



Results of the inter-laboratory comparison exercise for TC and EC measurements  
(ref.: OCEC-2017-2)

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## Summary

The European Centre for Aerosol Calibration (ECAC) under ACTRIS-2 completed in September 2017 an inter-laboratory comparison for the measurement of total carbon (TC), elemental carbon (EC) and organic carbon (OC) in particulate matter collected on filters. The aim of this comparison was to evaluate the performances of the measurement method (i.e. reproducibility and repeatability) and of individual laboratories (biases).

This exercise was based on ambient PM<sub>2.5</sub> aerosol samples collected on quartz fiber filters at a regional background site in Italy and an urban background site in Spain. A solution of phthalic acid prepared at JRC-ERLAP (the inter-laboratory comparison exercise coordinator) was also distributed.

Fifteen laboratories participated in this exercise running their usual thermal-optical protocol (thirteen applied EUSAAR\_2 and two a QUARTZ/NIOSH protocol) with their usual analytical instrument. Among those, thirteen are AQUILA - National Air Quality Reference Laboratories responsible for OC and EC measurements in their countries (i.e. Germany, Greece, Poland, France, The Netherlands, Finland, Austria, Lithuania, Estonia, Switzerland, Croatia, United Kingdom, and Hungary).

Measurement method performance: for TC determination, repeatability and reproducibility relative standard deviations ranged from 3% to 6% and from 6% to 11% (as one relative standard deviation), respectively.

For the *EC/TC ratio*, *repeatability* ranged from 3% to 12%. The *reproducibility* was calculated in two cases, i.e. case a) including all participants and case b) excluding participants 5 and 8 applying QUARTZ/NIOSH protocol and ranged from 10% to 48% in the case a) and from 6% to 46% in case b). The reproducibility standard deviation for EC/TC improves significantly for all samples, on average of 35%, when a single common thermal-optical protocol is applied.

Based on last six inter-laboratory comparisons, repeatability and reproducibility standard deviations show an inverse dependence on TC loadings and on EC/TC ratios becoming exponentially poorer toward lower TC contents i.e. <10 µgC / cm<sup>2</sup> and EC/TC ratio. i.e. <0.07, respectively.

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 and among all participants applying the European standard protocol EUSAAR\_2 for EC/TC ratio. The assigned value for the concentration of phthalic acid was determined from primary gravimetric and volumetric measurements.

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* ( $\sigma^*$ ) *from the data obtained in the round of the proficiency testing scheme*.

For TC loadings, one outlier and three stragglers were identified; and 87% of all entries were within 10% from the assigned TC concentration value.

Regarding EC/TC ratios, eight outliers and nine stragglers were identified. 47% of all entries were within 10% of the assigned value and 79% were within 25% of the assigned value. More than half of outliers and stragglers were reported by laboratories applying a QUARTZ/NIOSH-like thermal-optical protocol.

Although the contribution of localized sample heterogeneities and/or contaminations to biased data cannot be totally excluded, the random scheme adopted to distribute sub-samples was such that the recurrence of stragglers or outliers (more than two) for single laboratories most probably indicates an unsatisfactory laboratory performance as compared to the other participants. Laboratories showing unsatisfactory precision (both in terms of repeatability and reproducibility) or significant 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.

## 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 due to inhalation and indication of air pollution sources. For these reasons requirements for measuring EC and OC in PM<sub>2.5</sub> at rural background locations have been included in Air Quality Directive 2008/50/EC.

The Directive states that measurements should be made in a manner consistent with those of the cooperative programme for monitoring and evaluation of the long range transmission of air pollutants in Europe (EMEP). Thermal-optical analysis has been recognized as the most suitable method for the determination of EC and OC collected on filters and the thermal protocol EUSAAR\_2 with a transmittance optical correction for pyrolysis has been recently selected as the European standard thermal protocol (EN16909:2017).

Addressing a request from the AQUILA network (<https://ec.europa.eu/jrc/en/aquila>), ERLAP as a partner of the European center for aerosol calibration (ECAC) within the European project ACTRIS-2 has organized in July-September 2017 an inter-laboratory comparison exercise (ILCE) (ref. OCEC-2017-2) among National Air Quality Reference Laboratories responsible for OC and EC measurements in their countries (i.e. Germany, Greece, Poland, France, The Netherlands, Finland, Austria, Lithuania, Estonia, Switzerland, Croatia, United Kingdom, and Hungary). The air quality agency of Paris also participated.

## 1 Organization

### 1.1 Samples, sub-samples and sub-sample homogeneity

In lack of suitable certified reference material for atmospheric OC and EC, this ILCE made use of ambient (outdoor) PM aerosol collected with high-volume samplers on quartz fiber filters at two sites across Europe (Table 1). Upon receipt at ERLAP, filters were stored in a refrigerator.

**Table 1:** filter test samples used for the inter-laboratory comparison

Sampling location				Sample collection		
Station	Country	Symbol	Site type	Period	Size fraction	Filter type
Barcelona	Spain	TER1 _	Urban background	Dec.2016	PM2.5	Pallflex
Ispra	Italy	IPR_	rural	Dec.2016/Jan. 2017	PM2.5	Pallflex

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

The homogeneity of these test samples was investigated by ERLAP on one of the test samples for each location. From each sample, ten subsamples of 1 cm<sup>2</sup> were taken along two perpendicular axes across the filter surface and analysed for their TC, OC and EC contents. The filter homogeneity was assessed as the standard deviation of the average of the 10 replicate analyses. This leads to an upper limit for the filter homogeneity since it includes the repeatability

of the ERLAP laboratory (< 3 and 5% for TC and EC, respectively). The homogeneity was better than 4 and 3% for TC and EC/TC, respectively (Table 2). If sampling at each location occurred under repeatable conditions, it can be assumed that the remaining test samples had similar homogeneities.

**Table 2:** homogeneity of the deposits on filters collected with the samplers used to produce the eight test filters. Analyses were performed with the protocol EUSAAR\_2 and charring correction by transmittance monitoring.

Test sample and origin		Homogeneity for TC (%)	Homogeneity for EC/TC (%)
IPR_	Ispira (I)	3.8	2.7
TER1	Barcelona(E)	2.4	1.9

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

## 1.2 Participants

Participants were selected among applicants to ECAC choosing in a first place the National Air Quality Reference Laboratories, members of the AQUILA network, and then laboratories which could also benefit from the outcome of this exercise in term of their expertise development. The list of the fifteen participants is reported in Table 3. For brevity, the number assigned to each participant will be used in the remainder of the document.

## 1.3 Sample shipment and reporting of results

Test samples were shipped to all participants (except the “local” participant 19) on 04<sup>th</sup> July 2017 via courier at ambient temperature without temperature record in closed petri dishes. Participants were asked to report TC and EC concentration, in  $\mu\text{g C cm}^{-2}$  units with three decimal digits, from three replicates of test ambient PM samples, by the end of September 2017. In addition, participants were asked to report the OC content of 10  $\mu\text{l}$  of a phthalic acid solution ( $\mu\text{g} / 10 \mu\text{l}$ ) precisely prepared and traceable to primary measurements.

## 1.4 Thermal-optical analysis

The thermal protocol EUSAAR\_2 [Cavalli et al., 2010] with a transmittance optical correction for pyrolysis has been recently selected as the European standard thermal protocol for the measurements of TC, OC and EC in PM samples (EN16909:2017).

In this exercise all participants but two (5 and 8) applied the EUSAAR\_2 protocol (Table 4) with transmittance-based correction. Participant 5 applied the QUARTZ protocol and participant 8 the NIOSH870 protocol.

**Table 3:** List of participants in the inter-laboratory comparison 2017-2, and contact persons

Code	Participant	Acronym	Contact
1	Wesołowska Łucja, Stępniewska Alicja	JGORA-PIOS	izabela.kaluzinska@jgora.pios.gov.pl
2	Mr. Attila Machon	HMS	machon.a@met.hu
4	McGhee, Elizabeth	NPL	elizabeth.mcghee@npl.co.uk
5	Godec, Ranka	IMROH	rgodec@imi.hr
6	Koerner, Johannes	LANUV	Johannes.Koerner@lanuv.nrw.de
7	Szidat, Sönke	LARA Bern	szidat@dcb.unibe.ch
8	Arkadi Ebber	KLAB-EE	arkadi.ebber@klab.ee; toivo.truuts@klab.ee
11	Arnaud Papin	INERIS	Arnaud.papin@ineris.fr
13	Loreta Vitkauskaitė	AAA	loreta.vitkauskaitė@aaa.am.lt
14	Aurela, Minna	FMI_field	Minna.Aurela@fmi.fi
15	Svensson, Jonas	FMI_lab	Jonas.Svensson@fmi.fi
16	Henzing, J.S. (Bas)	TNO	Bas.henzing@tno.nl
17	Haller, Theresa and Schuh, Harald	UNIVIE	theresa.haller@gmx.at; harald.schuh@univie.ac.at
18	ARBOUCHE Chadia	AIRPARIF	chadia.kebbi@airparif.fr
19	Fabrizia Cavalli	EC JRC C5	fabrizia.cavalli@ec.europa.eu

**Table 4:** List of the analytical protocol and punch size used by each participant

Code	Participant	Instrument	Protocol	Punch size (cm <sup>2</sup> )
1	JGORA-PIOS	Serial Nr. 268-67	EUSAAR_2	1.50
2	HMS	Model 5L, Serial Nr. 386-167	EUSAAR_2	1.00
4	NPL	Model 5, Serial Nr. 185	EUSAAR_2	1.50
5	IMROH	Model 4L (2006), Serial Nr. 195	Quartz	1.50
6	LANUV	Model 4L, Serial Nr. 337-2013	EUSAAR_2	1.50
7	LARA Bern	Model 4L, Serial Nr. 232-5001	EUSAAR_2	1.50
8	KLAB-EE	Serial Nr. 364-152	NIOSH870	1.50
11	INERIS	Model 5, Serial Nr. 376	EUSAAR_2	1.50
13	AAA	Model 4L, Serial Nr. 249-49	EUSAAR_2	1.50
14	FMI_field	Model 4, Serial Nr. RT-3183	EUSAAR_2	2.27
15	FMI_lab	Model 5L, Serial Nr. 377-161	EUSAAR_2	1.00
16	TNO	Serial Nr. 209-24	EUSAAR_2	1.50
17	UNIVIE	Model 5, Serial Nr. 223-34	EUSAAR_2	1.50
18	AIRPARIF	Model 5L, Serial Nr. 400-178	EUSAAR_2	1.50
19	EC JRC C5	Serial Nr. 173-5	EUSAAR_2	1.00

**Table 5:** Details of the analytical protocol implemented by all participants

Carrier gas	EUSAAR_2		QUARTZ/NIOSH870	
	Time (s)	Temp. (°C)	Time (s)	Temp. (°C)
Helium	120	200	70/80	310
Helium	150	300	60/80	475
Helium	180	450	60/80	615
Helium	180	650	90/110	875/870
Helium			45	550
Oxygen in Helium (2%)	120	500	45	625
Oxygen in Helium	120	550	45	700
Oxygen in Helium	70	700	45	775
Oxygen in Helium	80/110	850	45	850
Oxygen in Helium			120/110	870

## 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 collected on filters as test samples.

In this report we focus on the *TC loadings* (in  $\mu\text{g cm}^{-2}$ ) and *EC/TC ratios* reported by each participants for each test sample. TC represents the most robust (and protocol-independent) output of TOA analyses, while EC/TC ratios are free from biases in the total carbon determination calibration, and reflect possible differences in the OC/EC split determination among participants. On average, reported TC loadings ranged from 5.6 to 18  $\mu\text{g cm}^{-2}$ , corresponding to atmospheric concentrations ranging from 1 to 4.3  $\mu\text{g m}^{-3}$  collected for 24h at a face velocity of 54  $\text{cm s}^{-1}$ . EC/TC ranged on average from 0.07 to 0.26. All submitted results (in  $\mu\text{g cm}^{-2}$ ) for TC, EC, OC (calculated as  $\text{OC} = \text{TC} - \text{EC}$ ) and EC/TC ratio are presented in tables in Annex 1.

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

### Assigned values:

As ambient PM collected on filters was used as test samples, the true values for *TC and EC/TC loadings* were not known. The assigned value and its standard uncertainty for TC on each test filter was calculated as the robust average among values from all participants- i.e. including also participants 5 and 8 applying the QUARTZ and NIOSH 870 protocol, respectively (see Par 2.2); whereas the assigned value and its standard uncertainty for EC/TC ratio on each filter was calculated among values from participants applying the EUSAAR\_2 protocol only, being the European standard thermal protocol (EN16909:2017).

It has been demonstrated that TC values from various thermal protocols do not significantly differ but EC/TC ratios can with EC/TC ratio from the QUARTZ/NIOSH870 protocol being typically lower than those from the EUSAAR\_2 protocol. In the present exercise EC/TC ratios from laboratories 5 and 8 were indeed the lowest values reported for seven out of eight test filters.

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

## **2.1 TEST FILTER SAMPLES - Method performance**

### **2.1.1 Data evaluation description**

The assessment of the *method performance* aims at deriving, from the results of the present exercise, the precisions of the measurement method in terms of repeatability and reproducibility standard deviations. For this, the consistency of the dataset is evaluated by means of Cochran's test and Grubbs' test [ISO5725-2] for possible outliers (i.e. observations greater than the critical value at the 99% confidence level) or stragglers (i.e. observations greater than the critical value at the 95% confidence level but less or equal to the critical value at the 99% confidence level). Cochran's test verifies the within-laboratory consistency (repeatability). The critical values for *Cochran's test* (i.e. outlier and straggler) vary upon the number of participants and the number of replicate measurements. In this comparison exercise, all fifteen laboratories provided three replicates for every sample, thus Cochran's critical values are 0.407 (outlier) and 0.335 (straggler).

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

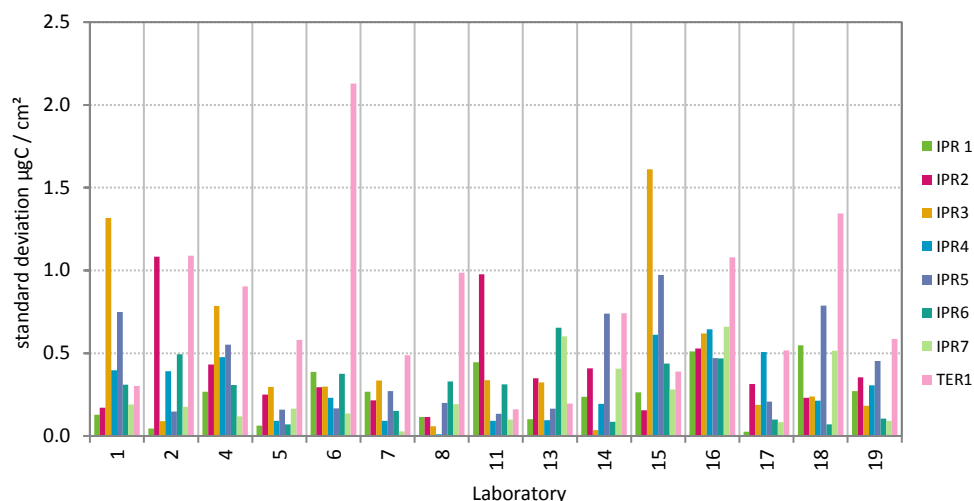
Grubb's test verifies the between-laboratory consistency (reproducibility) and is applied to test, at the first place, the significance of the largest observation (or two as for  $G_2$ ), and then the significance of the smallest observation (or two as for  $G_2$ ). For an inter-laboratory comparison among fifteen participants, the critical values for Grubb's test are 2.806 (outlier) and 2.549 (straggler).

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

### **2.1.2 Results: Method performance for TC**

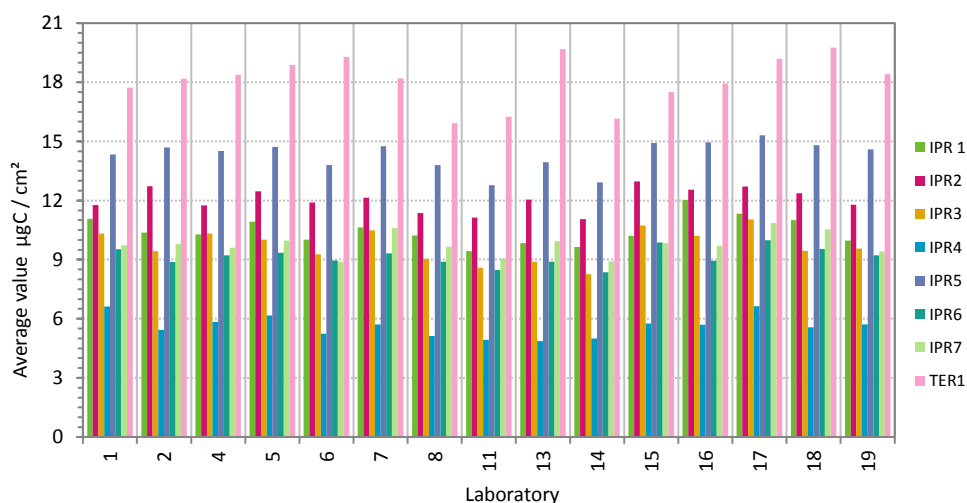
Within-laboratory consistency. In Figure 1, the standard deviations on the three replicates reported by laboratories for each test samples are presented grouped by laboratory. Cochran's test identifies as outliers 1/IPR3 and 15/IPR3 (laboratory/sample) and 2/IPR2 and 6/TER1 as stragglers (laboratory/sample).





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

Between-laboratory consistency. In Figure 2, the average values from three replicates reported by laboratories for each test sample are presented grouped for each laboratory. The  $G_1$  and  $G_2$  Grubbs' tests verify the absence of outliers and stragglers in the TC dataset.



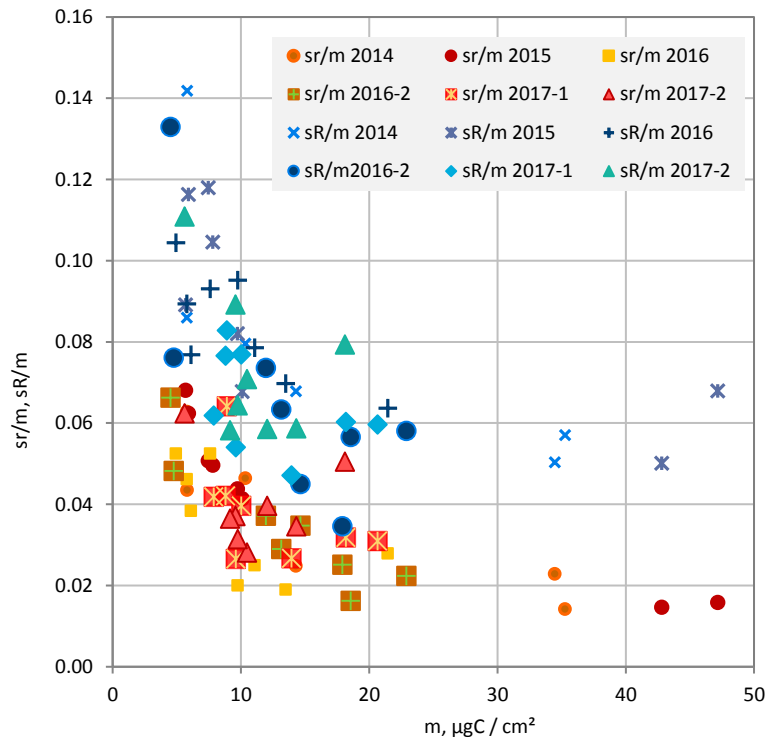
**Figure 2.** TC average values from three replicates reported by laboratories for each test sample, grouped by laboratory.

The entries identified as outliers by the statistical tests are discarded from the dataset, and from the retained values and for each sample separately, the mean value, the method repeatability ( $sr$ ) and reproducibility ( $sR$ ) standard deviations are calculated. The general means and values of  $sr$  and  $sR$  for the eight test filter samples are listed in Table 6. Both repeatability and reproducibility relative standard deviations tend to have an inverse dependence on TC for all samples expect for TER1 where, despite the highest TC loading, poor values for repeatability and reproducibility relative standard deviations are obtained. Localized sample heterogeneities and /or contaminations can be the cause of such poor precision.

**Table 6:** 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 1	10.47	0.29	2.8	0.74	7.1
IPR2	12.05	0.48	4.0	0.71	5.9
IPR3	9.58	0.36	3.7	0.85	8.9
IPR4	5.62	0.35	6.2	0.62	11.1
IPR5	14.32	0.50	3.5	0.84	5.9
IPR6	9.16	0.33	3.7	0.53	5.8
IPR7	9.75	0.31	3.1	0.63	6.4
TER1	18.10	0.91	5.0	1.44	7.9

Combining the repeatability and reproducibility relative standard deviation for the EUSAAR\_2 protocol obtained during the previous four ILCEs and the present one, we observe that the method precision (both *sr* and *sR*) for TC measurement becomes exponentially poorer toward lower TC contents i.e.  $< 10 \mu\text{gC} / \text{cm}^2$  (Fig. 3).



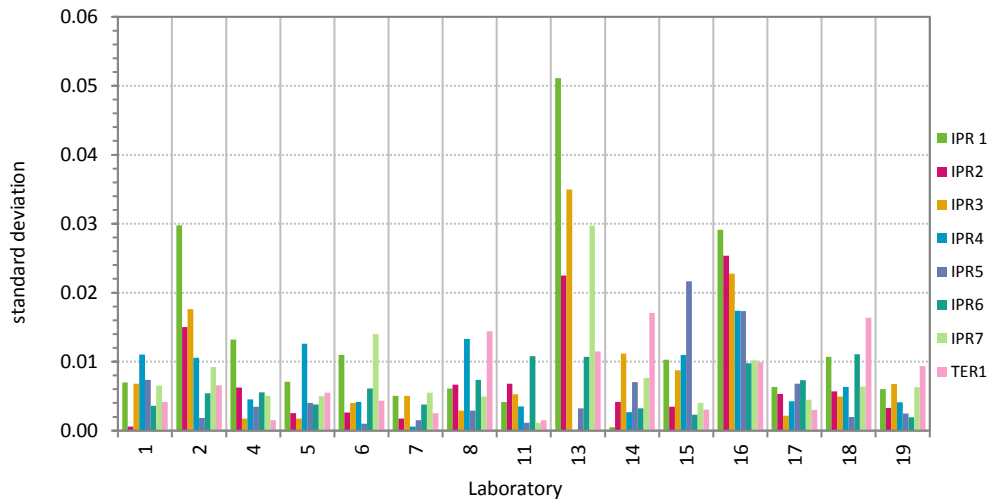
**Figure 3.** Repeatability and reproducibility relative standard deviation for the EUSAAR\_2 protocol for TC measurement obtained during the previous inter-laboratory comparisons and the present one.

### 2.1.3 Results: Method performance for EC/TC

*Within-laboratory consistency.* As there is no evidence that the within-laboratory consistency depends on the thermal-optical protocol applied, the within-laboratory consistency is analyzed on the entire dataset, i.e. including also entries from QUARTZ/NIOSH-like protocols, i.e. from participants 5 and 8. In Figure 4, the standard deviations of the three replicates reported for

each test samples are presented grouped by laboratory. Cochran's test identifies 13/IPR1, 13/IPR3, 16/IPR3, 15/IPR5, 16/IPR5 and 13/IPR7 as outliers (laboratory/sample) and 16/IPR2 as straggler.

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



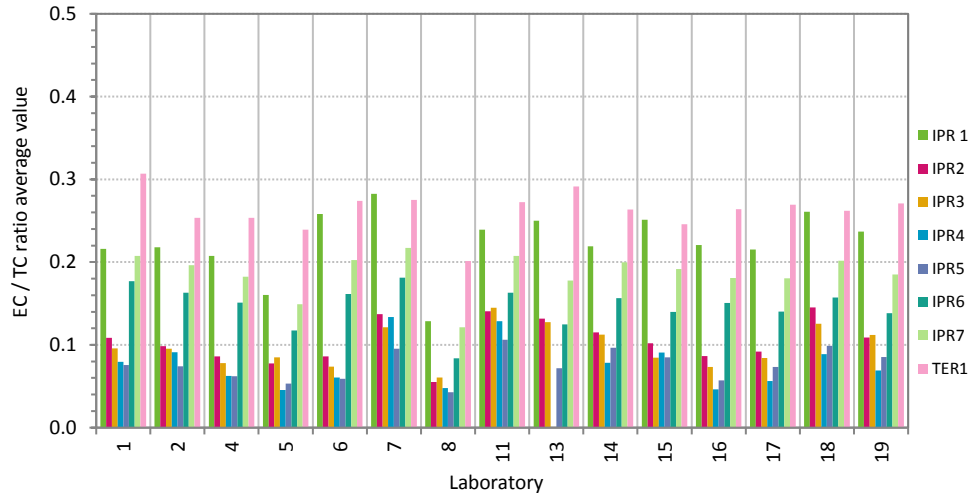
**Figure 4.** Standard deviation on the three replicates reported for each test filters, grouped by laboratory.

Between-laboratory consistency. It is well known that EC/TC ratio from different thermal-optical protocols might significantly differ with EC/TC ratios from QUARTZ/NIOSH-like protocols typically lower than those from the EUSAAR\_2 protocol (Cavalli et al., 2010). Therefore, the reproducibility among the participants is analysed for two cases separately, including all participants (case a), and excluding participants 5 and 8 -applying QUARTZ/NIOSH-like protocols (case b), respectively.

In Figure 5 the EC/TC ratio average values from three replicates reported by all laboratories for each test sample are presented grouped for each laboratory.

When including all participants, the  $G_1$  and  $G_2$  Grubbs' tests identifies no outliers and five stragglers (lab/sample) 5/IPR1, 8/IPR1, 8/IPR6, 8/IPR7 and 8/TER1, all from participants applying NIOSH/QUARTZ-like protocols.

When excluding participants 5 and 8, the  $G_1$  and  $G_2$  Grubbs' tests verifies the absence of outliers and stragglers in the database.



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

The entries identified as outliers by the statistical tests are discarded from the dataset, and the mean value, the repeatability ( $sr$ ) and the reproducibility ( $sR$ ) standard deviations for EC/TC are calculated for each sample from the retained values for both cases, i.e. including entries from all participants and excluding participants 5 and 8 (Table 7).

**Table 7:** General mean, repeatability ( $sr$ ) and reproducibility ( $sR$ ) standard and relative standard deviations for EC/TC. (Case a including all participants, case b excluding participants 5 and 8).

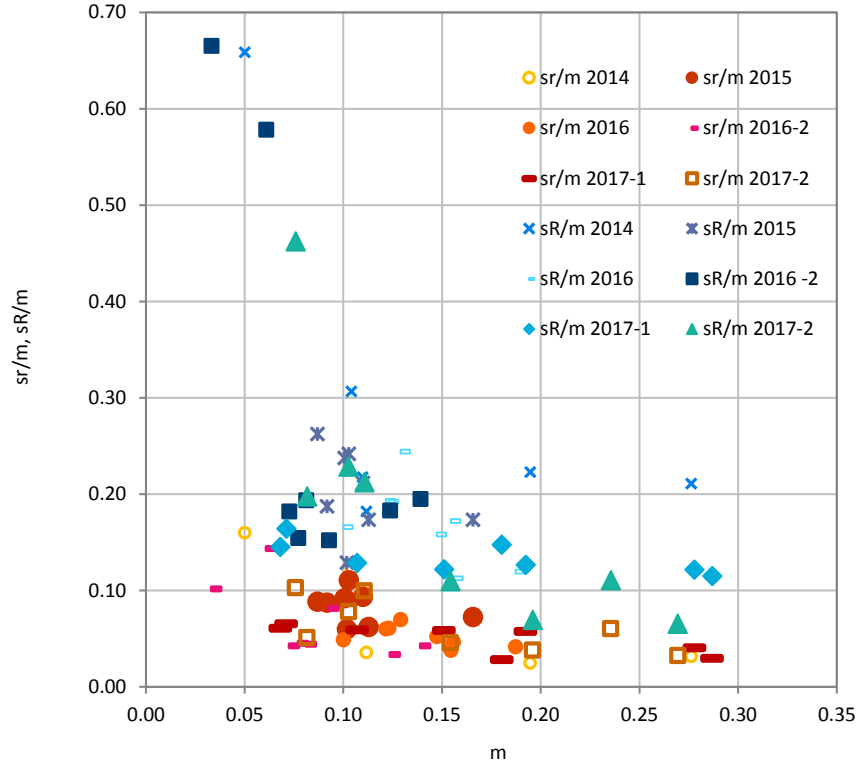
#### Case a

test sample	general mean	$sr$		$sR$	
			%		%
IPR 1	0.22	0.01	6.0	0.04	18.6
IPR2	0.10	0.01	9.9	0.03	25.9
IPR3	0.10	0.01	7.6	0.02	25.2
IPR4	0.07	0.01	12.0	0.03	47.7
IPR5	0.08	0.00	5.3	0.02	25.6
IPR6	0.15	0.01	4.7	0.03	17.3
IPR7	0.19	0.01	3.8	0.03	14.0
TER1	0.26	0.01	3.4	0.03	9.5

#### Case b

test sample	general mean	$sr$		$sR$	
			%		%
IPR 1	0.24	0.01	6.0	0.03	11.1
IPR2	0.11	0.01	9.9	0.02	21.2
IPR3	0.10	0.01	7.8	0.02	22.8
IPR4	0.08	0.01	10.3	0.04	46.2
IPR5	0.08	0.00	5.1	0.02	19.8
IPR6	0.15	0.01	4.6	0.02	11.0
IPR7	0.20	0.01	3.8	0.01	7.0
TER1	0.27	0.01	3.2	0.02	6.5

The reproducibility standard deviation for EC/TC improves significantly for all samples, on average of 35%, when a single common thermal-optical protocol is applied. Combining the repeatability and reproducibility relative standard deviation for the EUSAAR\_2 protocol obtained during the previous four ILCEs and the present one (Case b with participants 5 and 8 excluded), we observe that the method precision (both  $sr$  and  $sR$ ) for EC/TC ratio measurement becomes exponentially poorer toward lower EC/TC ratio, i.e.  $< 0.07$  (Fig. 6).



**Figure 6.** Repeatability and reproducibility relative standard deviation for the EUSAAR-2 protocol for EC/TC measurement obtained during the previous inter-laboratory comparisons and the present one (Case b with participants 5 and 8 excluded).

## 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 ( $\sigma^*$ ), the approach of calculating  $\sigma^*$  *from data obtained in a round of a proficiency testing scheme* was chosen. With this approach,  $\sigma^*$  is the robust standard deviation calculated, with a recursive algorithm, from the results reported by all participant testing (See ISO 13528:2005(E), Annex C).

These approaches might become statically 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 obtained values do not significantly differ from those obtained by the *consensus value from participant results*, in Table 8, which are then used for the following elaboration.

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

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

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

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

In Annex 1 Tables 5, 6 and 7 are reported statistics (percentage bias and variability)

### 2.2.2 Results: Laboratory performance for TC

The assigned values  $X$  and the related standard deviations for proficiency assessment  $\sigma^*$  calculated from the entire database for each sample, are reported in Table 8. Following ISO13528,  $\sigma^*$  were calculated *from data obtained in a round of a proficiency testing scheme*.

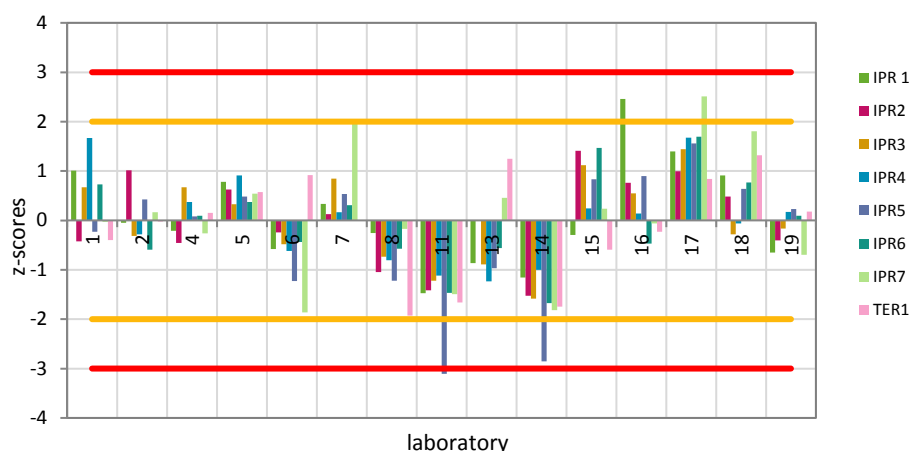
**Table 8:** Assigned values and standard deviations for proficiency assessment  $\sigma^*$  *from data obtained in a round of a proficiency testing scheme* for TC.

		IPR 1	IPR2	IPR3	IPR4	IPR5	IPR6	IPR7	TER1
assigned value	µg/cm2	10.4	12.1	9.7	5.6	14.5	9.2	9.7	18.2
standard deviation	µg/cm2	0.7	0.7	0.9	0.6	0.5	0.5	0.4	1.2
	%	6.4	5.4	9.5	10.8	3.7	5.2	4.6	6.5
2 $\sigma^*$	%	13	11	19	22	7	10	9	13
3 $\sigma^*$	%	19	16	28	33	11	16	14	19

Figure 7 shows z-scores calculated from  $\sigma^*$ . One outlier, 11/IPR5 (lab/sample) and three stragglers 16/IPR1, 14/IPR5, 17/IPR7 are identified.

For each sample, nine to ten out of fifteen participants show deviations from the assigned values within  $\pm 1 \sigma^*$  as listed in Table 8 (i.e. within 1 z-score). 87% of all entries are within 10% from the assigned value.

A few participants show the systematic tendency (larger than + or – 5% on average) of overestimating –i.e. lab 17 - or underestimating –i.e. labs 8, 11, and 14- the assigned TC concentrations. A more accurate determination of the instrument's calibration constant (e.g. implementing CO<sub>2</sub> calibration where possible) would correct this tendency.



**Figure 7.** z-scores for TC calculated using  $\sigma^*$  from data obtained in a round of a proficiency testing scheme.

### 2.2.3 Results: Laboratory performance for EC/TC

The assigned values,  $X$ , and the related standard deviations for proficiency assessment,  $\sigma^*$ , are reported in Table 9. Following ISO13528,  $\sigma^*$  are calculated from data obtained in a round of a proficiency testing scheme including all participants applying the EUSAAR\_2 protocol.

The corresponding z-scores are shown in Figure 8.

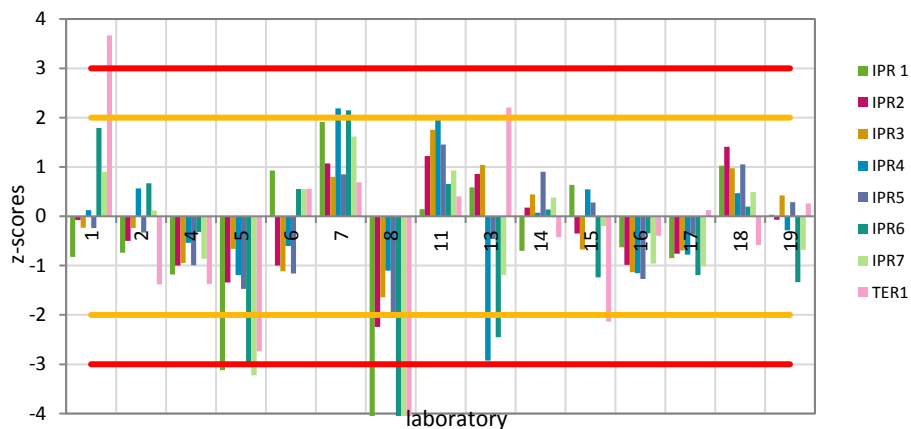
		IPR 1	IPR 2	IPR 3	A210	A223	A224	TER10	TER11
assigned value	ratio	0.24	0.11	0.10	0.08	0.08	0.15	0.19	0.27
standard deviation	ratio	0.02	0.02	0.02	0.03	0.02	0.01	0.01	0.01
	%	10.3	22.2	24.5	34.2	22.6	8.0	7.3	3.9
$2\sigma^*$	%	21	44	49	68	45	16	15	8
$3\sigma^*$	%	31	67	73	103	68	24	22	12

**Table 9:** Assigned values and standard deviations for proficiency assessment  $\sigma^*$  from data obtained in a round of a proficiency testing scheme for EC/TC.

Eight outliers -5/IPR1, 8/IPR1, 5/IPR6, 8/IPR6, 5/IPR7, 8/IPR7, 1/TER1, 8/TER1 (lab/sample)- and nine stragglers -8/IPR2, 7/IPR4, 13/IPR4, 8/IPR5, 7/IPR6, 13/IPR6, 13/TER1 and 15/TER1- (lab/sample) are identified. For each sample, 7 to 10 out of fifteen laboratories show deviations from the assigned values within  $\pm 1 \sigma^*$  as listed in Table 9 (i.e. within 1 z-score).

47% of all entries are within 10% of the assigned value and 79% are within the 25% of the assigned value.

A contribution of filter heterogeneities to poor laboratory performances cannot be completely excluded. However, the recurrence (more than two) of stragglers and/or outliers for single laboratories as observed in this exercise most probably suggest biases in EC/TC determination compared to the other laboratories. The recurrent biases observed for participants 5 and 8 are most probably caused by the application of a different thermal-optical protocol than EUSAAR\_2. Participants showing large biases ( $|z\text{-scores}| > 2$ ) shall carefully examine their procedures and identify appropriate corrective actions that are likely to prevent the recurrence of such results in the future.



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

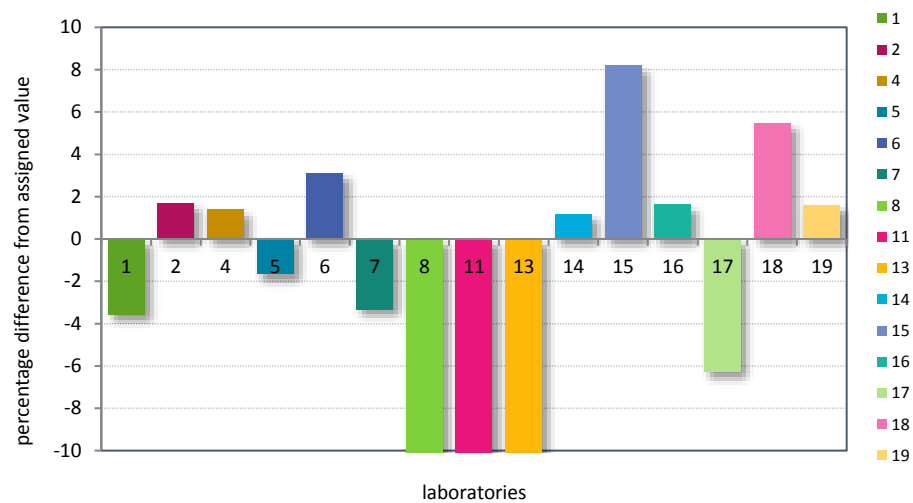
### 2.3 PHTHALIC ACID SOLUTION – Percentage differences

Participants were asked to report the OC content of 10  $\mu\text{l}$  of phthalic acid solution. This included the analysis of samples prepared by spiking a pre-cleaned filter punch with 10  $\mu\text{l}$  solution. This is the procedure normally used by laboratories to determine and verify the FID calibration constant.

Figure 9 shows the percentage differences from the assigned value ( $1.57 \pm 0.02 \text{ gC l}^{-1}$ , calculated from primary mass and water volume measurements) for each participant. Nine laboratories out of fifteen laboratories reported OC deviating from the assigned value by less than  $\pm 5\%$ . Since each phthalic acid solution flask was not checked individually, contaminations cannot be completely excluded.

This exercise did not aim at identifying systematic tendency of a laboratory to underestimate or overestimate the C content of analysed samples but rather to highlight the potential uncertainty (and variability) that can affect carbon determination, when the spiking procedure is applied to determine the FID calibration constant. As an example, the tendency of underestimating the C content of the phthalic acid solution observed for participants 8 and 11 is consistent with the same tendency of systematically underestimating the TC content of the test samples (par 2.2.2). It is recommended to implement the calibration with  $\text{CO}_2$  injections where possible, or to carefully revise the accuracy of all steps involved in the external solution spiking procedure (calibration of the pipette volume, complete deposition of the volume onto a punch filter, drying etc.).





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

## Conclusions

This inter-laboratory comparison involved fifteen participants all applying thermal-optical analyses. Thirteen applied the EUSAAR-2 protocol, and two applied Quartz/NIOSH-like protocols. The measurement method **repeatability and reproducibility for TC** ranged from **3% to 6%** and from **6% to 11%** (as one relative standard deviation), respectively.

For the **EC/TC ratio, repeatability** ranged from **3% to 12%**. The **reproducibility** was calculated in two case, i.e. case a) including all participants and case b) excluding participants 5 and 8 applying QUARTZ/NIOSH-like protocols and ranged from **10% to 48%** in the case a) and from **6% to 46%** in case b). The reproducibility standard deviation for EC/TC improves significantly for all samples, on average by 35%, when a single common thermal-optical protocol is applied.

Combining the repeatability and reproducibility relative standard deviation for the EUSAAR-2 protocol obtained during the previous four ILCEs and the present one, we observed that the method precision (both sr and sR) becomes exponentially poorer toward lower TC contents i.e.  $<10 \mu\text{gC} / \text{cm}^2$  and EC/TC ratio. i.e.  $<0.07$ .

Although the contribution of localized sample heterogeneities and /or contaminations to biased data cannot be totally excluded (particularly for TER1 sample), 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 for TC and among all participants applying the European standard protocol EUSAAR-2 for EC/TC ratio.

**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, one outlier and three stragglers were identified; and 87% of all entries were within 10% from the assigned TC concentration value.

A few participants show the systematic tendency (larger than + or - 5% on average) of overestimating -i.e. lab 17 - or underestimating -i.e. labs 8, 11, and 14- the assigned TC concentrations. A more accurate determination of the instrument's calibration constant (e.g. implementing CO<sub>2</sub> calibration where possible) would correct this tendency.

Regarding EC/TC ratios, eight outliers and nine stragglers were identified. 47% of all entries were within 10% of the assigned value and 79% were within the 25% of the assigned value. More than half of outliers and stragglers were EC/TC ratios reported by laboratories applying a QUARTZ/NIOSH-like thermal-optical protocol.

Participants showing large biases ( $|z\text{-scores}| > 2$ ) 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<sub>2</sub> phases; iii) temperature calibration and iv) transit time would correct this behavior and reduce the observed variability in EC/TC ratio determination.

## References

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## **Annex 1. Numerical results reported by participants**

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

TC								
Laboratory	ISP1	ISP2	ISP3	ISP4	ISP5	ISP6	ISP7	TER 1
1	11.086	11.884	9.598	6.169	14.141	9.165	9.923	17.492
	10.938	11.865	11.845	6.888	15.166	9.736	9.549	18.073
	11.195	11.579	9.529	6.819	13.707	9.657	9.677	17.639
2	10.410	12.387	9.448	5.263	14.704	8.732	10.006	19.437
	10.323	11.840	9.322	5.166	14.836	9.435	9.723	17.472
	10.391	13.930	9.497	5.888	14.543	8.485	9.680	17.639
4	10.271	12.220	9.619	6.271	14.081	8.859	9.513	17.509
	9.997	11.676	10.187	5.911	15.129	9.374	9.743	18.325
	10.533	11.367	11.170	5.329	14.309	9.407	9.582	19.314
5	10.958	12.737	9.707	6.073	14.905	9.322	9.896	19.511
	10.957	12.247	10.026	6.167	14.675	9.429	10.162	18.767
	10.849	12.405	10.300	6.257	14.598	9.295	9.862	18.367
6	9.676	12.031	9.207	4.995	13.723	9.347	9.006	21.686
	10.441	12.099	8.998	5.251	13.683	8.598	8.928	18.538
	9.950	11.559	9.585	5.456	13.990	8.928	8.741	17.629
7	10.376	11.901	10.811	5.690	14.620	9.366	10.621	18.698
	10.907	12.325	10.141	5.633	15.065	9.146	10.638	18.157
	10.599	12.177	10.507	5.812	14.576	9.435	10.584	17.723
8	10.100	11.300	9.100	5.110	14.000	8.570	9.870	16.600
	10.300	11.300	9.000	5.130	13.800	8.880	9.590	14.800
	10.300	11.500	9.000	5.120	13.600	9.230	9.500	16.400
11	9.730	10.396	8.564	4.920	12.909	8.118	9.159	16.409
	9.640	10.751	8.934	4.846	12.641	8.557	8.959	16.088
	8.917	12.239	8.262	5.029	12.782	8.719	9.058	16.243
13	9.780	12.370	8.940	4.770	14.120	8.400	10.630	19.870
	9.950	11.680	9.190	4.850	13.890	8.660	9.620	19.480
	9.770	12.100	8.550	4.960	13.800	9.640	9.560	19.680
14	9.398	11.273	8.254	5.119	12.073	8.441	9.382	16.947
	9.872	10.583	8.217	4.778	13.460	8.271	8.695	15.485
	9.640	11.305	8.288	5.106	13.213	8.377	8.659	16.007
15	9.913	13.002	9.794	6.463	14.026	9.501	9.989	17.206
	10.301	12.808	9.820	5.352	14.765	9.762	9.513	17.363
	10.418	13.117	12.597	5.466	15.953	10.354	10.009	17.946
16	12.583	12.525	10.149	5.527	14.531	9.049	9.150	18.294
	11.572	12.477	10.288	6.000	15.080	9.138	9.893	17.815
	11.953	12.655	10.199	5.558	15.242	8.641	10.064	17.694
17	11.332	12.706	11.037	6.630	15.307	9.983	10.857	19.193
	11.308	13.207	10.676	7.511	14.895	10.167	10.692	19.797
	11.282	13.283	10.942	6.638	15.053	10.141	10.741	20.221
18	10.470	12.599	9.178	5.480	15.362	9.614	10.905	20.323
	10.986	12.371	9.610	5.817	15.163	9.478	10.176	20.726
	11.563	12.136	9.570	5.420	13.908	9.522	–	18.223
19	9.943	11.466	9.538	6.060	14.155	9.118	9.370	17.835
	9.716	11.728	9.382	5.476	14.549	9.198	9.357	18.407
	10.258	12.167	9.747	5.612	15.060	9.326	9.523	19.006

**Table 2:** Elemental carbon / total carbon (ratios)

EC/TC								
Laboratory	ISP1	ISP2	ISP3	ISP4	ISP5	ISP6	ISP7	TER 1
1	0.208	0.109	0.101	0.069	0.084	0.178	0.201	0.310
	0.219	0.108	0.088	0.079	0.073	0.173	0.207	0.308
	0.221	0.109	0.098	0.091	0.070	0.180	0.214	0.302
2	0.237	0.083	0.111	0.083	0.075	0.160	0.202	0.251
	0.184	0.113	0.099	0.103	0.072	0.160	0.186	0.261
	0.233	0.100	0.077	0.088	0.075	0.169	0.201	0.248
4	0.219	0.081	0.079	0.058	0.064	0.145	0.183	0.254
	0.210	0.084	0.076	0.067	0.064	0.152	0.187	0.252
	0.193	0.093	0.079	0.062	0.058	0.156	0.177	0.255
5	0.168	0.078	0.084	0.032	0.057	0.119	0.149	0.234
	0.154	0.075	0.087	0.047	0.054	0.113	0.154	0.245
	0.159	0.080	0.084	0.057	0.049	0.120	0.144	0.239
6	0.267	0.088	0.073	0.062	0.059	0.155	0.198	0.276
	0.246	0.083	0.078	0.064	0.058	0.163	0.218	0.277
	0.262	0.087	0.070	0.056	0.060	0.167	0.191	0.269
7	0.277	0.135	0.116	0.134	0.095	0.177	0.212	0.275
	0.283	0.138	0.126	0.134	0.097	0.183	0.217	0.278
	0.287	0.138	0.122	0.133	0.094	0.184	0.223	0.273
8	0.122	0.057	0.059	0.039	0.041	0.078	0.127	0.193
	0.134	0.048	0.059	0.041	0.041	0.092	0.118	0.218
	0.130	0.061	0.064	0.063	0.046	0.081	0.119	0.193
11	0.238	0.146	0.151	0.125	0.107	0.166	0.207	0.272
	0.244	0.143	0.141	0.132	0.107	0.172	0.207	0.274
	0.236	0.133	0.143	0.129	0.105	0.151	0.209	0.271
13	0.309	0.148	0.114	0.000	0.068	0.137	0.154	0.280
	0.220	0.106	0.101	0.000	0.074	0.119	0.168	0.303
	0.221	0.141	0.167	0.000	0.073	0.118	0.211	0.291
14	0.219	0.116	0.107	0.076	0.095	0.160	0.196	0.244
	0.218	0.119	0.125	0.078	0.090	0.153	0.209	0.274
	0.219	0.110	0.105	0.081	0.104	0.157	0.195	0.274
15	0.260	0.100	0.087	0.078	0.073	0.141	0.191	0.245
	0.254	0.100	0.092	0.097	0.072	0.141	0.196	0.249
	0.240	0.106	0.075	0.097	0.110	0.137	0.188	0.243
16	0.200	0.091	0.073	0.047	0.057	0.154	0.184	0.252
	0.208	0.086	0.079	0.049	0.059	0.150	0.181	0.271
	0.254	0.082	0.068	0.043	0.055	0.148	0.178	0.269
17	0.215	0.092	0.084	0.056	0.073	0.140	0.180	0.269
	0.212	0.081	0.081	0.049	0.060	0.135	0.171	0.264
	0.224	0.088	0.080	0.056	0.066	0.149	0.175	0.265
18	0.270	0.147	0.129	0.085	0.097	0.147	0.197	0.266
	0.263	0.150	0.120	0.096	0.099	0.156	0.206	0.244
	0.249	0.139	0.128	0.085	0.101	0.169	–	0.276
19	0.231	0.105	0.107	0.064	0.088	0.136	0.190	0.279
	0.243	0.111	0.120	0.073	0.085	0.140	0.178	0.273
	0.236	0.111	0.109	0.070	0.083	0.139	0.188	0.261

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

EC								
Laboratory	ISP1	ISP2	ISP3	ISP4	ISP5	ISP6	ISP7	TER 1
1	2.306	1.291	0.966	0.424	1.183	1.636	1.991	5.430
	2.395	1.281	1.045	0.542	1.104	1.685	1.981	5.558
	2.473	1.261	0.936	0.621	0.956	1.734	2.069	5.321
2	2.470	1.025	1.052	0.435	1.108	1.398	2.025	4.886
	1.897	1.334	0.920	0.532	1.067	1.509	1.805	4.561
	2.423	1.388	0.727	0.517	1.087	1.437	1.943	4.383
4	2.246	0.986	0.758	0.362	0.906	1.287	1.737	4.440
	2.095	0.986	0.771	0.397	0.975	1.422	1.822	4.615
	2.030	1.056	0.884	0.331	0.831	1.472	1.697	4.928
5	1.843	0.994	0.819	0.193	0.850	1.111	1.474	4.559
	1.691	0.923	0.872	0.287	0.789	1.070	1.565	4.606
	1.726	0.992	0.863	0.360	0.718	1.113	1.422	4.385
6	2.582	1.064	0.674	0.311	0.813	1.450	1.782	5.990
	2.571	1.009	0.702	0.338	0.799	1.401	1.949	5.144
	2.611	1.011	0.673	0.308	0.841	1.492	1.670	4.743
7	2.872	1.608	1.259	0.760	1.384	1.660	2.248	5.143
	3.087	1.702	1.275	0.757	1.459	1.671	2.306	5.043
	3.046	1.678	1.286	0.774	1.371	1.731	2.359	4.835
8	1.230	0.640	0.540	0.200	0.570	0.670	1.250	3.200
	1.380	0.540	0.530	0.210	0.570	0.820	1.130	3.220
	1.340	0.700	0.580	0.320	0.620	0.750	1.130	3.170
11	2.314	1.523	1.297	0.616	1.380	1.350	1.895	4.471
	2.352	1.537	1.260	0.640	1.354	1.465	1.856	4.406
	2.102	1.629	1.178	0.649	1.345	1.318	1.890	4.396
13	3.030	1.830	1.020	0.000	0.950	1.160	1.640	5.560
	2.190	1.230	0.930	0.000	1.030	1.030	1.610	5.900
	2.160	1.700	1.430	0.000	1.000	1.140	2.020	5.730
14	2.061	1.305	0.884	0.390	1.152	1.349	1.835	4.136
	2.156	1.256	1.029	0.371	1.209	1.268	1.814	4.237
	2.112	1.249	0.869	0.415	1.372	1.312	1.691	4.378
15	2.537	1.303	0.849	0.505	1.025	1.341	1.916	4.208
	2.613	1.284	0.900	0.517	1.070	1.380	1.865	4.317
	2.496	1.385	0.945	0.530	1.759	1.419	1.877	4.366
16	2.517	1.135	0.745	0.259	0.822	1.390	1.688	4.611
	2.403	1.074	0.814	0.292	0.883	1.374	1.789	4.830
	3.032	1.043	0.693	0.239	0.845	1.278	1.795	4.769
17	2.440	1.169	0.930	0.372	1.122	1.400	1.957	5.171
	2.400	1.075	0.867	0.366	0.889	1.372	1.832	5.219
	2.532	1.166	0.877	0.371	0.996	1.516	1.880	5.362
18	2.828	1.848	1.180	0.465	1.486	1.417	2.153	5.410
	2.895	1.860	1.151	0.556	1.494	1.477	2.100	5.054
	2.884	1.684	1.221	0.461	1.407	1.609		5.034
19	2.301	1.206	1.023	0.390	1.240	1.244	1.776	4.973
	2.364	1.302	1.123	0.397	1.241	1.290	1.664	5.028
	2.417	1.345	1.061	0.392	1.245	1.294	1.786	4.951

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

OC								
Laboratory	IPR 1	IPR 2	IPR 3	A 210	A 223	A 224	TER 10	TER 11
1	8.780	10.593	8.632	5.745	12.958	7.529	7.932	12.062
	8.543	10.584	10.800	6.346	14.062	8.051	7.568	12.515
	8.722	10.318	8.593	6.198	12.751	7.923	7.608	12.318
2	7.940	11.362	8.396	4.828	13.596	7.334	7.981	14.551
	8.426	10.506	8.402	4.634	13.769	7.926	7.918	12.911
	7.968	12.542	8.770	5.371	13.456	7.048	7.737	13.256
4	8.025	11.234	8.861	5.909	13.175	7.572	7.776	13.069
	7.902	10.690	9.416	5.514	14.154	7.952	7.921	13.710
	8.503	10.311	10.286	4.998	13.478	7.935	7.885	14.386
5	9.115	11.743	8.888	5.880	14.055	8.211	8.422	14.952
	9.266	11.324	9.154	5.880	13.886	8.359	8.597	14.161
	9.123	11.413	9.437	5.897	13.880	8.182	8.440	13.982
6	7.094	10.967	8.533	4.684	12.910	7.897	7.224	15.696
	7.870	11.090	8.296	4.913	12.884	7.197	6.979	13.394
	7.339	10.548	8.912	5.148	13.149	7.436	7.071	12.886
7	7.504	10.293	9.552	4.930	13.236	7.706	8.373	13.555
	7.820	10.623	8.866	4.876	13.606	7.475	8.332	13.114
	7.553	10.499	9.221	5.038	13.205	7.704	8.225	12.888
8	8.870	10.660	8.560	4.910	13.430	7.900	8.620	13.400
	8.920	10.760	8.470	4.920	13.230	8.060	8.460	11.580
	8.960	10.800	8.420	4.800	12.980	8.480	8.370	13.230
11	7.416	8.873	7.267	4.304	11.529	6.768	7.264	11.938
	7.288	9.214	7.674	4.206	11.287	7.092	7.103	11.682
	6.815	10.610	7.084	4.380	11.437	7.401	7.168	11.847
13	6.750	10.540	7.920	4.770	13.170	7.240	8.990	14.310
	7.760	10.450	8.260	4.850	12.860	7.630	8.010	13.580
	7.610	10.400	7.120	4.960	12.800	8.500	7.540	13.950
14	7.337	9.968	7.370	4.729	10.921	7.092	7.547	12.811
	7.716	9.326	7.189	4.407	12.251	7.003	6.880	11.248
	7.528	10.056	7.419	4.691	11.841	7.065	6.968	11.629
15	7.376	11.699	8.945	5.958	13.001	8.160	8.073	12.998
	7.688	11.524	8.920	4.835	13.695	8.382	7.648	13.046
	7.922	11.732	11.652	4.936	14.194	8.935	8.132	13.580
16	10.066	11.390	9.404	5.268	13.709	7.659	7.462	13.683
	9.169	11.403	9.474	5.708	14.197	7.764	8.104	12.985
	8.921	11.612	9.506	5.319	14.397	7.363	8.269	12.925
17	8.892	11.537	10.107	6.257	14.185	8.583	8.900	14.022
	8.908	12.131	9.809	7.146	14.006	8.795	8.860	14.578
	8.750	12.117	10.065	6.267	14.057	8.626	8.862	14.860
18	7.642	10.751	7.998	5.015	13.876	8.197	8.752	14.913
	8.091	10.511	8.459	5.261	13.669	8.001	8.076	15.672
	8.679	10.452	8.349	4.959	12.501	7.913	0.000	13.189
19	7.642	10.260	8.515	5.670	12.915	7.875	7.594	12.862
	7.352	10.426	8.259	5.079	13.307	7.908	7.693	13.379
	7.841	10.821	8.685	5.220	13.816	8.032	7.736	14.055