

2nd Interim Report on Grant Agreement for an Action SA/CEN/ENTR/503/2012-11 Ambient Air Quality

DRAFT

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CEN/TC 264/WG 35 "EC/OC in PM"
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1. Introduction

Directive 2008/50/EC requires the measurement of elemental and organic carbon (EC/OC) in the PM_{2.5} fraction in background areas (Article 6.5), with the objective to support air quality assessment and management. To meet these requirements, the European Commission has issued Mandate M/503 "Ambient air quality" for the development of standards regarding automated measurements of particulate matter in ambient air and the measurement of its chemical composition (organic and elemental carbon, inorganic components).

The task of CEN/TC 264/WG 35 is to prepare a new European Standard on the measurement of airborne elemental carbon (EC) and organic carbon (OC) in PM_{2.5} in accordance to Directive 2008/50/EC. No European Standard currently exists and this standard is seen as a prerequisite to ensure compliance with the European legislation.

Up to now, CEN/TC 264/WG 35 has prepared the Technical Report CEN/TR 16243 and an Interim Progress Report (CEN/TC 264/WG 35 N 205).

The validated method will focus on the harmonization and improvement of the data quality of thermal-optical measurement method for EC and OC used in monitoring networks, and develop guidance regarding the use of one protocol (analytical parameters).

The method should be suitable for practical use in routine monitoring networks. The method shall be applicable for rural background sites according to Directive 2008/50/EC. There is a strong need that the same sampling and analysis method should also be applicable for suburban and urban background sites as well, if possible, for street sites, to achieve coherence in the European approach.

This final report describes the work of CEN/TC 264/WG35 Ambient air – measurement of elemental carbon (EC) and organic carbon (OC) deposited on filters, in providing validation work for WI 00264164 "Ambient air – Measurement of elemental carbon (EC) and organic carbon (OC) deposited on filters"

This validation work has been split into 4 work packages as outlined below:

- WP1: Literature review
- WP2: Lab tests
- WP3: Field tests
- WP4: Statistical evaluation

WP1 is completed and the Literature Review has been published (CEN/TC 264/WG 35 N 220).

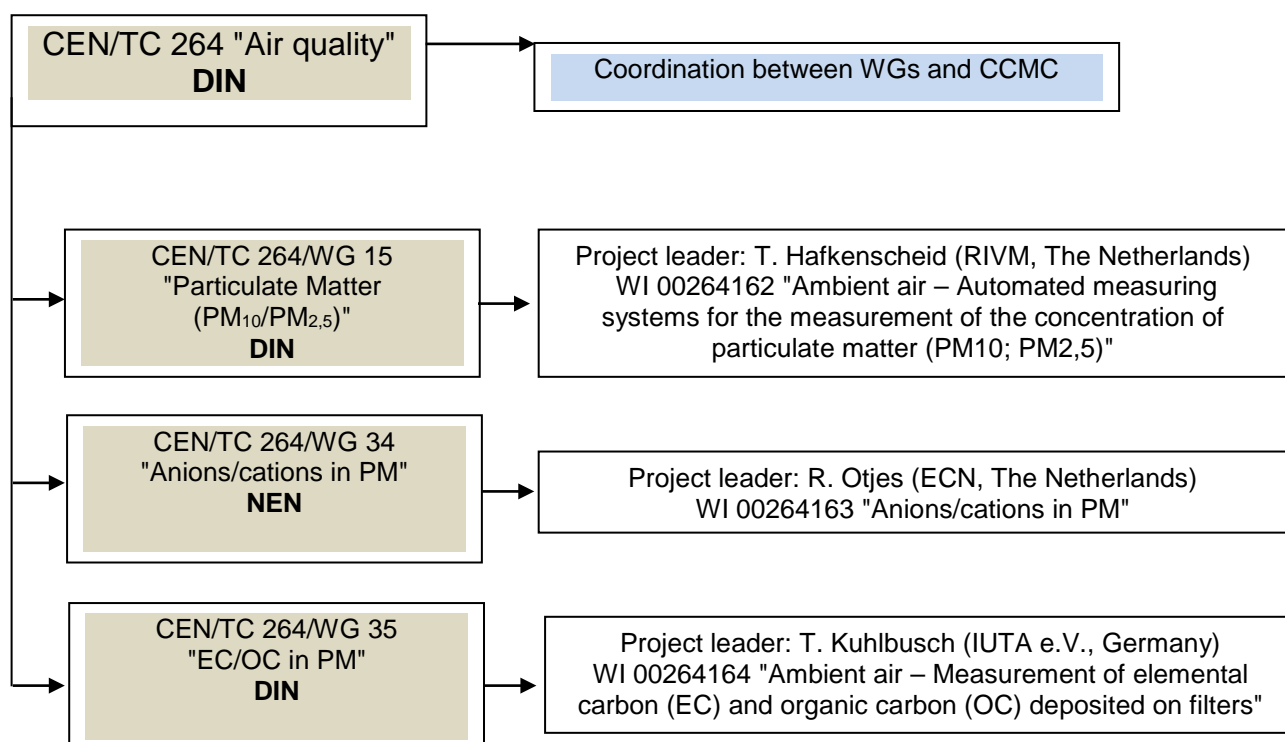
WP2 is completed with 2 inter laboratory comparisons being performed along with extensive laboratory tests. The report on the results of WP2 has been published (CEN/TC 264/WG 35 N 253).

WP3 is completed with field validation tests being performed in Ispra (Rural Background, Italy), Barcelona (Urban Background, Spain), Duisburg (Urban Background, Germany), Amsterdam (Roadside, Holland), Waldhof (Rural Background, Germany) and Cabauw (Rural Background, Holland). Samples from the field sites were distributed to the following laboratories for analysis: GGD Amsterdam, TNO Holland, IUTA Germany and NCSR "DEMOKRITOS" Greece.

WP4 is completed with statistical analysis performed on the field validation results to calculate the measurement uncertainty of a single measured result. A report on the results of the statistical analysis is included in *Annex F*.

2. Structure of the work in CEN/TC 264 Air Quality

In order to perform the work, the following structure was established. Only the working groups covered by mandate M/503 are shown:



It was decided that WG34 & 35 would share resources for the field sampling. WG35 undertook all of the field sampling and provided sampled filters to WG34 for analysis. A common sampling media for all sampling was agreed between the two working groups. Joint meetings between the two groups took place throughout the work packages to ensure efficient and complaint working practices.

3. Status of the work programme

Work Package 1:

The literature review has been published (CEN/TC 264/WG 35 N 220) and is included as *Annex A* of this report.

Work Package 2:

A laboratory intercomparison for the laboratories taking part in WP3 was performed. The main conclusions to be drawn from the 1st laboratory intercomparison are that oven temperature calibrations should be performed on a regular basis and that all instrumentation used to produce the final result should have their calibrations validated. For this reason the results from this intercomparison were only used for diagnostic purposes.

A 2nd intercomparison was performed and showed that there was good agreement between laboratories and analysis protocols when analysing both the sucrose solution and filter punches. When analyzing individual filter punches, results can be up to 10% different from the consensus value for total carbon (TC). The full results of the 2nd laboratory intercomparison are given in *Annex B* of this report. From the second laboratory intercomparison it can be concluded that laboratory performance was of good enough quality that valid conclusions could be drawn from the measurements of field samples.

The conclusions from the report on the laboratory tests (CEN/TC 264/WG 35 N 253) are:

1. The use of filters containing high concentrations of metals and /or binding material should be avoided. The POC/TC alters when such a filter is used and the split point may be shifted.
2. OC concentrations in blanks may vary per filter type, manufacturer, batch and/or filter. When relatively high concentrations are routinely observed, higher than 2 µg C/cm², pre-firing should be considered.
3. The initial OC concentration may or may not desorb from the filter material during sampling. Subtracting the field blank values from ambient concentrations is therefore not recommended.
4. Field exposure, handling and/or conditioning of a blank filter may alter the initial OC concentration. It is suggested that these are evaluated per filter type and each handling-conditioning step.
5. Standard solutions may be used for calibration and quality control. The organic compound selected for the standard solution shall be of such size and properties that does not fully desorb from the filter in temperatures less than 300 °C, e.g. sucrose and not oxalic acid. Sucrose solutions can be used up to a concentration of 300 µg C/cm² for all three protocols. The upper operational limit of the analyzer is defined by the full scale response of the detector per temperature step.
6. No clear correlation between laser signal intensity and EC/OC split point definition was identified for a laser intensity down to 500 Thermal/Optical Transmittance (TOT) (using the Sunset Labs instrument units) for a blank and EC concentrations up to ~40 µg/cm². EC for Thermal/Optical Reflectance (TOR) results showed more variation for all laser intensities.
7. Comparison exercises can serve as a QA/QC tool identifying deviating laboratory performance. The use of both standard solution and loaded quartz filters is recommended during such exercises.

8. Failure to measure and correct for temperature offsets may bias analysis results of filters with high concentrations. The temperature calibration application is recommended on an annual basis and after main oven maintenance, whichever is more frequent.
9. The homogeneity of the samples collected during the WG34-WG35 campaign is comparable with filters obtained by other samplers and reported on average a RSD of less than 5% for TC and less than 10% for EC and OC, TOT and TOR.
10. Long term daily repeated measurements of HVS filters provided similar results to the homogeneity tests for OC (TOT and TOR) and TC, less than 5%, while up to 17% for EC (TOT and TOR), indicating the stability of the performance of the analyzer.

The full report on the laboratory tests is included in *Annex C* of this report.

Work Package 3:

The six field validation tests have been performed in Ispra (Rural Background, Italy), Barcelona (Urban Background, Spain), Duisburg (Urban Background, Germany), Amsterdam (Roadside, Holland), Waldhof (Rural Background, Germany) and Cabauw (Rural Background, Holland). Samples from the field sites were distributed to the following laboratories for analysis: GGD Amsterdam, TNO Holland, IUTA Germany and NCSR "DEMOKRITOS" Greece.

The samples from each field site have been analysed, and the results sent to the National Physical Laboratory (WP4 - Statistical evaluation of data and reporting). Reports on each field validation site are included in *Annex D*, parts 1 to 6. Reports on the corresponding EC and OC results from the different laboratories are given in *Annex D*, parts 7 to 10.

Consistent site working procedures were implemented by Standard Operating Procedures (SOPs), written by the working group, for:

1. Operation of the Digitel high volume sampler
2. Filter handling, treatment and marking
3. ECOC analysis
4. Requirements for data exchange
5. Installation and operation of MAAP
6. Installation and operation of Aethalometer

These SOPs are included in *Annex E*, parts 1 to 6.

In addition to the filter sampling, real-time EC analysers (Multi Angle Absorption Photometer (MAAP) and a 7 wavelength Aethalometer) were also operated and their results compared to the EUSAAR2 transmittance results from the filter analysis.

Work Package 4:

The results from each sample, using the 6 thermal-optical protocols, were statistically analysed to calculate the uncertainty in a single measured result. The uncertainty analysis was performed on the whole data set as well as by site type and concentration range. In addition each thermal-optical protocol was ranked according to internal variability, between laboratory variability and between sampler variability.

The statistical analysis showed that the reflectance protocols were not suitable for the measurement of EC due to their inability to detect low levels of EC. The analysis showed that

all 3 transmittance protocols delivered similar performance with no protocol clearly performing better across all measurement site types and concentration ranges. Typical uncertainties of a single measurement result (95%, 2σ) were <25% for EC, <15% for OC and <8% for TC.

In addition to the statistical analysis, method detection limits from laboratory blank filters were calculated, along with field blank levels to assess the contamination of filters due to handling and storage.

The report covering the statistical analysis, detection limits, field blanks and the comparison of real-time EC analysers with the filter measurements is included in *Annex F* of this report.

3.1 Contract item 2012-11.3.1 EC/OC in PM

1/ Identification	<ul style="list-style-type: none"> • WI number 00264164, • Contract item 2012-11.3.1 • covers item 3 of mandate M/503
2/ Title	EC/OC in PM
3/ Progress of work	<p>present stage : Stage code 30.99 Dispatch Enquiry draft to CCMC</p> <p>next stage : Stage code xx.yy Launch CEN Enquiry</p>
4/ Milestones so far	<p>Validation work:</p> <ul style="list-style-type: none"> • WP1: Literature review: Published (CEN/TC 264/WG 35 N 220) see Annex A. • WP2: Lab intercomparisons and tests: Completed and results published (CEN/TC 264/WG 35 N 253), see Annex B & C • WP3: Field tests: Completed and reports on each site published, See Annex D & E • WP4: Statistical evaluation, See Annex F <p>Development of standard:</p> <ul style="list-style-type: none"> • Submission of modified prEN X (WI 00264164) to CEN enquiry, see Annex G
5/ Next steps and remaining work	<p>Listing of the milestones still be to achieved:</p> <p>Development of standard:</p> <ul style="list-style-type: none"> • Pre-evaluation of the technical comments given during CEN enquiry and preparation of a modified text of prEN X (WI 00264164) accordingly • Discussion and approval of the proposed answers to the CEN enquiry comments and modified text by WG • Submission of modified prEN X (WI 00264164) to CEN Formal Vote • Preparation of the final draft of prEN X (WI 00264164) <p>This project is in line with the original timeframe. In case of any unforeseen events that might influence these steps and the timeframe of the project, the Commission will be informed.</p>
6/ Documents	<p>Annex A: Literature Review</p> <p>Annex B: Laboratory Intercomparisons</p> <p>Annex C: Laboratory Tests</p> <p>Annex D: Field Measurement Sites</p> <p>Annex E: Standard Operating Procedures (SOPs)</p> <p>Annex F: Statistical Analysis of Filed Validation Measurements</p>

Annex A Literature Review (WP 1)

See separate document "Annex A_Literature Review (WP 1).pdf".

Annex B Laboratory Intercomparisons (WP 2)

First Laboratory Intercomparison

Each laboratory was sent:

- 1 of sucrose solution with a carbon content of $\sim 4 \mu\text{gC}/\text{ul}$
- 5 of 47mm diameter filter punches taken from 5 filters exposed by GGD. Duplicate analysis of each punch by the 3 protocols

GGD, TNO and IUTA results for the sucrose analysis agreed with a spread of $\sim 7\%$. Results from Demokritos were $\sim 25\%$ lower than the assigned value of the sucrose. Demokritos previously had problems with instrument and syringe calibration so were going back to investigate the reason for the discrepancy. Unfortunately the Demokritos representative at the January 2014 working group meeting had not performed the analysis himself so could not comment on their procedures.

Carbon loadings from the filters ranged from $1 - 10 \mu\text{g}\cdot\text{cm}^{-2}$. Results for total carbon did not follow the same agreement as was shown for the sucrose solution. All laboratories agreed with each other $\sim 10\%$. This would indicate that maybe Demokritos was not adding the correct amount of sucrose test solution to their filter punch for analysis.

GGD performed their analysis on the instrument as found and then performed an oven temperature calibration for each analysis protocol before repeating the analysis. The correction temperatures from this recalibration were in the order of -50°C , indicating the pre-calibration oven temperatures were lower than the protocol temperature. For TC, OC and EC there was better agreement between the GGD pre and post calibration results than with the other laboratories. The spread in results was different for each analysis protocol, with the largest spread using the NIOSH 870 protocol. Upon investigation it turned out that all laboratories had supplied their results using instruments in their as found states, with the gap between analysis and the last oven temperature calibration varying up to 6 months. As the temperatures reached by the NIOSH870 method are the largest it was concluded that poor oven temperature calibration was the probable cause for the variation between laboratories.

As a result of the filter intercomparison results it was recommended that each laboratory perform a protocol-specific oven calibration before analysing filters from each field location.

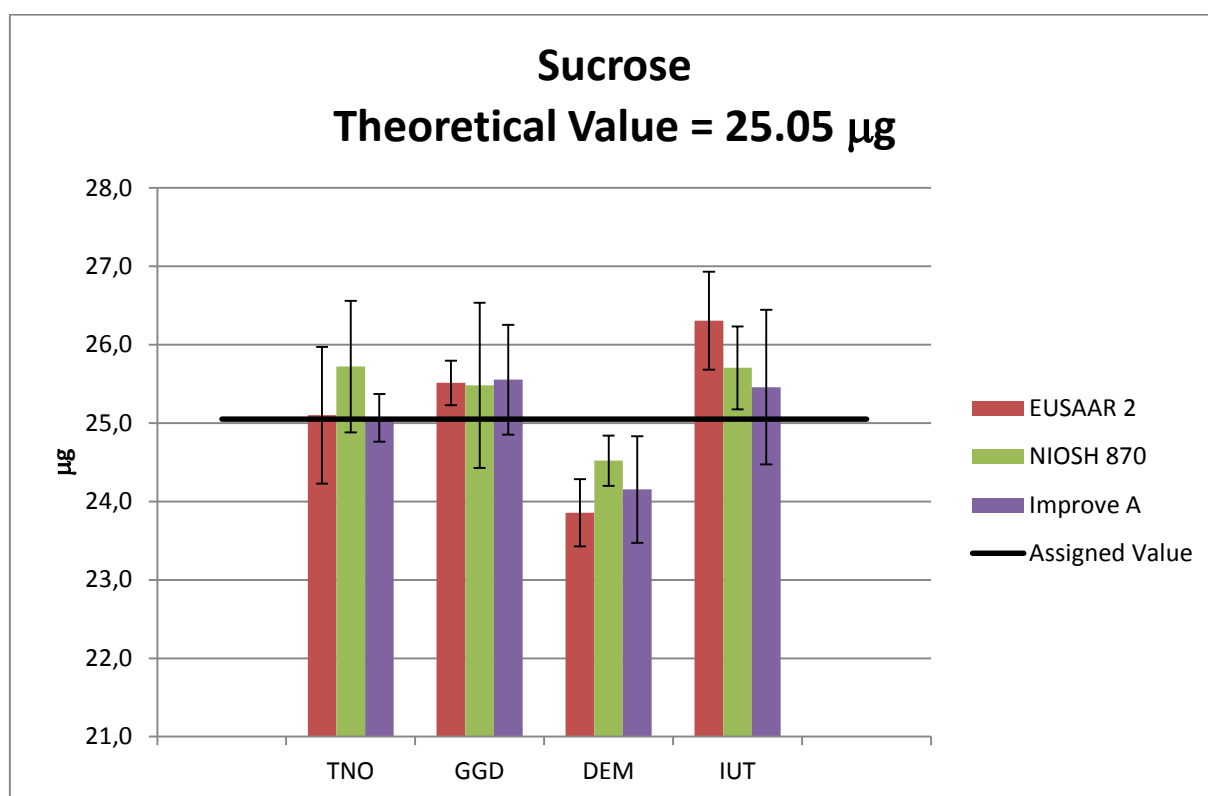
As the results of the sucrose and filter intercomparisons highlighted some significant differences between laboratories it was decided that this intercomparison should be used for diagnostic purposes only without any in depth statistical analysis. A second intercomparison exercise was organized.

Second Laboratory Intercomparison

Each laboratory was sent:

- 1 of sucrose solution with a carbon content of 2.505 µgC/ul
- 5 of 47mm diameter filter punches taken from 3 filters exposed by GGD. Duplicate analysis of each punch by the 3 protocols

For the analysis of the sucrose solution, all laboratories agreed with the theoretical value within ±5% for all three analysis protocols. The results for the sucrose analysis are given in Figure 1. The mean result of 3 measurements has been plotted and the error bars are 2 times the standard deviation of the measurements.



The assigned value is 25.05 µgC.

Results from sucrose solution analysed by EUSAAR 2, NIOSH 870 and IMPROVE A protocols

The uncertainty weighted average, x_{best} , and standard deviation, δx_{best} , of participant's results for each analysis protocol are calculated from the following:

$$x_{best} = \frac{\sum_{i=1}^n w_i \times x_i}{\sum_{i=1}^n w_i}$$

Where:

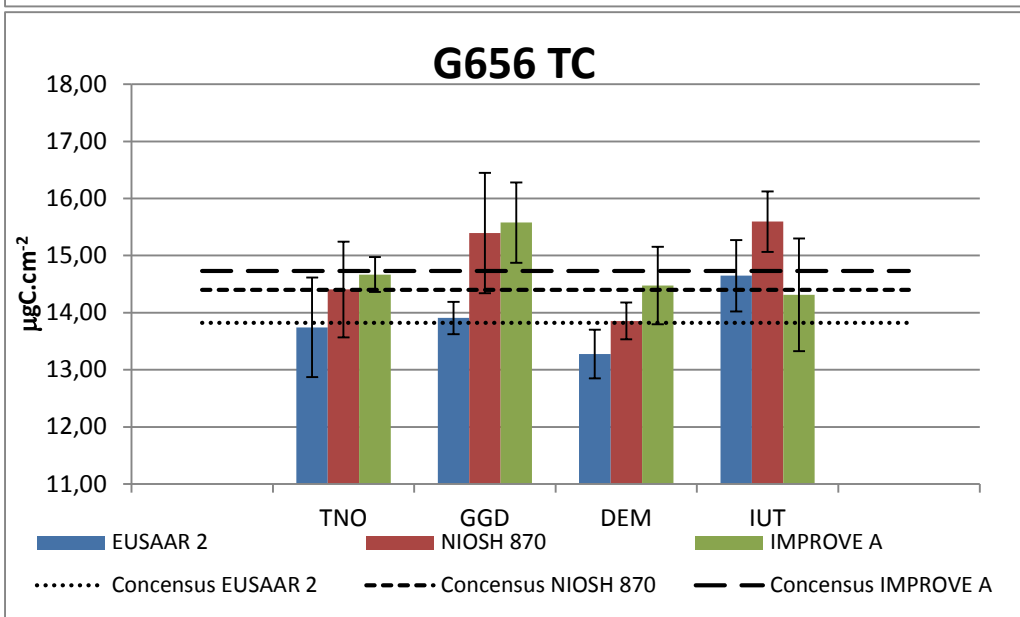
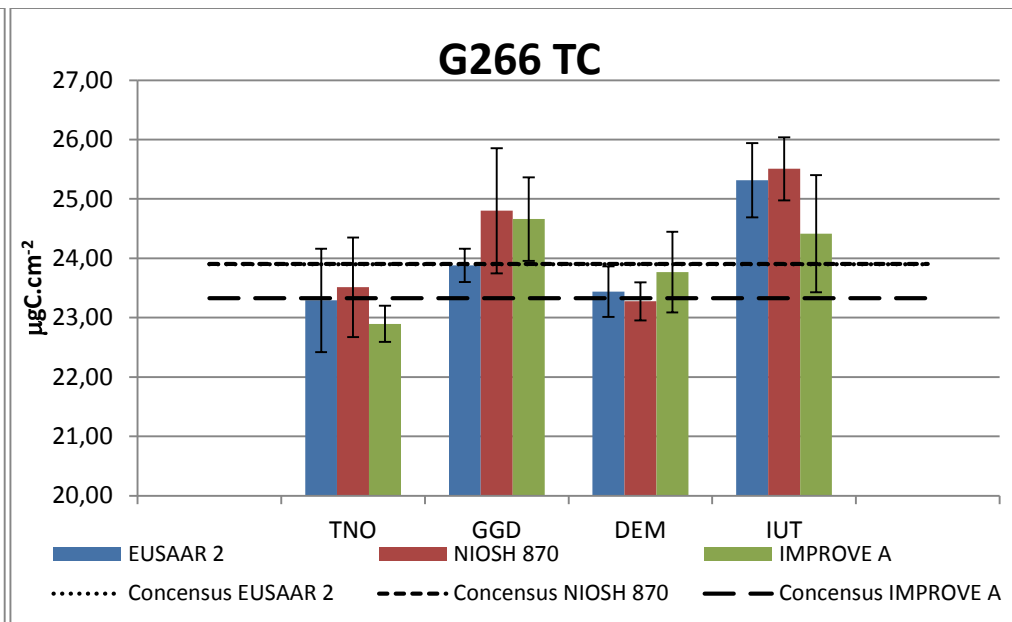
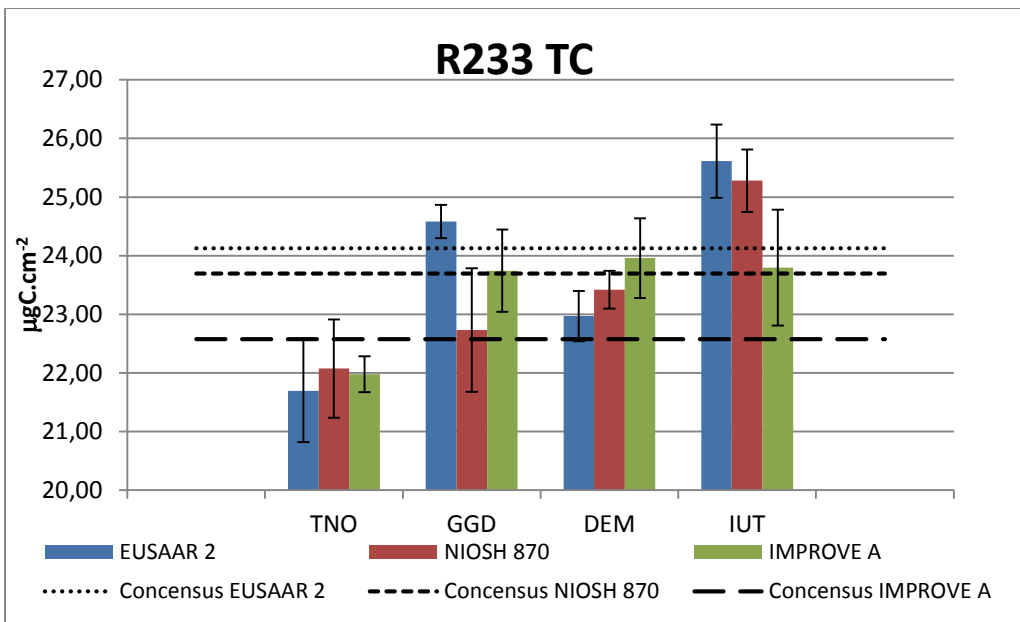
$$w_i = \frac{1}{\sigma_i^2}$$

$$\sigma_{x_{best}} = \frac{1}{\sqrt{\sum_{i=1}^n w_i}}$$

EUSAAR 2		NIOSH 870		IMPROVE A	
x_{best}	δx_{best}	x_{best}	δx_{best}	x_{best}	δx_{best}
25.17	0.11	24.96	0.13	25.03	0.13

Both the x_{best} values for the NIOSH 870 and IMPROVE A protocols agree with the assigned value within δx_{best} and the EUSAAR value for x_{best} is 0.01 outside of agreeing with the assigned value within δx_{best} . Therefore the uncertainty weighted average agrees with the assigned value for all protocols.

As well as sucrose solutions, 3 sampled filters were measured by each participant using all 3 protocols. The results are shown below. The error bars are 2 times the standard deviation of the individual laboratory sucrose measurements. The consensus value is the uncertainty weighted average of the participant's results.



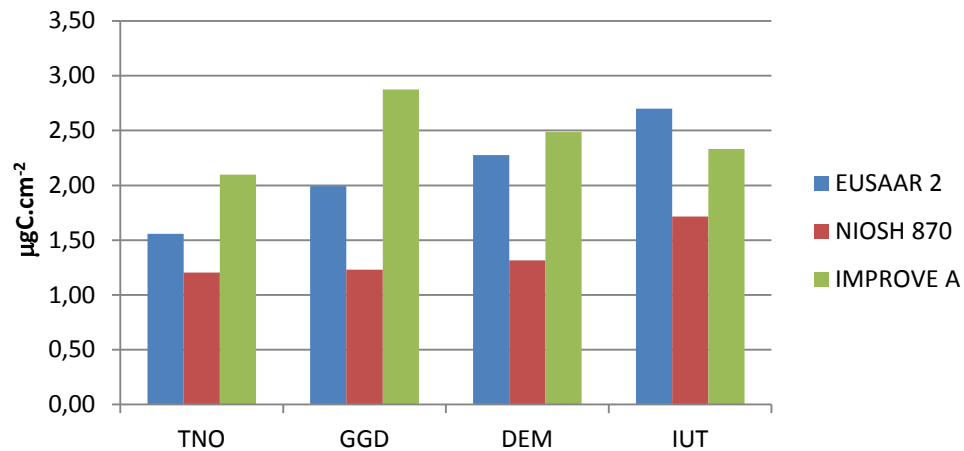
For filter G266 the consensus values for EUSAAR2 and NIOSH870 are identical.

Total Carbon results for filters analysed by EUSAAR 2, NIOSH 870 and IMPROVE A protocols

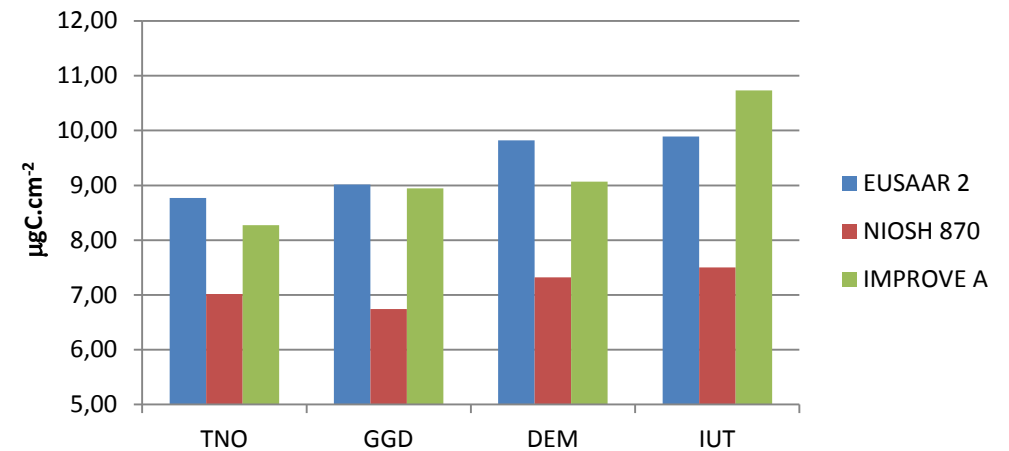
It can be seen that the difference between each lab is much larger than for the sucrose results with uncertainties encompassing the uncertainty weighted mean for filters G656 and G266, but not for filter R233.

Participant results for EC and OC are shown below.

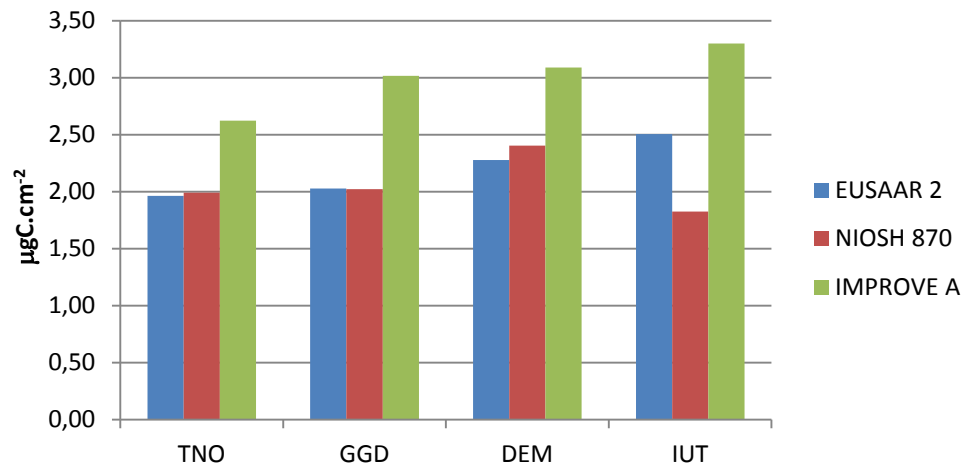
R233 EC 8% EC



G266 EC 35% EC

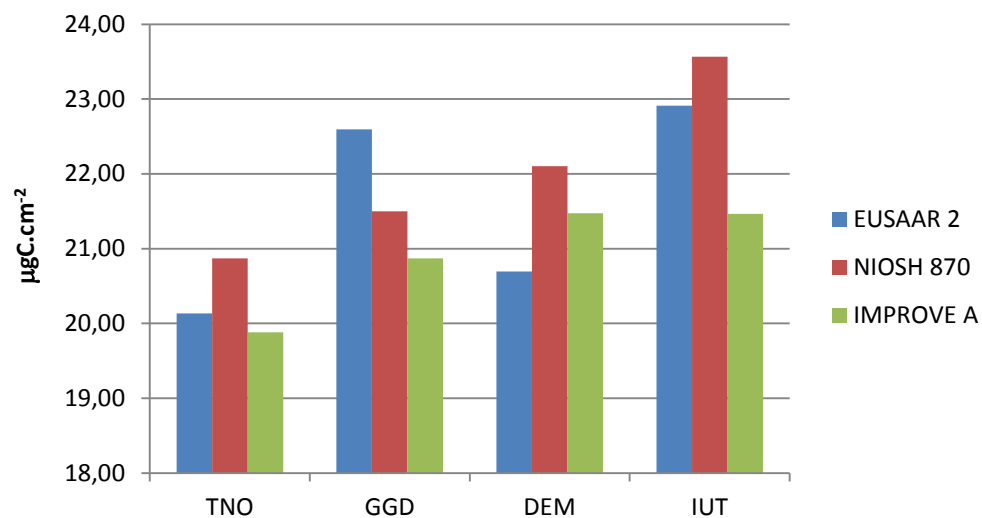
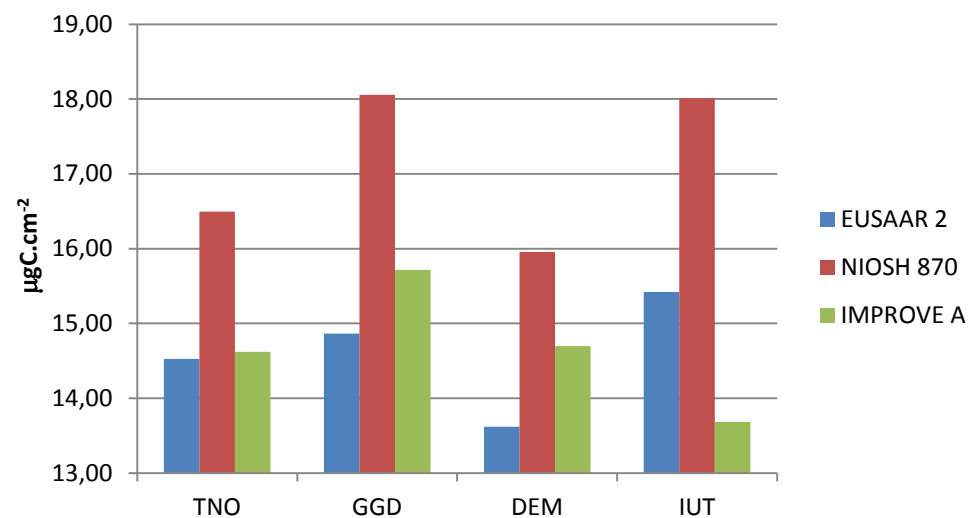
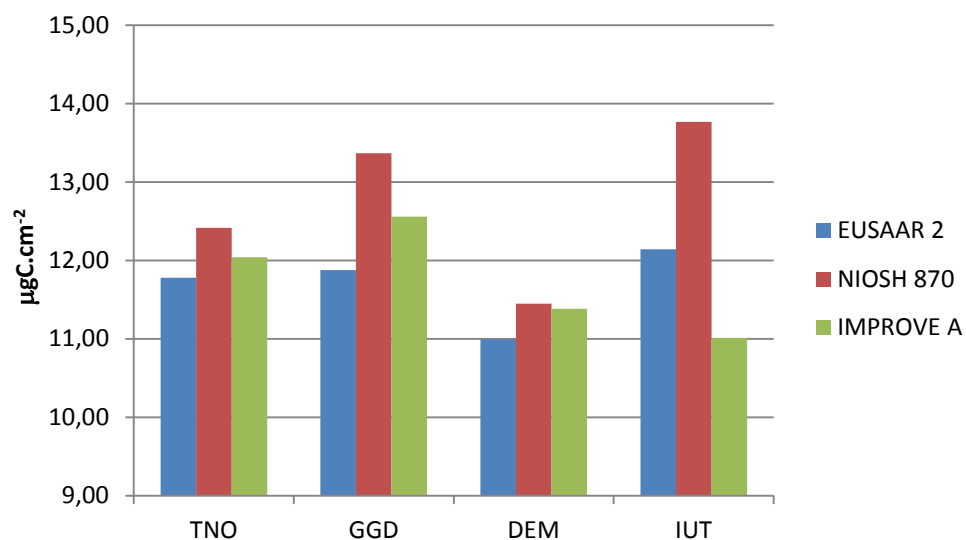


G656 EC 17% EC



Note that the y-axis scale for G266 is twice that for the other 2 filters.

Elemental Carbon results for filters analysed by EUSAAR 2, NIOSH 870 and IMPROVE A protocols

R233 OC**G266 OC****G656 OC**

Organic Carbon results for filters analysed by EUSAAR 2, NIOSH 870 and IMPROVE A protocols

Annex C Results of Laboratory Tests (WP 2)

See separate document "Annex C_Results of Laboratory Tests (WP 2).pdf".

Annex D Field Validation Site Reports (WP 3)

D1 Ispra (Rural Background, Italy)

See separate document "Annex D1_Field_Report_Ispra_rural_background.pdf".

D2 Barcelona (Urban Background, Spain)

See separate document "Annex D2_Field_Report_Barcelona_urban_background.pdf".

D3 Duisburg (Urban Background, Germany)

See separate document "Annex D3_Field_Report_Duisburg_urban_background.pdf".

D4 Amsterdam (Roadside, Holland)

See separate document "Annex D4_Field_Report_Amsterdam_roadside.pdf".

D5 Waldhof (Rural Background, Germany)

See separate document "Annex D5_Field_Report_Waldhof_rural background.pdf".

D6 Cabauw (Rural Background, Holland)

See separate document "Annex D6_Field_Report_Cabauw_rural background.pdf".

D7 Field Tests EC OC Analysis Lab1

See separate document "Annex D7_Field_Tests_EC OC Analysis_Lab1.pdf".

D8 Field Tests EC OC Analysis Lab2

See separate document "Annex D8_Field_Tests_EC OC Analysis_Lab2.pdf".

D9 Field Tests EC OC Analysis Lab3

See separate document "Annex D9_Field_Tests_EC OC Analysis_Lab3.pdf".

D10 Field Tests EC OC Analysis Lab4

See separate document "Annex D10_Field_Tests_EC OC Analysis_Lab4.pdf".

Annex E Standard Operating Procedures (SOPs) (WP 3)

E1 Operation of the Digitel high volume sampler

See separate document "Annex E1_Operation of the Digitel high volume sampler.pdf".

E2 Filter handling, treatment and marking

See separate document "Annex E2_Filter handling, treatment and marking.pdf".

E3 EC OC analysis

See separate document "Annex E3_EC OC analysis.pdf".

E4 Requirements for Data Exchange

CEN/TC 264/WG 35 N 174

Laboratory analysis of field samples

NPL expects to get results stored in the Excel result file generated by the Sunset peak integration software. A single version of analysis software needs to be decided on by the analysis laboratories. We expect to only get results from samples, filter blanks and field blanks.

We do not expect to get results from instrument calibrations and performance checks. These can be provided by the analysis lab in a separate file if necessary, but they should be used for internal quality control. We will be comparing calculated ambient concentrations, not scaling participant's analysis runs.

We expect separate result files for separate analysis protocols. Results calculated by reflectance and by transmission can be reported in 1 file as long as it is clearly marked in the file which optical correction method is used for each result line (See template).

Each analysis lab should generate 3 results files per sampler (3 analysis protocols including both optical correction methods). Each file should contain one result line per sample analysed. Each file will be between 80 and 120 lines long (depending on number of filters exposed at each site and if both transmission and reflectance optical correction methods are used to calculate the results). Results in these files need to use the standard filter identification code used to identify the original sampled filter (SOP on filter marking).

Results files should use the following naming convention:

IPA_12345_EUSAAR2_GGD	site=Ispra (IPA), sampler serial number=12345, analysis protocol=EUSAAR2, analysis lab=GGD
IPA_12345_NIOSH870_GGD	site=Ispra (IPA), sampler serial number=12345, analysis protocol=NIOSH870 analysis lab=GGD
IPA_12345_IMPROVEA_GGD	site=Ispra (IPA), sampler serial number=12345, analysis protocol=IPROVEA analysis lab=GGD

Each sample will follow the SOP on filter marking as detailed below:

STATION - PM2.5 -. Sampler # Holder # - Date Sampling Start (dd mmm yyyy)
e.g. IPR - PM2.5 - 12345 - 07 - 11 Dec 2013

An excel template file has been produced for the OCEC analysis results. The first 2 data lines are for example only.

Each file should contain separate columns for each parameter as follows:

Sample ID
Optics Mode
OC(ug/sq cm)
OC unc
EC(ug/sq cm)
EC unc
CC(ug/sq cm)
CC unc
TC(ug/sq cm)
TC unc
EC/TC ratio
Pk1 C ug/sqcm to Pkn C ug/sqcm (1 column per peak)
Pyrol C ug/sqcm
EC1 C ug/sqcm to ECn C ug/sqcm (1 column per peak)
Date
Time
CalConst
Punch Area
FID1
FID2
calibration area
Points
Split time(sec)
Manual split?(sec)
Init.Abs.
Abs.Coef.
Inst. Name
Atm.Pres.mmHg
Optical EC
Analyst
Laser Correction
Begin Int
End Int
TranTime
Analysis Parameter File
SB version
VBasic Version

Filter blanks and sample blanks can be contained in the 3 results files but results need to be clearly identified as such.

Each analysis laboratory will need to follow the SOP for identifying themselves and the field site which the samples including blanks come from.

Field Measurements

NPL expect to get sample times, sample volumes (expressed at ambient conditions), other PM measurements, any meteorological data and relevant comments on every filter sample taken. Predominantly our analysis will be on the carbon per square cm results produced by the analysis laboratories, but we will also convert these into ambient air concentrations.

Filter sampling data should be in the standard form as defined by the SOPs. Any flow calibration data should also be supplied to allow for the correct sample volume to be calculated.

Automatic BC data should be supplied in an Excel file per instrument at the time base used by the instrument. The file should contain the site and instrument used. Results shall be in mass concentration units ($\mu\text{g.m}^{-3}$). If results have not been corrected for filter loading then attenuation data also needs to be supplied. No averaging should be done.

The instrument configuration should be recorded including whether or not automatic filter loading correction was enabled or not. Any calibration data should also be supplied.

Site owned automatic and manual PM data and meteorological data should be supplied in an Excel file per instrument as daily averaged values, already corrected for calibrations. For PM data, results shall be in mass concentration units ($\mu\text{g.m}^{-3}$).

E5 Installation and Operation of MAAP

See separate document "Annex E5_Installation and Operation of MAAP.pdf".

E6 Installation and Operation of Aethalometer

See separate document "Annex E6_Installation and Operation of Aethalometer.pdf".

Annex F Statistical Analysis of Field Validation Data (WP 4)

See separate document "Annex F_Statistical Analysis of Field Validation Data (WP 4).pdf".