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EMEP Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe

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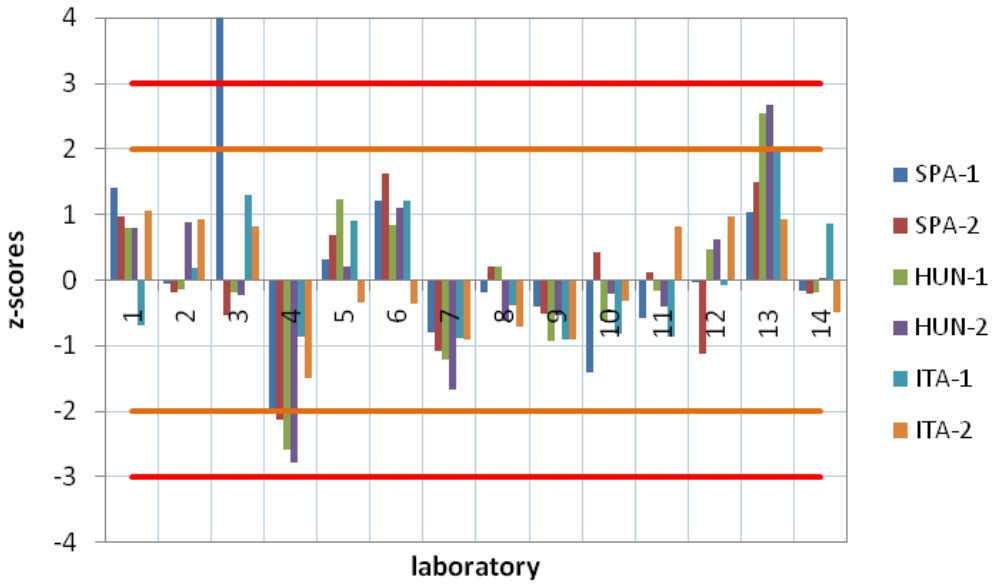

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Availability and quality of the OC and EC measurements within EMEP, including results of the fifth inter-laboratory comparison of analytical methods for OC and EC within EMEP (2012)

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Summary

22 sites within the EMEP (European Monitoring and Evaluation Programme) reported concentrations of organic carbon (OC) and elemental carbon (EC) in atmospheric particulate matter to EBAS (www.ebas.nilu.no) for 2012. The reported data were produced by 15 different institutes, covering measurements in 13 European countries. Despite nearly a doubling in the sites reporting OC and EC since 2010, large parts of Europe are still not covered, including in particular the westernmost and the easternmost parts. Only two of the time series extend 10 years or more back in time, and both experience a shift in the analytical methodology, as EUSAAR-2 first became available in 2008. Five sites performed measurements of OC and EC in more than one size fraction.

All 22 sites reported values obtained by thermal-optical analysis, of which 21 reported data obtained by the EUSAAR-2 analytical protocol recommended by EMEP, which is an important step towards harmonized and comparable data for OC and EC within EMEP. A SOP for OC and EC measurements was made available in the EMEP manual in 2014 (http://www.nilu.no/projects/ccc/manual/index.html), and in June 2015 EUSAAR -2 was proposed as the European standard method for analysis of OC and EC by the CEN TC264 WG35.

Comparable data, in particular for OC, requires that both the analytical and the sampling protocols are harmonized; this is currently not the case. Sampling procedures vary widely between sites with respect to sampling time and whether sampling artifacts are accounted for. Only three sites attempt to account for both positive and negative sampling artifacts.

The quality of the OC/EC data reported to EMEP has improved with respect to sampling time and sampling frequency; i.e., these parameters are constant for consecutive years, which substantially reduces the uncertainties when comparing data from one year to the other. The data capture is however too low for the majority of the sites; only one third of the sites have a sampling scheme that can fulfil the criterion of 75%. Further, 80% of the OC/EC datasets did not use any QA/QC flags, which is essential to provide data with a known quality.

45% of the sites reported OC/EC data to EBAS using the EBAS template for OC/EC data. From 2015 all whom report OC/EC data to EBAS have to use the EUSAAR format. With the increased information following from this format, increased transparency on how sampling and subsequent analysis of OC/EC are performed within EMEP will improve one more step.

The 5th EMEP inter-laboratory comparison for the measurement of carbonaceous aerosol performed in 2013/2014 involved all the fifteen laboratories that had reported 2012 data. They all applied thermal-optical analysis with two different thermal-optical protocols; i.e., EUSAAR-2 and NIOSH or NIOSH-like protocols.

For TC loadings, the measurement method repeatability relative standard deviation (S_r) and the reproducibility relative standard deviation (S_R) ranged from

1% to 6% and from 5% to 14% (based on 1 standard deviation), respectively. For EC/TC ratios, S_r and S_R ranged from 3% to 16% and from 18% to 31% (excluding 1 sample where the EC/TC ratio was close to the detection limit). The uncertainty of the EC/TC determination is thus much bigger than that of the TC determination. Repeatability and reproducibility showed a clear to marginal inverse dependence with respect to TC and the EC/TC ratio, respectively; i.e., the method performance was poorer for low TC contents and low EC/TC ratios.

With respect to the precedent inter-laboratory comparison, no significant improvements were observed.

Laboratories' performances were assessed for both TC loading and EC/TC ratio determination based on z-scores using as standard deviation for proficiency assessment, σ^*, the one calculated from data obtained in a round of a proficiency testing scheme. Note that the values of σ^* are larger for the EC/TC ratios compared to the TC loadings, i.e., the test based on z-scores is much more stringent for the TC loading than for the EC/TC-ratios. Eight outliers were identified in the TC data set, of which four came from 1 single laboratory. Only one outlier was detected among the EC/TC ratios. The laboratory which produced this outlier, also produced 4 stragglers. Laboratories reporting several outliers or stragglers (here: laboratory 5 and 11), shall carefully examine their procedures and instrument set-up and identify appropriate corrective actions that are likely to prevent the repetition of such results in the future. To link the laboratory's performance in an ILC and the data available in EBAS, an additional metadata point will be added to the reporting format for OC/EC with information of results in the ILC the representative year.

Availability and quality of the OC and EC measurements within EMEP, including results of the fifth inter-laboratory comparison of analytical methods for OC and EC within EMEP (2012)

1. Introduction

Organic (OC) and elemental (EC) carbon are abundant fractions of the ambient aerosol particle, thus contributing to the aerosol particle influence on the radiation budget both directly, by scattering and absorption of sunlight, and indirectly, by cloud formation. Likewise does the carbonaceous fraction contribute to the adverse health effects observed; i.e., respiratory and cardiovascular diseases. Despite the importance of the carbonaceous aerosol, detailed apportionment and quantification of its sources is still difficult due to the large number of sources (both natural and anthropogenic), the complexity of atmospheric formation, and the vast number of organic compounds associated with the aerosol. These are reasons why the Quality Directive 2008/50/EC requires measurement of OC and EC in $PM_{2.5}$ at rural background sites in Europe. The European Monitoring and Evaluation Programme (EMEP) lists OC and EC (in PM_{10}) as core variables for the same reasons, and has included these variables at EMEP level 2 sites (UNECE, 2004; UNECE, 2009).

Here we report about the status of sampling and measurements of OC and EC reported to EMEP for the year 2012, as well as the quality of OC and EC measurements within the EMEP monitoring network. The latter includes 15 laboratories responsible for ongoing (i.e., those reporting for 2012) measurement of OC and EC at stations within the EMEP monitoring network, and which apply thermal-optical analysis for such analysis.

To assess the data comparability and to get a picture of the method and laboratories' performance, an interlaboratory comparison was organized by the Joint Research Centre of the European Commission (JRC) in agreement with the EMEP Chemical Coordinating Centre (CCC) at NILU-Norwegian Institute for Air Research (NILU). The current interlaboratory comparison (ILC) is the fifth inter-laboratory comparison arranged and was organized in 2013-2014 with the support of the project ACTRIS (grant agreement no. 262254) funded by the European Union Seventh Framework Programme (FP7/2007-2013).

2. Status of sampling and measurements of carbonaceous matter in PM within the EMEP network – 2012

The EMEP OC and EC campaign (Yttri et al., 2007) and the CARBOSOL project (Pio et al., 2007), with data for the period 2002–2004, has for a long time been the only possibility to address the spatial and temporal variation of OC and EC in Europe on a regional scale. These two data sets dates more than 10 years back in time, thus more recent measurements must be made available to get an overview of the current situation, and to validate the progress made with respect to model development.

An increased number of countries and sites have started to report levels of OC and EC following from the development of the EUSAAR-2 protocol. 22 sites reported measurements of OC and EC for 2012, which is close to a doubling since 2010. There are, however, large areas that are poorly covered with respect to OC and EC measurements, being in particular the westernmost and the easternmost part of Europe. See Table 2.1 for all sites reporting levels of OC and EC for 2012, and Figure 2.1 for their spatial distribution. Only two of the time series extend 10 years or more back in time, at the Norwegian site Birkenes and at the Italian site Ispra, and there is a shift in the analytical methodology for both time series, as EUSAAR-2 first became available in 2008. This does not have an effect on TC, only on the split between OC and EC.

Figure 2.1: Overview of sites reporting OC/EC data obtained by thermal-optical analysis to EMEP for 2012. Sites with measurements covering less than 6 months of the year are not included in the figure.

The quality of the OC and EC data reported to EMEP has improved with respect to sampling time and sampling frequency; i.e., these parameters are constant for consecutive years, which substantially reduces the uncertainties when comparing data from one year to the other. 7 sites have a sampling scheme that allows for a

100% data capture, whereas 1 allow for a 50% data capture. For the remaining sites the data capture was between 8% and 33%. The data capture has improved for some sites, but is still too low for the majority of the sites to fulfil the criterion of 75%. All sites have arranged their sampling to include year-round measurements, making it possible to study seasonal variability.

All the 22 sites listed in Table 2.1 quantified OC and EC using thermal-optical analysis, and 21 according to the EUSAAR-2 protocol, which is an important step towards harmonized and comparable data for OC and EC within EMEP. A detailed description of the EUSAAR-2 protocol and its performance can be found in Cavalli et al. (2010), and since 2014 a SOP for OC and EC measurements has been available in the EMEP manual (http://www.nilu.no/projects/ccc/manual/index.html). How to handle samples impacted by carbonate carbon is still not settled. Different methods have been explored within the EU-funded project ACTRIS, and will continue within ACTRIS-2. Guidelines for how to deal with such samples will be developed based on the results obtained in ACTRIS-2 and will subsequently be added to the SOP for OC and EC analyses.

Table 2.1: Sites reporting OC and EC for 2012, including for which size fraction(s) and year(s).

Site (Country)	Code	PM_1	$PM_{2.5}$	PM_{10}	Period
Aspvreten (Sweden)	SE12			x	2008 - 2012
Ayia Marina (Cypros)	CY02		x		2011 - 2012
Birkenes (Norway)	NO02		x	x	2001 - 2012
Cabauw (The Netherlands)	NL644		x		2012
Diabla Gora (Poland)	PL05		x		2011 - 2012
Finokalia (Greece)	GR02			x[1)]	2009 - 2012
Hurdal (Norway)	NO56		x	x	2010 - 2012
Iskrba (Slovenia)	SI08		x		2010 - 2012
Ispra (Italy)	IT04		x		2002[2)] – 2012[3)]
Košetice (Czech Rep.)	CZ03		x		2009 – 2012
Kårvatn (Norway)	NO39		x	x	2010 – 2012
Melpitz (Germany)	DE44		x	x	2006 – 2012
Montseny (Spain)	ES1778	x	x	x	2007 – 2012
Neuglobsow (Germany)	DE07		x		2012[4)]
Payerne (Schwitzerland)	CH02		x		2012
Puy de Dome (France)	FR30		x		2008 - 2012
Rigi (Schwitzerland)	CH05		x		2012
San Pablo de Los Montes (Spain)	ES01		x		2012
Schauinsland (Germany)	DE03		x		2012[4)]
Schmücke (Germany)	DE08		x		2012[4)]
Vavihill (Sweden)	DE11			x	2008 - 2012
Waldhof (Germany)	DE02		x		2012[4)]

1. PM_1 in 2009
2. EMEP EC and OC campaign
3. Both $PM_{2.5}$ and PM_{10} for the period 2002 – 2005
4. Measurements were initiated in 2011, but 2012 was the first full year of measurements

*Three Finish sites performed measurements for the first 5 months of 2012 (EC/OC monitor).

The EUSAAR-2 protocol is commonly used for other site categories than the rural background, and has been one of the candidate methods tested for a standardized method for OC and EC measurements within CEN. In June 2015, EUSAAR-2 was proposed as the European standard method for analysis of OC and EC by the CEN TC264 WG35, hence comparable OC and EC data for a wider range of site categories can be obtained in the near future.

Comparable data, in particular for OC, requires that both the analytical and the sampling protocols are harmonized, which currently is not the case. The variability amongst the various sampling approaches currently used is apparent from the parameters listed in Table 2.2. Most sites sample for 24 hours, however the sampling time extends up to one week for some of the low loading sites in Scandinavia. The three sites Aspvreten, Ispra and Vavihill attempted to account for both positive and negative sampling artifacts, whereas at Košetice the QBQ-approach (Quartz-behind-Quartz) was used to account for the positive artifact. 18 of the 22 sites did not address sampling artifacts on a regular basis. However, the positive sampling artifact has been reported for several of these sites based on results from intensive measurements periods, and at Puy de Dome such results have been used to provide an estimate of the positive artifact for annual time series.

There are likely various reasons why so few sites account for sampling artifacts of OC on a regular basis. One is that it is cost efficient to obtain several variables from the same filter sample. OC/EC and particle mass concentration are often obtained from the same filter sample, but using a denuder to account for the sampling artifact of OC would be in conflict with the standard method for gravimetric determination of the mass concentration (EN12341 and EN14907). A tandem filter set up is less likely to interfere with the previously mentioned reference methods, but equivalence ought to be addressed to be on the safe side. Operating a filter sampler with a denuder requires only slightly more effort than a sampler without a denuder. The denuder has to be cleaned on a regular basis, and as such facilities are typically not present on the sampling site one must either allow for a stop in the sampling while the denuder is being cleaned, or have a duplicate one. It is likely that some experience a certain reluctance towards making changes to a time series that has run for several years. This would also require a period of concurrent sampling and analysis to address the differences between the previous and the new sampling approach. However, operating a filter sampler with a carbon monolith denuder is simple and both investment and running costs are low.

Table 2.2: Sampling - and analytical approach used at the sites reporting OC and EC to EMEP for 2012.

Site (Country)	Sampling time/frequency	Filter face velocity	Sampling equipment	Analytical approach
Aspvreten (Sweden)	24 hr, every 3rd day	55 cm s^{-1}	Denuder/Backup filter (Pos/neg artifact)	Sunset TOT (EUSAAR-2)
Ayia Marina (Cypros)	24 hr, irregular	51 cm s^{-1}	Single filter (No correction)	Sunset TOT (EUSAAR-2)
Birkenes (Norway)	168 hr, every 7th day	52 cm s^{-1}	Single filter (No correction)	Sunset TOT (EUSAAR-2)
Cabauw (The Netherlands)	24 hr, every 4th day	48 cm s^{-1}	Single filter (no correction)	Sunset TOT (EUSAAR-2)
Diabla Gora (Poland)	24 hr, daily	54 cm s^{-1}	Single filter (No correction)	Sunset TOT (EUSAAR-2)
Finokalia (Greece)	24 hr, daily	24 cm s^{-1}	Single filter (No correction)	Sunset TOT (EUSAAR-2)
Hurdal (Norway)	168 hr, every 7th day	51 cm s^{-1}	Single filter (No correction)	Sunset TOT (EUSAAR-2)
Iskrba (Slovenia)	24 hr, every 2nd day	56 cm s^{-1}	Single filter (No correction)	Sunset TOT (EUSAAR-2)
Ispra (Italy)	24 hr, daily	20 cm s^{-1}	Denuder/Backup filter (Pos/neg artifact)	Sunset TOT (EUSAAR-2)
Košetice (The Czech Rep)	24 hours, every 6th day	20 cm s^{-1}	QBQ (Pos. artifact)	Sunset TOT (EUSAAR-2)
Kårvatn (Norway)	168 hr, every 7th day	50 cm s^{-1}	Single filter (No correction)	Sunset TOT (EUSAAR-2)
Melpitz (Germany)	24 hr, daily	54 cm s^{-1}	Single filter (No correction)	Sunset TOT (EUSAAR-2)
Montseny (Spain)	24 hr, every 4th day	55 cm s^{-1}	Single filter (no correction)	Sunset TOT (EUSAAR-2)
Neuglobsow (Germany)	24 hours, every 6th day	54 cm s^{-1}	Single filter (No correction)	Sunset TOT (EUSAAR-2)
Payerne (Schwitzerland)	24 hours, every 12th day	54 cm s^{-1}	Single filter (No correction)	Sunset TOT (EUSAAR-2)
Puy de Dome (France)	48 hr, every 7th day	69 cm s^{-1}	Single filter Pos. artifact/camp	Sunset TOT (EUSAAR-2)
Rigi (Schwitzerland)	24 hours, every 12th day	54 cm s^{-1}	Single filter (No correction)	Sunset TOT (EUSAAR-2)
San Pablo de Los Montes (Spain)	24 hours, every 8th day	54 cm s^{-1}	Single filter (No correction)	Sunset TOT (NIOSH-like)
Schauinsland (Germany)	24 hours, every 6th day	54 cm s^{-1}	Single filter (No correction)	Sunset TOT (EUSAAR-2)
Schmücke (Germany)	24 hours, every 6th day	54 cm s^{-1}	Single filter (No correction)	Sunset TOT (EUSAAR-2)
Vavihill (Sweden)	72 hr, every 3rd day	55 cm s^{-1}	Denuder/Backup filter Pos/neg artifact	DRI TOT (EUSAAR-2)
Waldhof (Germany)	24 hours, every 6th day	54 cm s^{-1}	Single filter (No correction)	Sunset TOT (EUSAAR-2)

Five of the 22 sites performed measurements of OC and EC in both PM_{10} and $PM_{2.5}$, hence providing valuable information on the size distribution of these variables, which also add to the understanding of sources and atmospheric processes.

Several sites have reported OC and EC levels to EMEP (see: http://ebas.nilu.no) on a non-regular basis. These are measurements typically performed during EMEP intensive measurement periods (EIMPs), or during dedicated campaigns or projects such as the EMEP OC and EC campaign in 2002 – 2003 (Yttri et al., 2007). There are also EMEP sites where filter samples are collected and analyzed with respect to OC and EC, but for which data are currently not reported to EMEP. Effort will be made to improve this. Two of the sites (Harwell and Campisabalos) that reported OC and EC for 2011 did not do so for 2012.

The OC and EC concentration range possible to measure by TOA is poorly constrained. According to the manufacturer of the sunset lab instrument, TC can be measured within the range 0.2 µg C cm^{-2} to 400 µg C cm^{-2}, depending on the linearity of the instrument's flame ionization detector (FID). This range is however not applicable for OC and EC, being operational defined variables for which no standard reference material exist. The TOA instrument would have no problem providing reliable values for OC or EC within the same range as for TC if OC or EC was the only fraction on the filter. Problems occur when OC and EC are mixed, which is the case for all ambient aerosol filter samples. There are two elements that are crucial: The laser´s ability to detect changes in the transmittance of a filter sample high in initial EC. 15 µg EC cm^{-2} has been suggested as an upper limit (Subramanian et al., 2006; Wallén et al., 2010), but this value is likely to vary. The ranges of applicability in the draft of the CEN standard for analysis of OC and EC using TOA, range from 0.2 – 16 µg EC/cm^2 and from 1.8 – 45 µg OC/cm^2. Further, a non-biased separation between OC and EC requires that either pyrolytic carbon (PC) evolves before EC during analysis or that PC and EC have the same light absorption coefficient. It is well known that this is not always the case (Yang and Yu, 2002), and there is a lack of information on the magnitude of this imperfection. Action should be undertaken to establish the range for which OC and EC can be analyzed using TOA to greatly reduce the uncertainty in OC/EC measurements.

There is a large number of participating laboratories within the EMEP network. The data quality is complex and can vary substantially from one data set to the other. Consequently, documentation of the data quality is highly important, and within EMEP this has been put into system with objective criteria estimating the uncertainties in the data. A list containing more than 120 flags, designed to describe individual measurements submitted to EBAS according to whether they are "valid", "invalid", or "missing" for various reasons exists, and should be applied for all observational data, including OC and EC. The aim of these flags is to warn about issues that could affect data quality

18 of the 22 OC/EC data sets submitted to EBAS for 2012 did not make use of flags to describe the quality of the data. Here, exception is made for flag 999 (missing data). Lack of flagging is likely attributed to the submitters omitting to perform this task, rather than the lack of need to do so. Examining data sets with respect to Flag 470, "Particulate mass concentration higher than parallel mass concentration measurement with higher cut off, i.e., PM_1 mass > $PM_{2.5}$ mass and $PM_{2.5}$ mass > PM_{10} mass", can be done after they have been submitted, and thus give insight into whether flagging has been assessed or not. The 470 flag was

relevant for 2 of the 18 datasets that have not used flags, and when examining those two it was found that flag 470 should have been used extensively. The reasons for not flagging in general might be several, but omitting this step noticeably reduces the quality of the dataset and in the end introduces needless uncertainties to the answers that we seek from these data.

For ACTRIS, and previously EUSAAR partners, reporting of OC/EC data to EBAS is made according to the ebas template for OC/EC data, http://ebas-submit.nilu.no/SubmitData/RegularAnnualDataReporting/ECOC.aspx, which includes requested meta-data in addition to the observational data itself. From 2015, OC/EC data reported to EBAS is to be reported according to the EBAS format for all submitting such data. With the added information following on from the EUSAAR format, transparency with respect to how sampling and subsequent analysis of OC/EC are performed within EMEP will improve one more step. Further, laboratory analytical performance will be included in the metadata part of the OC/EC reporting format in the near future to create a link between the laboratory's performance in an ILC and the data available in EBAS.

3. The 5th inter-laboratory comparison of analytical methods for carbonaceous particulate matter within EMEP – Organization

All institutes that submitted OC, EC and TC data to EMEP in 2012 were strongly encouraged to participate in *"the 5th inter-laboratory comparison of analytical methods for carbonaceous particulate matter within EMEP"*. TC and the EC/TC ratio were inter-compared. The results from this inter-laboratory comparison (ILC) are presented in the following section.

3.1 Test samples, sub-samples and homogeneity

High-volume samplers were used to collect two PM_{10} filter samples at each of the following three regional background sites: Birkenes, Norway (NOR); Montseny, Spain (SPA); Ispra, Italy (ITA).

The filter samples were collected during the month of December 2013 in order to assess the potential influence from biomass burning emissions on measurement consistency. Upon receipt at the Joint Research Centre (JRC), filters were stored in a freezer at -18 °C. From each filter sample, a rectangular punch of 3.6 cm x 1.8 cm was prepared for each laboratory, which allowed for three replicate measurements. Hence, a set of six punches, based on random selection, was dispatched to each of the participants in closed petri dishes. The participants were asked to report the TC and EC concentration (for each punch in µg C cm^{-2}) with three decimal digits, from three replicates.

The homogeneity of each of the six filter samples used in the inter-comparison was investigated by the JRC. From each filter sample ten subsamples of 2 cm x 2 cm, uniformly distributed over the filter sample surface, were punched, from which two aliquots were analyzed for its TC content. According to ISO 13528:2005 EC, the filter homogeneity was assessed as the between samples standard deviation (i.e., subtracting the within-samples standard deviation obtained from the analysis of two aliquots, and accounting for the JRC laboratory

repeatability, from the standard deviation of sample average) and was better than 3% for the NOR samples and better than 1% for the SPA and ITA samples. If sampling at each location occurred under similar conditions, then one could infer that the test filter samples have similar homogeneity.

A standard solution of phthalic acid, with a concentration (1.528 μg C μl^{-1}) unknown to the participants, was distributed amongst the participants in addition to the six filter samples. The participants were asked to report the OC content of a 10 μl solution. The solution homogeneity was estimated as the between-samples standard deviation: i.e., i) analyzing 10 replicates of the stock solution and a one-time analysis of the 15 aliquots shipped to the participants ii) subtracting the within-samples standard deviation, obtained from the 10 replicated analyses of the stock solution, accounting for the JRC laboratory repeatability, from the standard deviation obtained from the average of the 15 aliquots.

The overall uncertainty of the phthalic acid solution was less than 1.05% and included the uncertainty from the formulation and the between-bottle homogeneity. No study was performed to investigate the short-term stability of the solution.

3.2 Participants

Participants included all laboratories submitting OC, EC and TC data to EMEP for the year 2012, as well as two labs participating in the CEN TC264 WG35 on OC and EC. The participants are listed in Table 3.1. For brevity, a code was assigned to each participant.

Table 3.1: List of participants and contact persons

Code	Name of laboratory	Contact persons
1	ITM-Dept. of Appl. Environ. Sci., Stockholm Univ.	hans.areskoug@itm.su.se
2	NILU-Norwegian Institute of Air Research	key@nilu.no
3	ISCIII-Instituto de Salud Carlos-III	rosalia.fernandez@isciii.es
4	Inst. of Environ. Engi. of the Polish Academy of Sci.	basia@ipis.zabrze.pl
5	ECPL-Environ. and Chem. Proces. Lab., Univ. of Crete	mihalo@chemistry.uoc.gr
6	ARSO-KAL – Slovenian Environment Agency	irena.kranjc@gov.si
7	CHMI-Chezch Hydrometeorological Institute	novakj@chmi.cz
8	IfT-TROPOS – Leibniz Inst. for Tropospheric Res.	spindler@tropos.de
9	CSIC-IDAEA- Inst. of Environ. Assess. and Water Res.	andres.alastuey@idaea.csic.es
10	LGGE – Lab. de Glacio. et Géophys. de l'Environ.	jaffrezo@lgge.obs.ujf-grenoble.fr
11	UL-University of Lund	johan.martinsson@nuclear.lu.se
12	UBA-Umweltbundesamt, Deutschland	elke.bieber@uba.de
13	GGD Amsterdam	ppanteliadis@ggd.amsterdam.nl
14	EMPA- Lab. for Air Poll./Environ. Technol., Duebendorf	andrea.fischer@empa.ch
15 15.B	JRC-Joint Research Centre, Ispra	kevin.douglas@jrc.ec.europa.eu

3.3 Thermal-optical analysis

3.3.1 Protocol

Thermal-optical analysis (TOA) is the most commonly used technique to quantify OC, EC and TC in atmospheric particulate matter (PM) filter samples. In Europe, the two most commonly used protocols are the NIOSH protocol, and variations of it, (Peterson and Richard, 2002) and the EUSAAR-2 protocol (Cavalli et al., 2010). Because of differences in temperature and length of the temperature steps, the two protocols are known to give significantly different results, with the EC/TC ratio derived from NIOSH protocol(s) typically being lower than that of the EUSAAR-2 protocol. No standard protocol was defined at the time of this ILC. Thus, each participant was asked to analyze the samples with the protocol in-use in their respective laboratories (Table 3.2). Two laboratories applied the NIOSH protocol, or a slight variation of it, i.e., lab 3 and lab 13, but both having a temperature of 870° C as the highest temperature step in the He-mode of the analysis. Thirteen laboratories applied the EUSAAR-2 protocol (Table 3.3). Transmittance was used by all laboratories to correct for pyrolysis.

Table 3.2: List of the analytical protocol and punch size used.

Code	Name of laboratory	Protocol	Punch size (cm^2)
1	ITM-Dept. of Appl. Environ. Sci., Stockholm Univ.	EUSAAR-2	1.5
2	NILU-Norwegian Institute of Air Research	EUSAAR-2	1.50
3	ISCIII-Instituto de Salud Carlos-III	QUARTZ	1.50
4	Inst. of Environ. Engi. of the Polish Academy of Sci.	EUSAAR-2	1.00
5	ECPL-Environ. and Chem. Proces. Lab., Univ. of Crete	EUSAAR-2	1.50
6	ARSO-KAL – Slovenian Environment Agency	EUSAAR-2	1.50
7	CHMI-Chezch Hydrometeorological Institute	EUSAAR-2	1.50
8	IfT-TROPOS – Leibniz Inst. for Tropospheric Res.	EUSAAR-2	1.50
9	CSIC-IDAEA- Inst. of Environ. Assess. and Water Res.	EUSAAR-2	1.50
10	LGGE – Lab. de Glacio. et Géophys. de l'Environ.	EUSAAR-2	1.50
11	UL-University of Lund	EUSAAR-2	0.549
12	UBA-Umweltbundesamt, Deutschland	EUSAAR-2	1.50
13	GGD Amsterdam	NIOSH870	1-1.5
14	EMPA- Lab. for Air Poll./Environ. Technol., Duebendorf	EUSAAR-2	1.50
15 15.B	JRC-Joint Research Centre, Ispra	EUSAAR-2	1.00

Table 3.3: *Details of the two analytical protocols used by participants*

	NIOSH/QUARTZ		EUSAAR-2	
	Time (s)	Temp (°C)	Time (s)	Temp (°C)
Carrier gas				
Helium	80	310	120	200
Helium	80	475	150	300
Helium	80	615	180	450
Helium	110	870	180	650
Helium	45	550		
Oxygen in Helium	45	550	120	500
Oxygen in Helium	45	625	120	550
Oxygen in Helium	45	700	70	700
Oxygen in Helium	45	775	80	850
Oxygen in Helium	45	850		
Oxygen in Helium	110	870/890		
% Oxygen in Helium	2%		2%	

4. TC and EC/TC inter-laboratory comparison - Data evaluation

4.1 PM filter samples

In the present exercise, the *measurement method performance* (4.3) and *laboratory performances* (4.4) are evaluated for TC and the EC/TC ratio. TC represents the most robust, and protocol-independent measure of thermal-optical analysis, whereas the EC/TC ratio is free from biases in the carbon determination and allows us to investigate possible biases in the OC/EC split determination among laboratories applying the same protocol.

All results are presented in Annex 1: TC (in µg C cm^{-2}) in Table 1, and light transmittance-corrected EC/TC ratios in Table 2.

On average, reported TC amounts ranged from 5.7 to 35.0 µg C cm^{-2}, corresponding to atmospheric concentrations ranging from 1.3 to 8.0 µg C m^{-3} when collected for 24 hrs with a filter face velocity of 51 cm s^{-1}. The EC/TC ratio ranged from 0.05 to 0.27, on average (including all observations and regardless of the analytical protocol).

There are no technical reasons for which the thermal protocols used in the current ILC could result in a different TC determination, as samples are subjected to more than 3 min at temperatures > 500 °C in an oxidizing atmosphere for all protocols. Hence, potential differences in TC are considered random and thus the TC dataset is evaluated as a whole. The split between OC and EC is operational defined and potential differences in the EC/TC ratio thus may be protocol-dependent. It would have been more appropriate to evaluate the EC/TC data subsets separately according to the protocol used, but a subset of only two laboratories (i.e., those applying the NIOSH/NIOSH-like protocols) is statistically not significant. Thus, the dataset is evaluated as a whole also for the EC/TC ratio.

4.2 Phthalic acid solution samples

The assigned value for the phthalic acid solution's OC concentration was derived by calculation from the chemical formulation, i.e., 1.528 μg C μl^{-1}. Laboratories reported the OC content of a 10 μl solution. Percentage differences from the assigned value are evaluated and reported in section 4.5.

4.3 PM filter samples - Method performance

The assessment of the *method performance* aims at deriving the precision of the applied measurement method, including the repeatability and reproducibility standard deviations. For this, the consistency of the dataset is first evaluated graphically by means of Mandel's *h* and *k* statistics [ISO5725-2] for possible outliers (observations greater than its critical value at 1% confidence level) or stragglers (observations greater than its critical value at 5% confidence level and less or equal to its critical value at 1% confidence level). The Mandel's *h* parameter describes the between-laboratory consistency and was calculated for every laboratory and every sample, whereas the Mandel's *k* parameter estimates the within-laboratory consistency. Values for *Mandel's k* indicators (i.e. outlier and straggler) vary upon the number of replicate measurements. In the present comparison exercise, all laboratories provided three replicates for every sample (except lab 9 and lab 7 for sample SPA-1 and SPA-2, respectively). Thus, *Mandel's k* was calculated for an average case of three replicates.

To confirm the identified outliers and stragglers, G_1-Grubbs' and Cochran's statistical tests were applied for testing the between-laboratory variability and the within-laboratory variability, respectively [ISO5725-2]. Based on the outcomes of the abovementioned statistical treatments, outliers were not used for calculation of the reference value discarded.

From the retained values for each of the six filter samples, the mean value, the repeatability and reproducibility standard deviations were calculated. Subsequently, the dependence of the precision (i.e., repeatability and reproducibility standard deviations) upon the mean values was investigated [ISO5725-2].

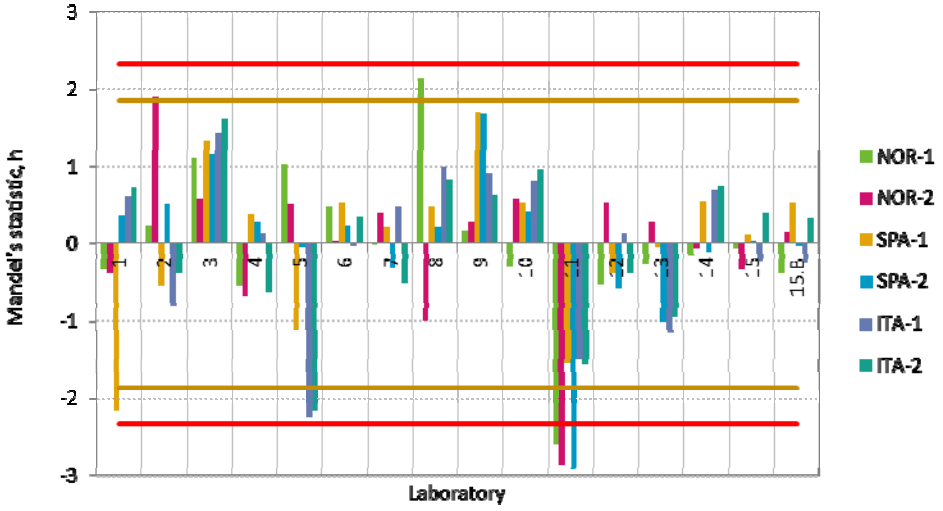
4.3.1 Results: Method performance for TC

In Figure 4.1, the *Mandel's h* statistical values are presented grouped for each laboratory (panel a) and for each sample (panel b).

In the TC dataset, three outliers (lab/sample: 11/NOR-1; 11/NOR-2 and 11 SPA-2), consistently negative from lab 11, and five stragglers (8/NOR-1; 2/NOR-2; 1/SPA-1; 5/ITA-1 and 5/ITA-2) were identified. The Grubbs' test confirmed the 11/SPA-2 as an outlier and the 11/NOR- and 11/NOR-2 as stragglers.

Although sample heterogeneities/contaminations could not be excluded, the random scheme adopted to distribute sub-samples to laboratories is such that the systematic recurrence of stragglers or outliers for a single laboratory indicates unsatisfactory laboratory reproducibility for TC determination, as compared to the other laboratories.

Panel a



Panel b

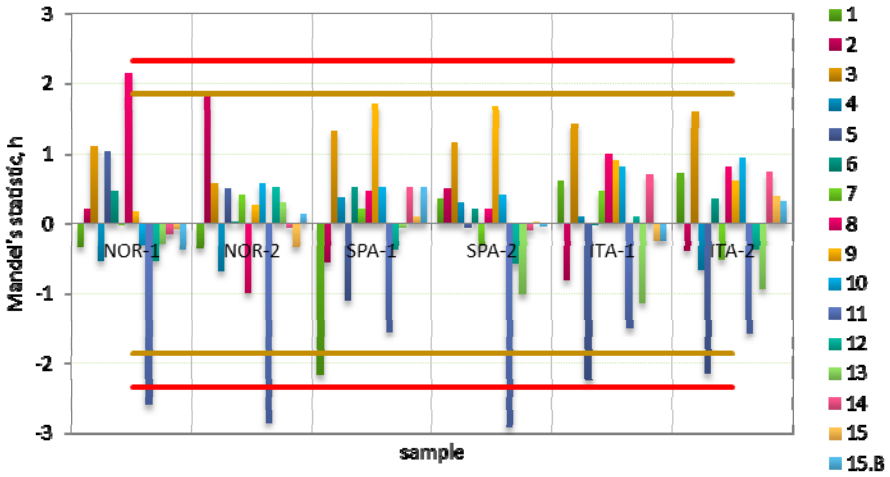
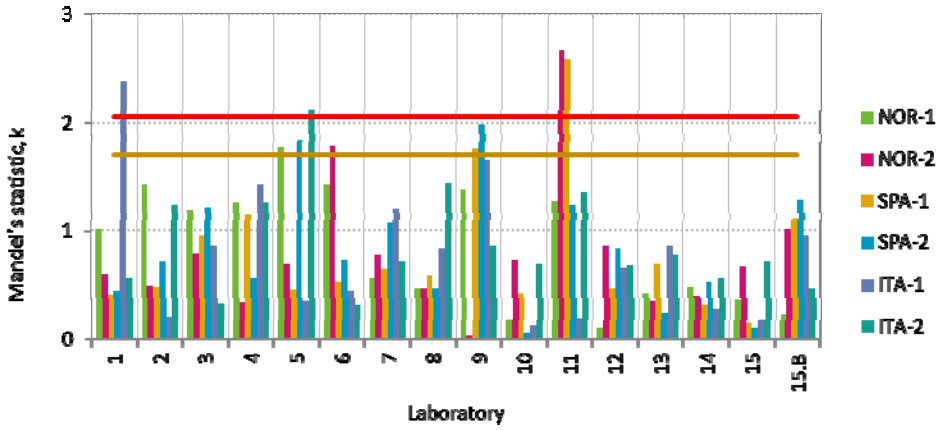


Figure 4.1: Mandel's h statistic values for between laboratory consistency on TC data, grouped by laboratory (panel a) and by sample (panel b). For 16 laboratories, h values should be < 2.33 at 1% significance level (red line) and < 1.86 at 5% significance level (orange line).

In figure 4.2., the *Mandel's k* statistic values are presented grouped for each laboratory (panel a) and for each sample (panel b). In the TC dataset, four outliers (lab/sample: 11/NOR-2; 11/SPA-1; 5/SPA-2 and 1/ITA-1) and five stragglers (lab/sample: 5/NOR-1; 5/NOR-2; 9/SPA-1; 9/SPA-2 and 5/ITA-2) were identified. The Cochran's test confirmed the 11/NOR-2 and 11/SPA-1 as outliers.

Panel a



Panel b

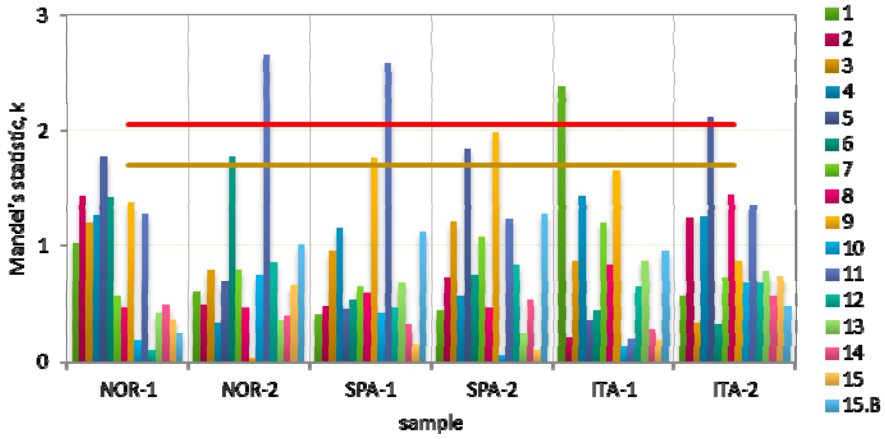


Figure 4.2: Mandel's k statistic values for within laboratory consistency on TC data, grouped by laboratory (panel a) and by sample (panel b). For 16 laboratories and 3 replicates, k values should be < 2.05 at 1% significance level (red line) and < 1.7 at 5% significance level (orange line).

Based on the outcome of the statistical tests and according to ISO 5725-2 7.6, all entries from lab 11 were discarded from the dataset before further elaborations.

From the retained values and for each of the six filter samples, the mean value, the repeatability, s_r, and reproducibility, s_R, standard deviations were calculated. Both repeatability and reproducibility relative standard deviations show an inverse dependence on TC, i.e., the method precision becomes poorer for lower TC contents.

The values of s_r and s_R for the six samples included in the inter-comparison are reported as relative standard deviations in Table 4.1.

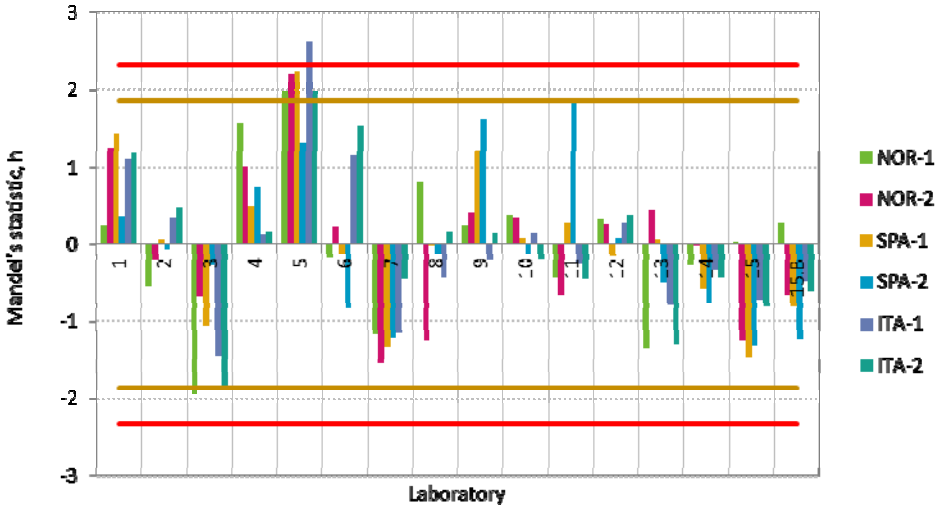
Table 4.1: Repeatability (s_r) and reproducibility (s_R) relative standard deviations for TC.

	Arithmetic mean (µg C cm^{-2})	***s_r* (%)**	***s_R* (%)**
NOR-1	14.294	2.5	6.8
NOR-2	5.780	6.3	8.6
SPA-1	5.815	4.3	14.2
SPA-2	10.340	4.6	8.0
ITA-1	34.470	2.3	5.0
ITA-2	35.260	1.4	5.7

4.3.2 Results: Method performance for the EC/TC ratio

Figure 4.3 shows the *Mandel's h* statistic values for the EC/TC ratios calculated for the entire data set for each laboratory (panel a) and for each sample (panel b). One outlier (lab/sample: 5/ITA-1) and seven stragglers (lab/sample: 3/NOR1-; 5/NOR-1; 5/NOR-2; 5/SPA-2; 11/SPA-2; 3/ITA-2; and 5/ITA-2) were identified. The Grubbs' test identified 5/ITA-1 only as a straggler.

Panel a



Panel b

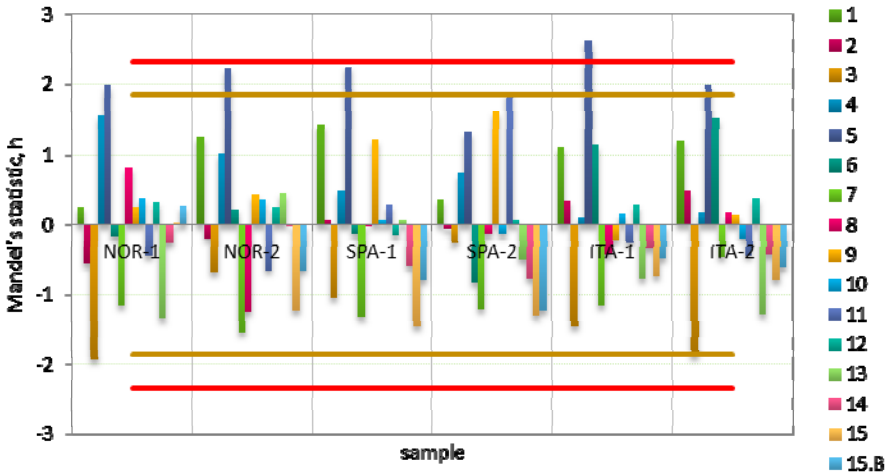


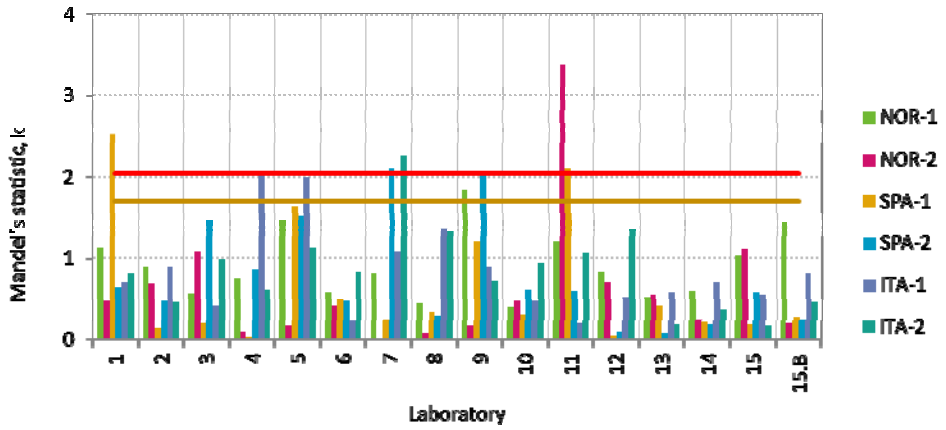
Figure 4.3: Mandel's h statistic values for between laboratory consistency of the EC/TC ratio obtained from the entire data set, grouped by laboratory (panel a) and by sample (panel b). For 16 laboratories h values should be < 2.33 at 1% significance level (red line) and < 1.86 at 5% significance level (orange line).

Although localized sample heterogeneities/contaminations could not be excluded, the random scheme adopted to distribute sub-samples to laboratories is such that the systematic recurrence of stragglers or outliers for a single laboratory indicates

unsatisfactory laboratory reproducibility for the EC/TC ratio determination, as compared to the other laboratories.

In Figure 4.4 the *Mandel's k* statistic values are presented grouped for each laboratory (panel a) and for each sample (panel b). In the EC/TC dataset, six outliers (lab/sample: 11/NOR-2; 1/SPA-1; 11/SPA-1; 7/SPA-2; 4/ITA-1 and 7/ITA-2) and three stragglers (lab/sample: 9/NOR-1; 9/SPA-2; and 5/ITA-1) were identified. The Cochran's test confirmed 11/NOR-2 and 1/SPA-1 as outliers and 7/ITA-2 as a straggler.

Panel a



Panel b

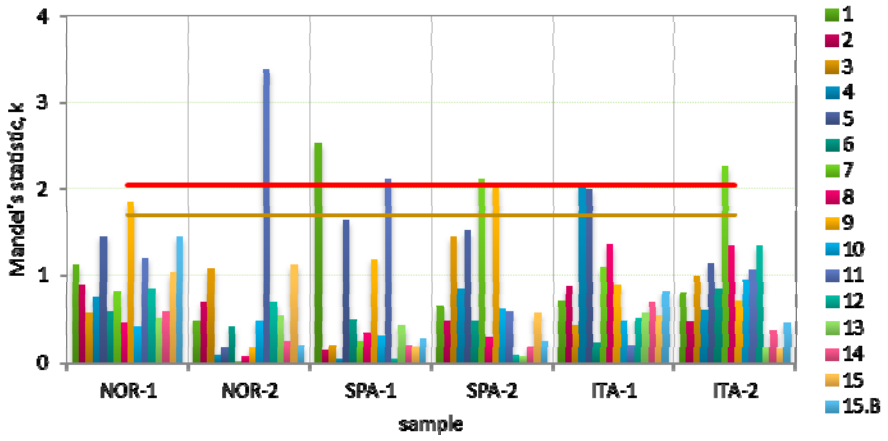


Figure 4.4: Mandel's k statistic values for within laboratory consistency on the EC/TC ratio obtained from the entire data set, grouped by laboratory (panel a) and by sample (panel b). For 16 laboratories k and two replicates values should be < 2.05 at 1% significance level (red line) and < 1.70 at 5% significance level (orange line).

Entries identified as outliers by the statistical tests, i.e. 11/NOR-2 and 1/SPA-1, were discarded from the dataset before further analysis.

From the retained values, the mean value, the repeatability, s_r, and reproducibility, s_R, standard deviations were calculated for the EC/TC ratio for each sample. A clear dependence on the EC/TC ratio was found only for the repeatability standard deviation. In general, repeatability and reproducibility relative standard deviation showed values particularly high for the NOR-2 sample. This might be due to its very low EC/TC ratio value, but could also indicate a poor homogeneity of this test filter with respect to the EC/TC ratio.

Table 4.2: Repeatability (s_r) and reproducibility (s_R) relative standard deviations for the EC/TC ratio.

	Arithmetic mean	s_r (%)	s_R (%)
NOR-1	0.112	3.6%	18.2%
NOR-2	0.050	16.0%	65.9%
SPA-1	0.104	12.1	30.7%
SPA-2	0.110	9.8%	21.7%
ITA-1	0.276	3.1%	21.1%
ITA-2	0.195	2.5%	22.3%

4.4 Filter Samples - Laboratory performance

4.4.1 Data evaluation description

In the present study, the assessment of the *laboratory performance* aims at describing the laboratory bias in terms of *z-scores,* i.e., a standardized measure of the laboratory capacity to comply with the limits defined by a standard deviation. To calculate this, an assigned value and the related standard deviation have to be determined for each of the six samples subject to comparison.

- *Determining the assigned value*: Among the five methods described in the ISO 13528:2005(E) for determining the assigned value, the approach of the *consensus value from participants* was chosen, in absence of a reference or certified reference material. With this approach, the assigned value X for each of the six test samples used in a round of proficiency testing scheme is the robust average calculated, with a recursive algorithm, from the results reported by all participant in the round (See ISO 13528:2005(E), Annex C).

- *Determining the standard deviation for proficiency assessment*: Among the five methods described in the ISO 13528:2005(E) of determining the standard deviation for proficiency assessment, σ*, the approach of calculating σ* *from data obtained in a round of a proficiency testing scheme* was chosen. With this approach, σ* is the robust standard deviation calculated, with a recursive algorithm, from the results reported by all participants in the round proficiency testing (See ISO 13528:2005(E), Annex C).

A *z-Score* for each laboratory, and for each of the six samples subject to comparison, was calculated as $z = (x\text{-}X)/\sigma^*$, where x is the result obtained by each of the participants; X is the assigned value for the actual sample; and σ* is the standard deviation for proficiency assessment.

When a participant reports an entry that produces a *z-Score* greater than +3 or less than -3 (i.e., deviating from the assigned value by more than 3 times the standard deviation), then this entry is considered to give an "action signal". Likewise, if a *z-Score is* greater than +2 or less than -2 (i.e., deviating from the assigned value by more than 2, but less than 3, times the standard deviation), a "warning signal" is given. A laboratory bias between -2 and +2 times σ^* indicates a satisfactory performance.

4.4.2 Results: Laboratory performance for TC

The assigned values X, and the related standard deviations for proficiency assessment, σ*, calculated based on the entire data set for each of the six samples subject to inter comparison, are reported in Table 3 of Annex 2.

z-Scores less than -3 and greater than +3 (Fig. 4.5) indicate that the reported values deviated from the assigned value by more than ±13.3% for NOR-1, ±16.6% for NOR-2, ±24.3% for SPA-1, ±15.0% for SPA-2, ±14.34% for ITA-1 and ±16.5% for ITA-2.

z-Scores less than -2 and greater than +2 indicate that the reported values deviated from the assigned value by more than ±8.9% for NOR-1, ±11.1% for NOR-2, ±16.2% for SPA-1, ±10.0% for SPA-2, ±9.5% for ITA-1 and ±11.0% for ITA-2.

In the TC data set, eight outliers (lab/sample: 8/NOR-1 11/NOR-1; 2/NOR-2; 11/NOR-2; 1/SPA-1; 11/SPA-1 9/SPA-2 and 11/SPA-2) and 10 stragglers (lab/sample: 3/NOR-1; 5/NOR-1; 8/NOR-2: 3/SPA-1; 5/SPA-1; 9/SPA-1; 3/SPA-2; 13/SPA-2; 5/ITA-1 and 5/ITA-2) were detected.

For all of the six samples subject to inter comparison, at least nine of the sixteen laboratories showed deviation from the assigned values within ±1 σ* (i.e., z-scores within [-1, +1]).

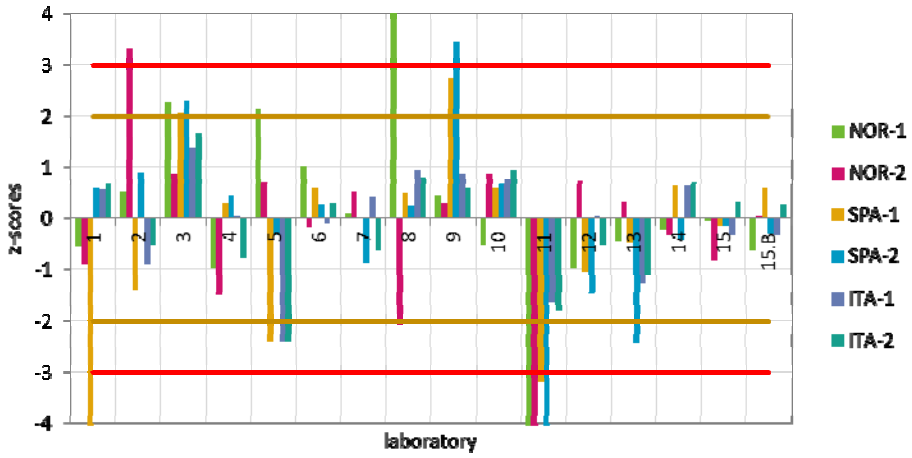


Figure 4.5: z-scores for TC calculated using σ from data obtained in a round of a proficiency testing scheme.*

4.4.3 Results: Laboratory performance for EC/TC

The assigned values, X, and the related standard deviations for proficiency assessment, σ*, are reported in Table 4 of Annex 2. Following ISO13528, σ* were calculated *from data obtained in a round of a proficiency testing scheme* and the obtained z-scores are shown in Figure 4.6.

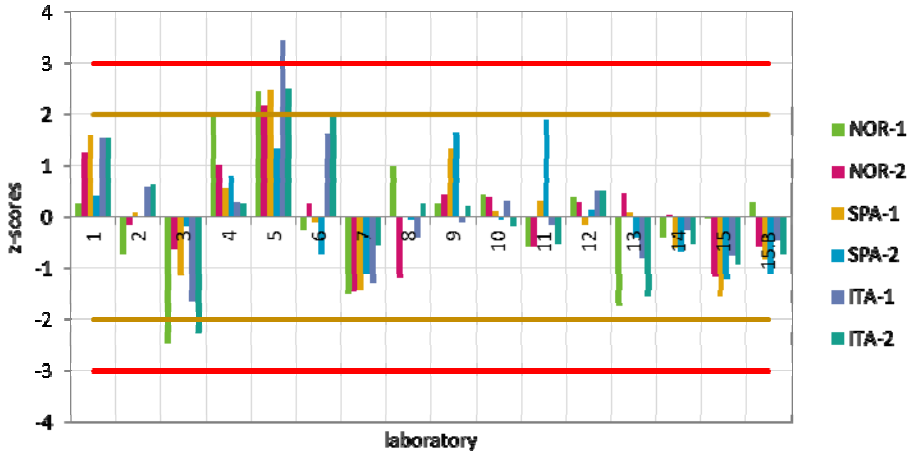


Figure 4.6: z-scores for EC/TC ratio calculated using σ from data obtained in a round of a proficiency testing scheme.*

z-Scores less than -3 and greater than +3 indicated that the reported value deviated from the assigned value by more than ±42.4% for NOR-1; ±206% for NOR-2; ±82.1% for SPA-1; ±63.9% for SPA-2; ±51.3% for ITA-1 and ±53.9% for ITA-2 . z-Scores less than -2 and greater than +2 indicated that the reported values deviated from the assigned value by more than ±28.3% for NOR-1; ±138% for NOR-2; ±54.7% for SPA-1; ±42.6% for SPA-2; ±34.3% for ITA-1 and ±35.9% for ITA-2.

One outlier (lab/sample: 5/ITA-1) and six stragglers (lab/sample: 3/NOR-1; 5/NOR-1; 5/NOR-2; 5/SPA-1; 3/ITA-2 and 5/ITA-2) were identified. For all samples, at least 10 out of sixteen laboratories showed deviation from the assigned values within ±1 σ* (i.e., within 1 z-score).

The observed laboratory biases can partly be due to filter heterogeneity, which cannot be completely excluded. However, the random scheme adopted to distribute sub-samples to laboratories is such that the recurrence of stragglers or outliers for a single laboratory strongly indicates an unsatisfactory laboratory performance as compared to the other laboratories.

Laboratories showing repeated significant biases shall carefully examine their procedures and identify appropriate corrective actions that are likely to prevent the recurrence of such results.

4.5 Phthalic acid solution samples – Percentage differences

Participants were asked to report the OC content of 10 µl phthalic acid solution. This included the analysis of samples prepared by spiking a pre-cleaned filter punch with 10 µl solution. This is the procedure used by laboratories to determine and verify the FID calibration constant when the recommended calibration with CO_2 injections is not implemented.

Figure 4.7 shows the percentage difference from the assigned value for each participant. The observed percentage difference ranged from -9.5% to 11%, with six laboratories reporting OC levels deviating from the assigned value by more than ±5%.

This exercise did not aim at identifying a systematic tendency of a laboratory to underestimate or overestimate the carbon content of analyzed samples, but rather to highlight the potential uncertainty (and variability) that can affect TC determination when the spiking procedure is applied to retrieve the FID calibration constant.

It is recommended to implement the calibration with CO_2 injections where possible, or to carefully revise the accuracy of all steps involved in the external solution spiking procedure (calibration of the pipette volume, complete deposition of the volume onto the filter punch, drying etc.).

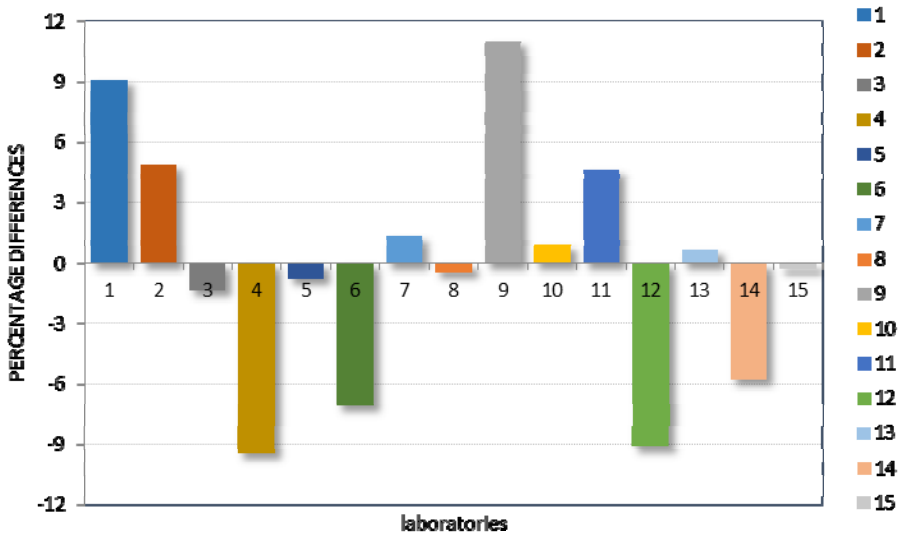


Figure 4.7: Difference in % from the assigned value of the phthalic acid solution.

5. Conclusions from the 5th EMEP inter-laboratory comparison for measurements of the carbonaceous aerosol

The 5th EMEP inter-laboratory comparison for measurement of the carbonaceous aerosol performed in 2013/2014 involved fifteen laboratories applying thermal-optical analysis with two different thermal-optical protocols, i.e. EUSAAR-2 (13 labs) and NIOSH/NIOSH-like (2 labs).

The measurement method repeatability and reproducibility for TC (as relative standard deviation) ranged from 1% to 6% and from 5% to 14%, respectively. For the EC/TC ratio, repeatability and reproducibility (as relative standard deviation) ranged from 3% to 16% and from 18% to 31%, respectively. This range does not include the reproducibility of 66% for the NOR-2 sample, which was likely due to the very low levels of EC. Repeatability and reproducibility show a marginal to clear inverse dependence on TC and EC/TC ratio, i.e. the method performance becomes poorer toward lower levels of TC content and EC/TC ratio.

With respect to the precedent inter-laboratory comparison, only slight improvements, if at all, were observed.

The measurement method performance for TC determination is mainly user-dependent and can therefore be improved by a more accurate implementation of the recommended standard operating procedures. The measurement method performance for the EC/TC ratio is in contrast mainly controlled by the instrument characteristic and set-up, e.g. the actual temperature of the temperature steps, laser alignment, laser temperature-dependence, etc. A more solid and stable in time instrument set-up by the producers would reduce the inter-instrument variability and, in turn, the observed variability in the EC/TC ratio determination.

The laboratory performance was assessed for both the TC loading and the EC/TC ratio determination based on z-scores using as *standard deviation for proficiency assessment,* σ^*, the one calculated *from data obtained in a round of a proficiency testing scheme.*

Eight outliers were identified in the TC data set, of which 50% were reported from one single laboratory, which shall undertake actions. Only one outlier was detected for the EC/TC ratio. Note though, that the values of σ^* are quite big for the EC/TC ratios compared to the TC loadings. The stragglers in EC/TC all came from two laboratories: one using a "NIOSH-like" protocol, reporting EC/TC ratios lower than average, which is as expected, whereas the other one, using the EUSAAR-2 protocol, reported systematically higher EC/TC ratios.

Although localized sample heterogeneities/contaminations could not be excluded, the random scheme adopted to distribute sub-samples is such that the recurrence of stragglers or outliers for a single laboratory indicates an unsatisfactory laboratory performance as compared to the other laboratories. Thus, laboratories showing recurrent biases shall carefully examine their procedures and instrument set-up and identify appropriate corrective actions that are likely to prevent the repetition of such results.

6. References

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Annex 1

Raw Data

Table A 1: Total carbon loadings (µg C cm^{-2})

	NOR-1	NOR-2	SPA-1	SPA-2	ITA-1	ITA-2
	14.009	5.343	3.974	10.274	34.537	36.224
1	13.279	5.241	3.692	10.675	34.071	36.740
	13.743	5.779	3.858	10.627	37.427	36.718
	13.770	6.620	5.430	10.840	32.780	34.950
2	14.750	6.710	5.110	10.930	32.920	34.060
	14.550	7.060	5.190	10.280	33.100	33.710
	15.095	5.594	6.866	11.270	36.066	38.614
3	15.327	6.310	7.229	10.901	36.748	38.369
	15.934	6.140	6.568	12.065	37.385	38.284
	13.798	5.254	6.500	10.175	33.754	33.125
4	13.521	5.433	5.737	10.449	34.040	33.590
	12.905	5.117	5.909	10.730	35.768	34.403
	15.776	5.875	4.709	9.999	30.248	31.469
5	14.619	5.699	4.930	9.190	30.787	30.812
	15.680	6.335	4.626	10.992	30.448	29.333
	14.52	6.632	6.386	10.788	34.163	35.591
6	14.24	5.382	6.148	10.123	33.956	35.874
	15.24	5.04	6.02	10.19	34.626	35.878
	14.316	5.505	5.689		34.543	33.539
7	13.958	6.018	6.138	9.401	34.603	34.160
	13.962	6.222	5.891	10.146	36.161	34.201
	16.628	5.321	6.264	10.498	36.534	37.446
8	16.680	4.885	6.243	10.094	35.294	36.881
	16.944	5.034	5.898	10.481	36.155	35.972
	14.804	5.825	7.646	13.110	37.197	36.824
9	14.287	5.845	6.785	11.563	35.622	36.244
	13.805	5.819		11.307	34.699	35.951
	13.735	6.383	6.015	10.604	35.638	36.676
10	13.635	5.964	6.243	10.605	35.608	37.063
	13.769	5.690	6.292	10.556	35.791	37.388
	10.640	3.530	5.380	6.420	31.890	31.090
11	10.580	3.010	4.120	7.560	31.810	32.480
	11.410	5.400	3.650	6.630	31.600	31.700
	13.388	6.256	5.364	9.077	34.213	34.299
12	13.457	6.161	5.254	9.468	34.244	33.872
	13.399	5.512	5.573	9.895	35.101	34.575
	13.573	5.788	5.935	8.936	31.698	32.620
13	13.796	6.035	5.463	8.904	33.012	33.396
	13.864	5.721	5.629	9.125	32.367	33.177
	13.706	5.410	6.078	9.730	35.305	36.273
14	14.057	5.737	6.274	10.030	35.734	36.832
	13.901	5.743	6.266	10.253	35.479	36.710
	14.110	5.128	5.782	10.143	33.786	36.010
15	14.005	5.555	5.886	10.111	33.845	36.189
	13.849	5.741	5.824	10.209	34.059	35.462
	13.530	6.298	6.635	9.489	33.369	35.500
15 B	13.636	5.410	5.930	10.739	33.550	35.984
	13.703	5.558	5.999	9.990	34.715	35.690

Table A 2: Elemental carbon/total carbon ratios

	NOR-1	NOR-2	SPA-1	SPA-2	ITA-1	ITA-2
	0.118	0.090	0.123	0.114	0.341	0.245
1	0.112	0.095	0.199	0.113	0.346	0.243
	0.120	0.081	0.136	0.126	0.333	0.251
	0.105	0.035	0.107	0.103	0.302	0.215
2	0.098	0.039	0.112	0.114	0.287	0.213
	0.100	0.054	0.110	0.107	0.300	0.218
	0.073	0.009	0.071	0.099	0.190	0.117
3	0.071	0.032	0.072	0.090	0.191	0.108
	0.075	0.039	0.077	0.122	0.197	0.116
	0.143	0.080	0.123	0.138	0.291	0.199
4	0.140	0.082	0.124	0.121	0.297	0.204
	0.146	0.080	0.123	0.120	0.263	0.204
	0.145	0.117	0.165	0.145	0.448	0.274
5	0.156	0.122	0.162	0.153	0.414	0.284
	0.153	0.118	0.210	0.120	0.425	0.283
	0.107	0.049	0.102	0.088	0.343	0.265
6	0.107	0.057	0.096	0.087	0.345	0.256
	0.111	0.061	0.112	0.097	0.341	0.262
	0.091	0.000	0.070	-	0.207	0.176
7	0.085	0.000	0.062	0.082	0.201	0.163
	0.090	0.000	0.063	0.083	0.220	0.185
	0.128	0.008	0.101	0.109	0.238	0.200
8	0.127	0.010	0.110	0.103	0.258	0.197
	0.130	0.010	0.110	0.109	0.258	0.209
	0.108	0.063	0.160	0.126	0.260	0.197
9	0.118	0.059	0.132	0.140	0.273	0.202
	0.123	0.064	-	0.172	0.259	0.203
	0.120	0.054	0.104	0.111	0.287	0.188
10	0.120	0.058	0.114	0.098	0.288	0.182
	0.117	0.068	0.110	0.111	0.280	0.190
	0.105	0.000	0.097	0.157	0.263	0.181
11	0.097	0.000	0.097	0.144	0.260	0.171
	0.106	0.085	0.156	0.154	0.260	0.175
	0.122	0.051	0.103	0.111	0.297	0.205
12	0.117	0.050	0.101	0.112	0.294	0.218
	0.116	0.069	0.102	0.110	0.288	0.209
	0.087	0.054	0.101	0.098	0.236	0.138
13	0.083	0.065	0.113	0.099	0.232	0.138
	0.084	0.069	0.114	0.099	0.226	0.140
	0.109	0.045	0.091	0.092	0.254	0.177
14	0.104	0.049	0.085	0.095	0.264	0.174
	0.106	0.052	0.090	0.091	0.252	0.177
	0.111	0.028	0.057	0.079	0.234	0.160
15	0.109	0.000	0.063	0.088	0.238	0.160
	0.117	0.000	0.062	0.075	0.229	0.161
	0.121	0.029	0.082	0.085	0.254	0.169
15 B	0.111	0.031	0.077	0.083	0.251	0.170
	0.120	0.025	0.086	0.079	0.240	0.165

Annex 2

Statistics

Table A 3: Assigned values and standard deviations for proficiency assessment, σ(from data obtained in a round of a proficiency testing scheme) for TC*

	NOR-1	**NOR-2**	**SPA-1**	**SPA-2**	**ITA-1**	**ITA-2**
Assigned value, X (µg C cm^{-2})	14.022	5.738	5.902	10.228	34.426	35.209
Standard deviation, σ*	0.624	0.317	0.478	0.510	1.642	1.936
Standard uncertainty of X	0.195	0.099	0.149	0.159	0.513	0.605

Table A 4: Assigned values and standard deviations for proficiency assessment, σ(from data obtained in a round of a proficiency testing scheme) for EC/TC*

	NOR-1	**NOR-2**	**SPA-1**	**SPA-2**	**ITA-1**	**ITA-2**
Assigned value, X	0.112	0.047	0.106	0.108	0.269	0.193
Standard deviation, σ*	0.016	0.033	0.029	0.023	0.046	0.035
Standard uncertainty of X	0.005	0.010	0.009	0.007	0.014	0.011