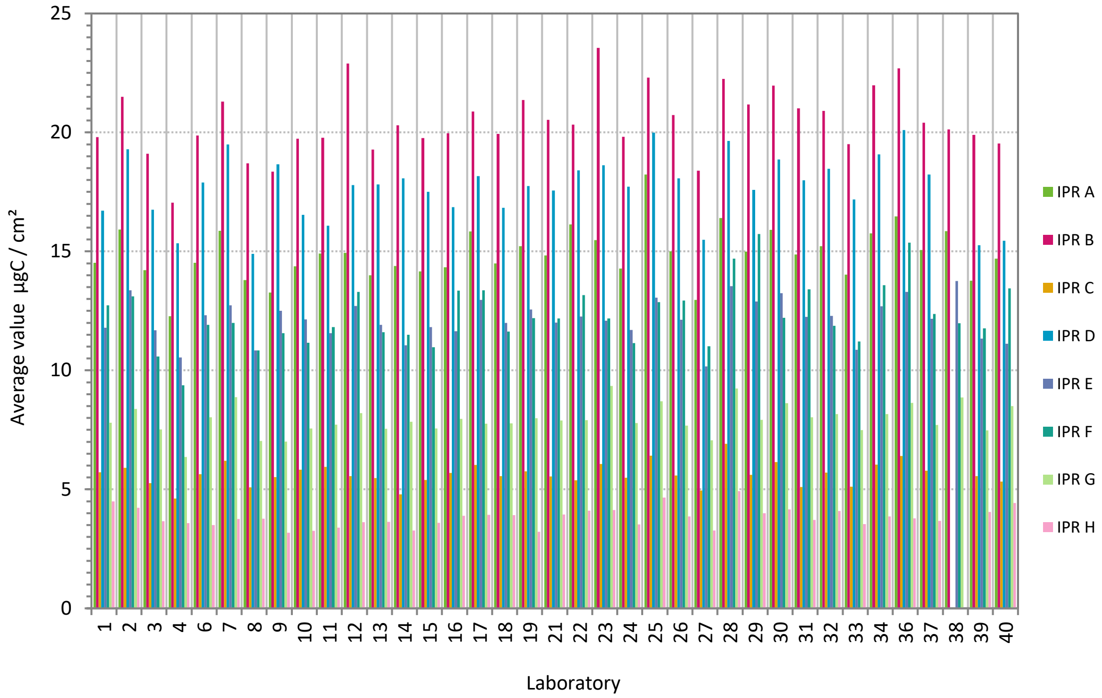


Source: JRC 2024.

Between-laboratory consistency. In Figure B2, 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 25/IPRA as straggler (participant/sample), and no outliers.

Figure B2. TC average values from three replicates reported by participants for each test sample, grouped by participant.



Source: JRC 2024.

Localized sample heterogeneities or contaminations cannot be rigorously excluded, but the occurrence of several outliers and/or stragglers from a single participant 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 B1.

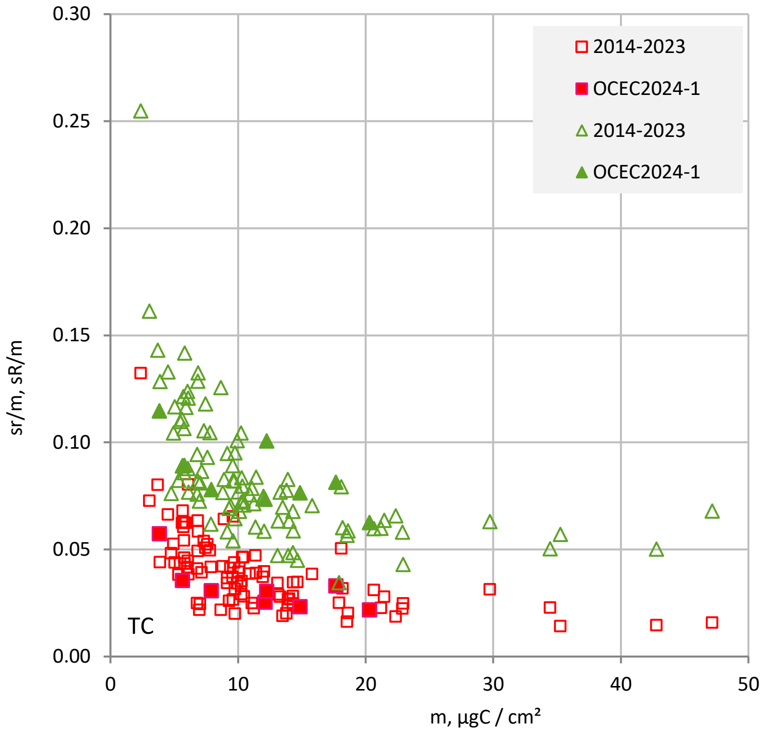
Table B1: General mean**,** repeatability (*sr*) and reproducibility (*sR*) standard and relative standard deviations for TC.

PT item	general mean	sr		sR	
	µgC / cm²	µgC / cm²	%	µgC / cm²	%
IPR A	14.9	0.345	2.3	1.14	7.6
IPR B	20.3	0.443	2.2	1.27	6.3
IPR C	5.64	0.201	3.6	0.503	8.9
IPR D	17.7	0.584	3.3	1.44	8.1
IPR E	12.1	0.307	2.5	0.889	7.3
IPR F	12.2	0.372	3.0	1.23	10
IPR G	7.91	0.244	3.1	0.617	7.8
IPR H	3.83	0.220	5.7	0.440	11

Source: JRC 2024.

Combining the repeatability and reproducibility relative standard deviations of the EUSAAR_2 protocol obtained during the previous ILCEs and the present one, we observe that the method precision (both *sr* and *sR*) for TC measurement becomes exponentially poorer toward lower TC contents i.e. < 10 µgC / cm² (Fig. B3).

Figure B3. Repeatability (squares) and reproducibility (triangles) relative standard deviation of the EUSAAR_2 protocol for TC measurement obtained during the previous inter-laboratory comparisons and the present one.



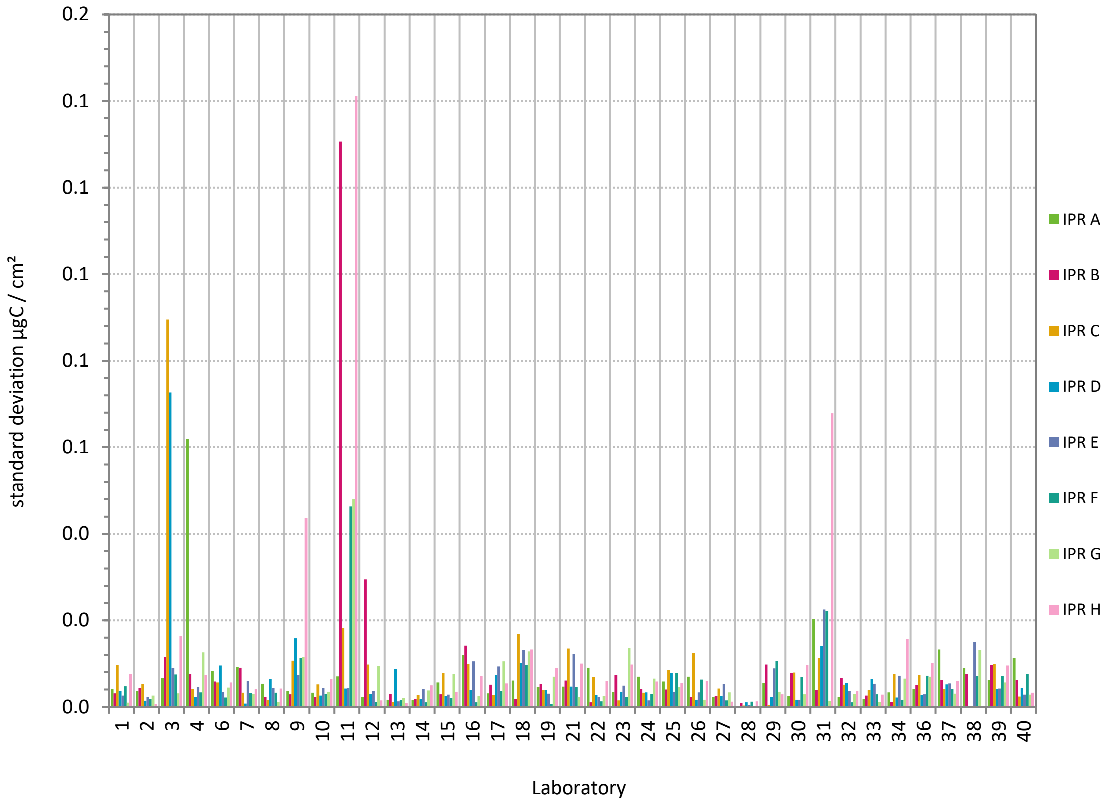
Source: JRC 2024.

B.2 Method performance for EC/TC

Within-laboratory consistency. In Figure B4, the standard deviations of the replicates reported for each test samples are presented grouped by participant.

Cochran's test identifies entries 4/IPRA, 31/IPRA, 11/IPRB, 12/IPRB, 3/IPRC, 3/IPRD, 9/IPRD, 31/IPRE, 11/IPRF, 31/IPRF, 11/IPRG, 11/IPRH and 31/IPRH as outliers and 17/IPRE and 19/IPRG (participant/sample). and no stragglers

Figure B4. Standard deviation on the EC/TC ratio replicates reported for each test filters, grouped by participant.

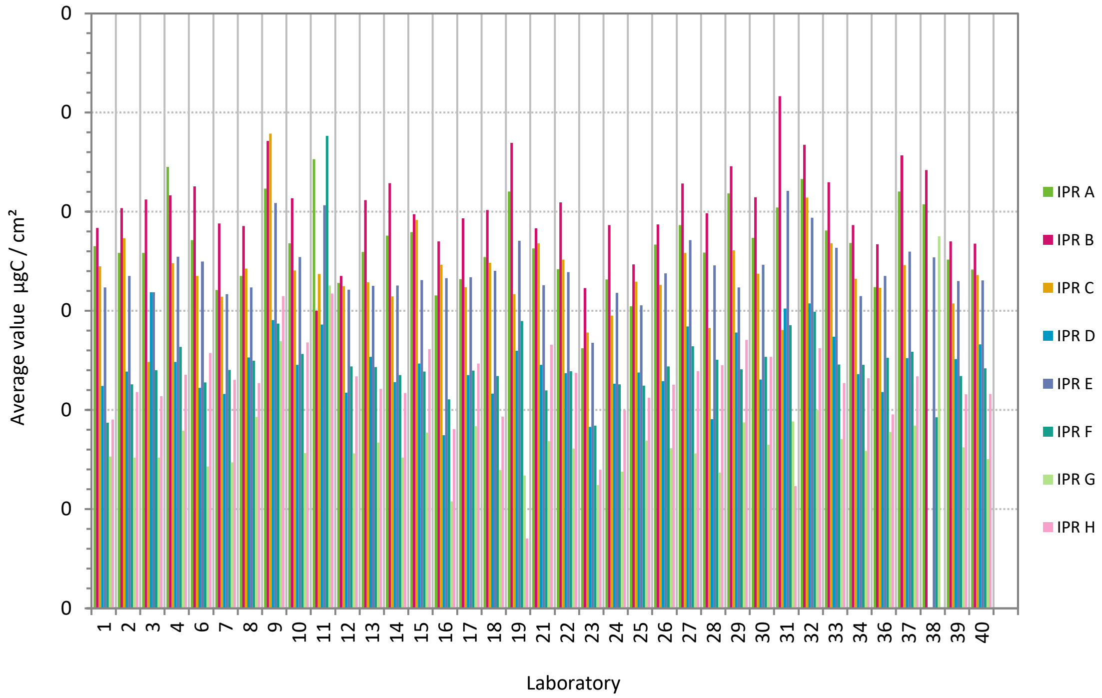


Source: JRC 2024.

__Between-laboratory consistency__. In Figure B5, 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 9/IPRC and 11/IPRF as outliers and no stragglers. Participant 23 applies the NIOSH-870 thermal protocol.

Figure B5. EC/TC average ratios from the replicates reported by participants for each test sample, grouped by participant.



Source: JRC 2024.

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 B2).

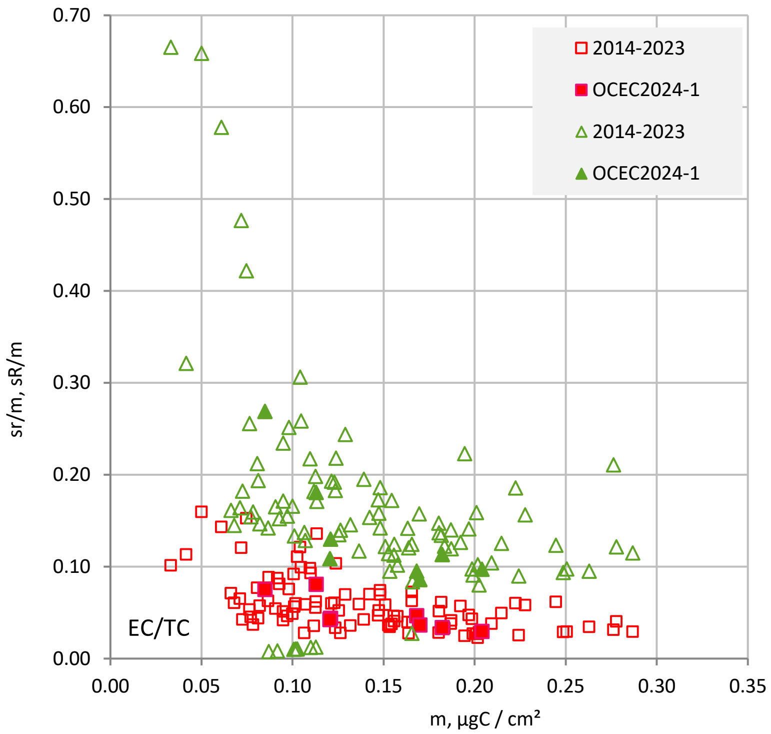
Table B2: General mean, repeatability (*sr*) and reproducibility (*sR*) standard and relative standard deviations for EC/TC.

PT item	general mean M, ratio	sr	%	sR	%
IPR A	0.182	0.006	3.4	0.021	11
IPR B	0.204	0.006	3.0	0.020	10
IPR C	0.168	0.008	4.7	0.016	10
IPR D	0.121	0.005	4.4	0.016	13
IPR E	0.170	0.006	3.7	0.015	8.6
IPR F	0.120	0.005	4.3	0.013	11
IPR G	0.085	0.006	7.5	0.023	27
IPR H	0.113	0.009	8.1	0.020	18

Source: JRC 2024.

Combining the repeatability and reproducibility relative standard deviation of the EUSAAR_2 protocol obtained during the previous four ILCEs and the present one, we observe that the method precision (*sR* and possibly *sr*) of EC/TC ratio measurement can become poorer at lower EC/TC ratios and exceptionally poor only for EC/TC ratios <0.070 (Fig. B6).

Figure B6. Repeatability (squares) and reproducibility (triangles) relative standard deviation for the EUSAAR_2 protocol for EC/TC measurement obtained during the previous inter-laboratory comparisons and the present one.



Source: JRC 2024.

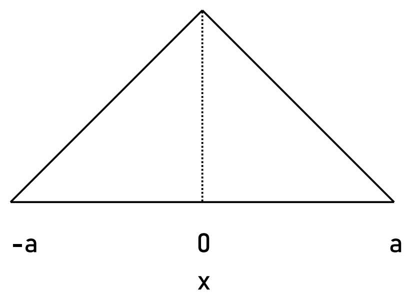
Annex C. QA MEASURES

Based on the results from the present inter-laboratory comparison and for the purpose of harmonizing the TC, OC and EC mass concentrations reported to the EBAS database, quality control measures, i.e. percentage bias and variability, were calculated for TC, OC and EC determination for each participant.

C.1 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).

Figure C1. Triangular distribution.



Source: 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

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

Equation C.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:

$$D_i = (L_i - T_i) / T_i$$

Equation C.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

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

Equation C.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:

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

Equation C.4

C.2 Calculation of QA bias = systematic error (RB%)

An estimation of bias in single measurements requires a long data series, and only a few samples in an 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 is considered approximate constant for the concentrations range used in the comparison. The differences D_i, as defined above are calculated as relative difference, and a median of these relative difference is defined as the QA bias. Median is chosen instead of average to avoid that one outlier get too high influence on the results.

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

Equation C.5

In Table C1 are reported the assigned values for TC, OC and EC calculated as described in par. 2.2.1. In Tables C2-4 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 C1. Assigned values for TC, OC and EC in µg cm^{-2}.

Assigned values								
	IPR A	IPR B	IPR C	IPR D	IPR E	IPR F	IPR G	IPR H
TC	14.9	20.5	5.63	17.7	12.2	12.3	7.95	3.83
OC	12.2	16.3	4.68	15.5	10.1	10.8	7.26	3.42
EC	2.73	4.13	0.950	2.15	2.07	1.50	0.653	0.435

Source: JRC 2024.

Table C2: QA bias and QA variability for TC.

		QA_bias	QA_variability	Systematic
1	CNR-ISAC	-2.2%	9.4%	no
2	UNIGE/INFN	6.9%	2.4%	high
3	UBA	-5.3%	4.0%	low
4	LAERO	-17.2%	7.1%	low
6	IMI	-1.3%	4.1%	no
7	HMS	5.7%	5.6%	no
8	IDAEA-CSIC	-10.3%	5.9%	low
9	IDAEA-CSIC	-8.1%	9.2%	no
10	TROPOS	-4.3%	7.4%	low
11	FMI	-3.5%	6.9%	no
12	LVGMC	1.9%	6.9%	no
13	RIVM	-5.1%	2.7%	low
14	LANUV	-4.8%	6.9%	low
15	SEA	-4.5%	3.8%	low
16	ARPA Umb	-1.2%	5.6%	no
17	INERIS	4.6%	4.6%	high
18	TU Wien	-2.5%	3.0%	low
19	ECPL_UOC	1.4%	8.2%	no
21	LISA	-0.6%	1.9%	no
22	ISSeP	2.5%	5.2%	no
23	CLP-B	6.4%	7.4%	no
24	NPL	-3.6%	3.8%	low
25	NCSR D	11.2%	7.1%	high
26	CyI	0.8%	3.6%	no
27	ICPF	-12.2%	2.5%	low
28	IPIŚ PAN	13.8%	8.2%	high
29	NILU	1.9%	11.8%	no
30	LSCE	7.8%	3.8%	high
31	GIOS	0.9%	7.7%	no
32	ECPL_UoC	2.1%	4.1%	high
33	SLBV	-6.7%	3.1%	low
34	UNIVIE	6.5%	4.0%	high
36	LU_Physics	10.6%	10.8%	high
37	UCD AQRC	0.5%	2.9%	no
38	IPH Bg	6.4%	6.3%	no
39	SU-ACES	-4.9%	7.9%	low
40	EC -JRC	-3.1%	11.7%	no

Source: JRC 2024.

Table C3: QA bias and QA variability for OC.

		QA_bias	QA_variability	Systematic
1	CNR-ISAC	-1.1%	9.6%	no
2	UNIGE/INFN	7.8%	3.1%	high
3	UBA	-4.4%	4.5%	low
4	LAERO	-17.5%	6.9%	low
6	IMI	-0.8%	5.5%	no
7	HMS	7.9%	6.5%	no
8	IDAEA-CSIC	-10.1%	5.6%	low
9	IDAEA-CSIC	-12.0%	10.1%	low
10	TROPOS	-3.8%	8.5%	low
11	FMI	-9.9%	12.9%	low
12	LVGMC	3.0%	6.1%	no
13	RIVM	-5.0%	2.5%	low
14	LANUV	-4.8%	7.2%	low
15	SEA	-5.3%	3.7%	low
16	ARPA Umb	0.4%	6.1%	no
17	INERIS	5.3%	5.0%	high
18	TU Wien	-1.9%	3.2%	low
19	ECPL_UOC	0.0%	5.3%	no
21	LISA	-0.2%	2.1%	no
22	ISSeP	2.8%	6.1%	no
23	CLP-B	11.2%	7.5%	high
24	NPL	-1.9%	3.8%	no
25	NCSR D	13.5%	8.5%	high
26	CyI	0.6%	3.3%	no
27	ICPF	-13.5%	3.1%	low
28	IPIŚ PAN	16.5%	7.2%	high
29	NILU	0.0%	12.9%	no
30	LSCE	7.3%	4.1%	high
31	GIOS	-2.0%	5.4%	no
32	ECPL_UoC	-1.7%	4.1%	no
33	SLBV	-7.5%	3.0%	low
34	UNIVIE	7.0%	4.4%	high
36	LU_Physics	13.7%	10.0%	high
37	UCD AQRC	-1.6%	3.1%	no
38	IPH Bg	0.8%	6.5%	no
39	SU-ACES	-4.3%	8.0%	no
40	EC - JRC	-0.9%	12.0%	no

Source: JRC 2024.

Table C4: QA bias and QA variability for EC

		QA_bias	QA_variability	Systematic
1	CNR-ISAC	-7.9%	10.0%	low
2	UNIGE/INFN	5.6%	7.6%	no
3	UBA	-10.0%	20.6%	low
4	LAERO	-11.8%	7.2%	low
6	IMI	-1.0%	6.6%	no
7	HMS	-1.0%	3.8%	no
8	IDAEA-CSIC	-11.0%	7.9%	low
9	IDAEA-CSIC	18.9%	17.1%	high
10	TROPOS	-2.1%	5.6%	no
11	FMI	18.7%	36.6%	high
12	LVGMC	-3.9%	7.6%	low
13	RIVM	-5.5%	5.3%	low
14	LANUV	-9.2%	10.6%	low
15	SEA	-0.5%	9.8%	no
16	ARPA Umb	-13.9%	15.5%	low
17	INERIS	3.7%	6.2%	no
18	TU Wien	-7.5%	7.9%	low
19	ECPL_UOC	10.0%	38.9%	no
21	LISA	-0.6%	12.6%	no
22	ISSeP	0.7%	5.8%	no
23	CLP-B	-21.1%	10.6%	low
24	NPL	-14.0%	5.2%	low
25	NCSR D	6.1%	8.0%	no
26	CyI	-1.8%	4.2%	no
27	ICPF	-7.4%	7.4%	low
28	IPIŚ PAN	7.5%	21.0%	no
29	NILU	14.1%	10.3%	high
30	LSCE	9.0%	8.0%	high
31	GIOS	20.5%	30.5%	no
32	ECPL_UoC	22.0%	6.3%	high
33	SLBV	-2.1%	7.2%	no
34	UNIVIE	4.0%	6.0%	no
36	LU_Physics	5.0%	18.1%	no
37	UCD AQRC	7.1%	7.0%	high
38	IPH Bg	-7.6%	104.1%	no
39	SU-ACES	-10.0%	4.6%	low
40	EC DG JRC	-5.0%	9.5%	no

Source: JRC 2024.

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