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Statistical Analysis of Organic Carbon (OC), Elemental Carbon (EC) & Total Carbon (TC) Concentrations Collected on Filters from the CEN TC 264 WG 35 Field Validation Exercise

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Executive Summary

Daily $PM_{2.5}$ samples were collected from 6 monitoring stations over 2013 & 2014 and analysed by 4 different laboratories. Sub-samples of each daily filter were analysed twice using 6 thermal-optical protocols (EUSAAR2, NIOSH & IMPROVE) with optical corrections for OCEC split point performed by both reflectance and transmittance methods. This resulted in 12 results per laboratory, per sampled filter.

NPL performed a statistical analysis to determine the uncertainty of a single measured value based on between-laboratory variability, internal-laboratory variability and between sampler variability. NPL expanded this analysis to rank the different protocol / optical correction methodologies on a site specific and complete dataset basis.

The analysis shows that the reflectance protocols have problems detecting very low levels of elemental carbon and are unable to deliver the detection limits required.

The results from the transmittance protocols show no protocol clearly performing better than the others across all of the site types and concentrations encountered during the field validation tests. EUSAAR2 performs best for EC at urban background and roadside locations and second best at rural locations.

There was no significant between sampler variability detected for most components and most protocols. Where it was detected it was insignificant compared to the internal repeatability.

The uncertainty of a single measurement result (95%, 2σ) for the transmittance protocols is less than 25% above concentrations of 2 $\mu g.cm^{-2}$. For concentrations below this the relative uncertainty is greater than 25%, but probably limited by the detection limit. When performing repeat measurements of a single sampled filter the repeatability was similar to the calculated uncertainty of a single measurement result.

The OC detection limit measured from laboratory blank filters was close to or exceeded the requirements of the draft standard, with the NIOSH protocols over reporting OC levels compared to the other protocols. The mean EC detection limit for reflectance protocols is <0.1 $\mu g.cm^{-2}$, while the mean detection limit for transmittance protocols was ~0.4 $\mu g.cm^{-2}$. This was above the proposals for the draft standard and is higher than that seen in other measurement studies.

Field blank OC and EC content was at or below the detection limit results calculated from the laboratory blanks.

At all the field validation sites two different types of automatic optical black carbon analysers (Multi Angle Absorption Photometer & Aethalometer) were co-located with the filter samplers. Results from these automatic analysers were compared against the filter measurements using the EU Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods and the EU Excel spreadsheet.

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1. INTRODUCTION

Daily $PM_{2.5}$ samples were collected from 6 monitoring stations over 2013 & 2014 and analysed by 4 different laboratories. Sub-samples of each daily filter were analysed twice using 6 thermal-optical protocols (EUSAAR2, NIOSH & IMPROVE) with optical corrections for OCEC split point performed by both reflectance and transmittance methods. This resulted in 12 results per laboratory, per sampled filter. NPL performed a statistical analysis to determine the uncertainty of a single measured value based on between-laboratory variability, internal-laboratory variability and between sampler variability. NPL expanded this analysis to rank the different protocol / optical correction methodologies on a site specific and complete dataset basis.

Laboratory blanks analysed to determine detection limits for OC, EC and TC. Sampled filters with low EC content were also analysed to determine EC detection limits.

OC, EC and TC levels were also determined for field blank samples.

At all the field validation sites two different types of automatic optical black carbon analysers (Multi Angle Absorption Photometer & Aethalometer) were co-located with the filter samplers. Results from these automatic analysers were compared against the filter measurements using the EU Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods[1] and the EU Excel spreadsheet[2]. The results of these equivalence calculations can be seen in Annexes 1 & 2.

2. ANALYSIS METHODOLOGY

For the purpose of the data analysis described below, the data are divided into three data sets as follows:

1. Data set 1 relates to those sites for which a single sampler is used by all the laboratories. The sampler used at a particular site may be the same as that used at a different site or it may be different from the samplers used at all other sites. The data set is used to investigate between- and within-laboratory effects and to quantify those effects.

2. Data set 2 relates to those sites for which at least two samplers are used by all the laboratories. As for data set 1, a sampler used at a particular site may be the same as that used at a different site, or it may be different from the samplers used at all other sites. The data set is used to investigate a between-sampler effect and to quantify that effect.

3. Data sets 1 & 2 were combined and split into:
    a. Sites to determine specific site classification (rural background, urban background & roadside) uncertainties.
    b. Four concentration ranges to determine uncertainty over the range of concentrations.

The objective of the data analysis is to evaluate the standard uncertainty to be associated with an individual measured value of concentration, which combines the within-laboratory, between-laboratory and between-sampler effects. For data sets 3a and 3b only the within-laboratory and between-laboratory effects were calculated.

2.1 CALCULATING BETWEEN- AND WITHIN-LABORATORY VARIABILITY

<u>Notation</u>

Let there be S sites identified by the index $i, i \in \{1, \dots, S\}$, and L laboratories identified by the index: $j, j \in \{1, \dots, L\}$. Suppose measurements are made by all L laboratories at site i on each of the days identified by the index $k, k \in K_i$. The measured values of concentration are then denoted by:

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1 Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods, Report by an EC Working Group on Guidance for the Demonstration of Equivalence, January 2010.
2 Ruben Beijk, Orthogonal regression and equivalence test utility, V2.9, RIVM, January 2010.

$$x_{ijk}, \qquad k \in K_i, \qquad j \in \{1, \dots, L\}, \qquad i \in \{1, \dots, S\}.$$

The data set is balanced in the sense that all laboratories make measurements at all sites. However, the days K_i on which measurements are made can be different from one site to another.

2.1.1 Data processing

The data processing comprises two stages. In a first stage, the L measured values corresponding to each site and each day are processed to remove outlying values, and normalised to remove effects associated with the factors of site, sampler and time. In a second stage, an ANalysis Of VAriance (ANOVA) is applied to the resulting data set corresponding to all sites and all days to decide whether a between-laboratory effect exists. If the effect exists, a calculation of the between- and within-laboratory standard deviations is undertaken. If the effect does not exist, a calculation of the within-laboratory standard deviation only is made. In either case, the within-laboratory standard deviation describes the repeatability standard deviation for the laboratories, which is assumed to be the same for all laboratories.

Each part of the data processing is described below.

2.1.2 Outlier rejection

Outlier rejection is applied to the set of measured values $x_{ijk}, j \in \{1, \dots, L\}$, provided by the L laboratories on day k at site i. Outlier rejection is applied separately for the sets of measured values provided on different days and at different sites.

Outlier rejection involves the following steps:

1. Remove any measured value that is zero, with zero interpreted as denoting a missing value;

2. For the non-zero measured values, evaluate the modified Z-score defined by

$$z_{ijk} = \frac{x_{ijk} - \mathrm{med}(\{x_{ijk}\})}{1.483 \times \mathrm{mad}(\{x_{ijk}\})},$$

   where:
   $\mathrm{med}(\{x_{ijk}\}) = \hat{x}_{ik}$ is the median of the non-zero values $\{x_{ijk}: x_{ijk} \neq 0, j = 1, \dots, L\}$, a robust measure of location, and $\mathrm{mad}(\{x_{ijk}\}) = \mathrm{med}(\{|x_{ijk} - \hat{x}_{ik}|\})$ is the median-absolute deviation of those values, a robust measure of dispersion;

3. Remove any measured value for which $|z_{ijk}| > 3.5$.

The procedure for outlier rejection described in steps 2 and 3 follows the recommendation made in section 1.3.5.17 of the NIST Engineering Statistics Handbook[3]. Outlier rejection can be problematic for small sample sizes, in this case when the number L of laboratories is small. The critical value (of, here, 3.5) for the absolute value of a modified Z-score, which is used to decide whether a measured value is to be considered as an outlier or not, can be adjusted to make outlier rejection easier (using a smaller value of the critical value) or harder (using a larger value). However, such an adjustment leads to a degree of “subjectivity” into the step of outlier rejection, and ought to be justified.

For the majority of the data analysis performed for this standard outlier rejection was not used in order to calculate the uncertainty of a single measured value.

3 www.itl.nist.gov/div898/handbook/

2.1.3 Data normalisation

Following outlier rejection, the data for site i and day k is denoted by:

$$x_{ijk}, \qquad k \in K_i, \qquad j \in J_{ik}, \qquad i \in \{1, \dots, S\},$$

where J_{ik} contains the indices of the laboratories for which measured values are retained.

Data normalisation involves the following steps:

1. Evaluate the average
$$\bar{x}_{ik} = \frac{1}{L_{ik}} \sum_{j \in J_{ik}} x_{ijk},$$
where L_{ik} is the number of indices in J_{ik};

2. Shift the measured values by the average $\bar{x}_{ik}$, and scale the shifted values by $\bar{x}_{ik}$ to obtain normalised values
$$v_{ijk} = \frac{x_{ijk} - \bar{x}_{ik}}{\bar{x}_{ik}}, \qquad j \in J_{ik}.$$

The average value calculated in step 1 is taken as a reference or consensus value for the concentration of OC, EC or TC at the specific site i on the specific day k. The aim of shifting the measured values is to remove, at least approximately, any dependence of measured concentration on the time of measurement, the site at which the measurement is made, and the sampler that is used to make the measurement. The aim of scaling the shifted values is to remove, at least approximately, any dependence of the variability of measured concentration on the value of concentration. The application of scaling is based on the assumption that the repeatability standard deviation is proportional to the measured concentration, i.e., the relative repeatability standard deviation is approximately constant. The normalised data is reported as a fraction (or percentage) of the reference value.

2.1.4 Analysis of variance

Following outlier rejection and data normalisation, the data is denoted by:

$$v_{ijk}, \qquad k \in K_i, \qquad j \in J_{ik}, \qquad i \in \{1, \dots, S\}.$$

Since there is no interest in the factors of site and time, an equivalent representation of the data is as

$$y_{lr}, \qquad r \in \{1, \dots, R_l\}, \qquad l \in \{1, \dots, L\},$$

which groups the measured values by laboratory. Here, R_l is the number of retained measured values for laboratory l over all sites and days, and each y_{lr} equates to one of the normalised values v_{ijk}.

An ANOVA is used to test the null hypothesis that the averages for the laboratories are equal, i.e., there is no laboratory effect. The ANOVA calculation must account for the fact that the data set may be unbalanced, because the numbers of measured values can be different from one laboratory to another. The function "anovan", which is provided in Matlab's Statistics Toolbox[4], can be used to perform a (multiway) ANOVA and allows for an unbalanced data set. The function returns a p value that is compared with a critical value p_c, usually 0.01 or 0.05, chosen before the analysis. If $p \geq p_c$, the null hypothesis of no laboratory effect is

4 Matlab®, The MathWorks Inc.

accepted at a $100p_{\rm c}$ % level of confidence. Otherwise, the null hypothesis is rejected at that level of confidence.

2.1.5 Calculation of standard deviations

The within-laboratory variance (squared standard deviation) is calculated as the pooled variance s^2 of the laboratory values, and is given by

$$s^2 = \frac{1}{(\sum_{l=1}^{L} R_l) - L} \sum_{l=1}^{L} (R_l - 1) s_l^2,$$

where

$$\bar{y}_l = \frac{1}{R_l} \sum_{r=1}^{R_l} y_{lr}\,, \qquad s_l^2 = \frac{1}{R_l - 1} \sum_{r=1}^{R_l} (y_{lr} - \bar{y}_l)^2.$$

If the ANOVA indicates the existence of a between-laboratory effect, then that effect is quantified by the standard deviation $s_{\rm lab}$ of the averages calculated for the laboratories, i.e.,

$$s_{\rm lab}^2 = \frac{1}{L-1} \sum_{l=1}^{L} (\bar{y}_l - \bar{\bar{y}})^2,$$

where

$$\bar{\bar{y}} = \frac{1}{L} \sum_{l=1}^{L} \bar{y}_l.$$

In the case that the null hypothesis of no laboratory effect is accepted, the between-laboratory standard deviation is taken to be zero.

2.2 CALCULATING BETWEEN-SAMPLER VARIABILITY

<u>Notation</u>

Let there be S sites identified by the index $i, i \in \{1, \ldots, S\}$, and L laboratories identified by the index $j, j \in \{1, \ldots, L\}$. Suppose measurements are made by all L laboratories at site i on each of the days identified by the index $k, k \in K_i$, using samplers identified by index $f, f \in F_i$. The measured values of concentration are then denoted by:

$$x_{ijkf}, \qquad f \in F_i, \qquad k \in K_i, \qquad j \in \{1, \ldots, L\}, \qquad i \in \{1, \ldots, S\}.$$

The data set is balanced in the sense that all laboratories make measurements at all sites. However, the days K_i on which measurements are made, as well as the samplers F_i used, can be different from one site to another.

2.2.1 Data processing

In a similar way to that for data set 1, the data processing comprises two stages. In a first stage, considering the data for each sampler separately, the measured values corresponding to each site and each day are processed to remove outlying values. Then, considering the data for the samplers together, the values corresponding to each site and each day are normalised to remove effects associated with the factors of site and time, but preserving any sampler effect. In a second stage, an ANOVA is applied to the resulting data set corresponding to all sites, all days and all laboratories to decide whether a between-sampler effect exists. If the effect exists, a calculation of the between-sampler standard deviations is undertaken.

Following outlier rejection and data normalisation, the data is denoted by:

$$v_{ijkf}, \qquad f \in F_i, \qquad k \in K_i, \qquad j \in J_{ikf}, \qquad i \in \{1, \dots, S\},$$

where J_{ikf} contains the indices of the laboratories for which measured values are retained for site i, day k and sampler f. Since there is no interest in the factors of site, time and laboratory, an equivalent representation of the data is as:

$$y_{fr}, \qquad r \in \{1, \dots, R_f\}, \qquad f \in F_1 \cup \dots \cup F_S,$$

which groups the measured values by sampler. Here, R_f is the number of retained measured values for sampler f over all sites, days and laboratories, and each y_{fr} equates to one of the normalised values v_{ijkf}. As for data set 1, the data set is generally unbalanced, because the numbers of measured values can be different from one sampler to another.

If an ANOVA indicates the existence of a between-sampler effect, then that effect is quantified by the standard deviation s_{sam} of the averages calculated for the samplers, i.e.,

$$s_{\mathrm{sam}}^2 = \frac{1}{F-1}\sum_{f=1}^{F}\left(\bar{y}_f - \bar{\bar{y}}\right)^2,$$

where

$$\bar{y}_f = \frac{1}{R_f}\sum_{r=1}^{R_f} y_{fr}, \qquad \bar{\bar{y}} = \frac{1}{F}\sum_{f=1}^{F}\bar{y}_f,$$

and F is the total number of samplers. In the case that the null hypothesis of no sampler effect is accepted, the between-sampler standard deviation is taken to be zero.

2.3 CALCULATING COMBINED STANDARD UNCERTAINTY

The relative standard uncertainty u_{rel} associated with an individual measured value of concentration is given:

$$u_{\mathrm{rel}}^2 = s^2 + s_{\mathrm{lab}}^2 + s_{\mathrm{sam}}^2,$$

which combines the standard deviations related to within-laboratory, between-laboratory and between-sampler effects.

The between sampler variability results showed that s_{sam}^2 was insignificant and was not included in the uncertainty calculation.

2.4 REMARKS

The data analysis described, including the use of ANOVA and the calculations of the standard deviations to quantify the various effects, depends on assumptions about the homogeneity of these effects for different concentrations, sites, laboratories, samplers and time. Graphical displays of the data, in which the data is plotted against these factors, can be useful to identify obvious departures from these assumptions. In cases that the assumptions do not hold, the results of the data analysis may not be reliable expressions of the various effects considered.

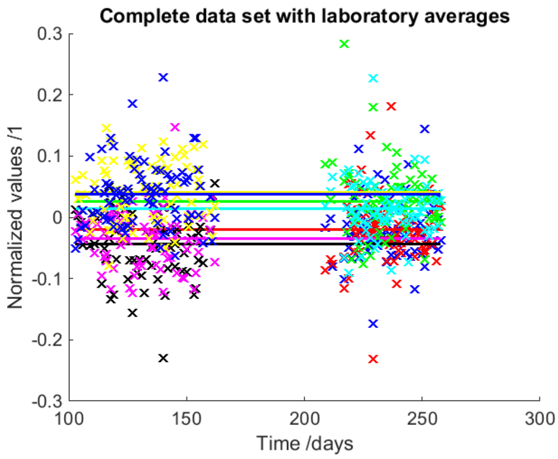
3.0 RESULTS

All results were calculated with the outlier rejection disabled.

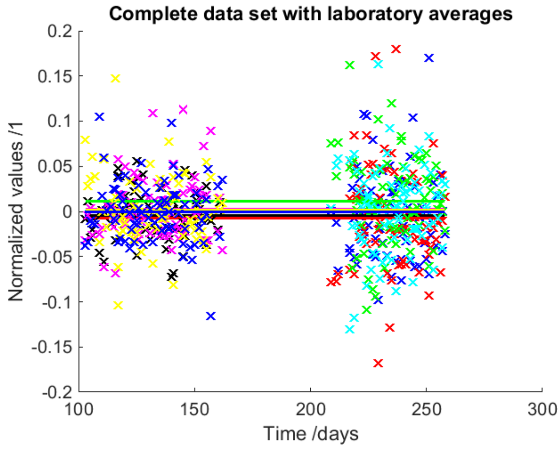
Spreadsheets containing all the input data and the results of all calculations can be viewed in Annex 3.

3.1 DATA SET 1 – BETWEEN LABORATORY AND INTERNAL LABORATORY VARIABILITY

The following 2 figures show the graphical output from the analysis for the determination of between laboratory variability. The first figure shows a clear between laboratory variance and the second figure shows minimal between laboratory variability.



NIOSH Reflectance – OC



NIOSH Transmittance - OC

Each colour represents a different laboratory's result. There are 8 data sets as repeat analyses were considered to be separate data sets to allow the calculation of the uncertainty from a single measured value.

The following table gives the p values from the analysis of variance for between laboratory effects. If $p \geq p_c$, the null hypothesis of no laboratory effect is accepted at a $100p_c$ % level of confidence. Otherwise, the null hypothesis is rejected at that level of confidence.

Protocol	EC	OC	TC
EUSAAR2 Trans	3.00E-04	0.0006	0.0003
IMPROVE Trans	1.61E-05	1.07E-09	8.80E-17
NIOSH Trans	8.92E-29	0.2399	1.20E-18
EUSAAR2 Refl	0.0003	0.0012	0.0003
IMPROVE Refl	0.0519	3.03E-09	8.65E-17
NIOSH Refl	0.3544	2.35E-38	1.19E-18

p Value Results from Between Laboratory Analysis of Variance

It can be seen that only IMPROVE reflectance (EC), NIOSH reflectance (EC) and NIOSH transmittance (OC) show no significant between laboratory effect at the 5% level of confidence. In all cases the between laboratory variability was calculated and included in the overall uncertainty calculations.

Between laboratory variability and internal laboratory variability were calculated for the 6 thermal / optical protocols and the results shown below. Protocols were ranked: 0.75, 2, 3, 4, 5 & 6 with a ranking of 0.75 denoting the lowest result, rising to a ranking of 6 for the highest result. Rankings for between laboratory variability and internal laboratory variability were combined to provide an overall performance rank for the protocols.

Score	Analysis Protocol	Component	Between laboratory variability, %
0.75	EUSAAR2 Trans	EC	2.2
2	IMPROVE Trans	EC	2.9
3	NIOSH Trans	EC	9.0
4	EUSAAR2 Refl	EC	12.9
5	IMPROVE Refl	EC	67.2
6	NIOSH Refl	EC	488.7
0.75	NIOSH Trans	OC	0.6
2	NIOSH Refl	OC	3.3
3	IMPROVE Trans	OC	2.1
4	EUSAAR2 Trans	OC	1.5
5	EUSAAR2 Refl	OC	1.5
6	IMPROVE Refl	OC	2.3
0.75	NIOSH Refl	TC	1.6
2	NIOSH Trans	TC	1.6
3	EUSAAR2 Trans	TC	1.3
4	EUSAAR2 Refl	TC	1.3
5	IMPROVE Trans	TC	2.4
6	IMPROVE Refl	TC	2.4

Between Laboratory Variability

Score	Analysis Protocol	Component	Internal laboratory variability, %
0.75	EUSAAR2 Trans	EC	9.4
2	IMPROVE Trans	EC	11.5
3	NIOSH Trans	EC	16.1
4	EUSAAR2 Refl	EC	55.6
5	IMPROVE Refl	EC	399.2
6	NIOSH Refl	EC	3922.5
0.75	NIOSH Trans	OC	4.3
2	EUSAAR2 Trans	OC	6.7
3	EUSAAR2 Refl	OC	7.1
4	IMPROVE Trans	OC	6.4
5	IMPROVE Refl	OC	7.0
6	NIOSH Refl	OC	5.1
0.75	EUSAAR2 Trans	TC	5.9
2	EUSAAR2 Refl	TC	5.9
3	NIOSH Refl	TC	3.5
4	NIOSH Trans	TC	3.5
5	IMPROVE Trans	TC	5.6
6	IMPROVE Refl	TC	5.6

Internal Laboratory Variability

EC	Between laboratory	Internal laboratory	Combined Rank
EUSAAR2 Trans	0.75	0.75	1.5
IMPROVE Trans	2	2	4
NIOSH Trans	3	3	6
EUSAAR2 Refl	4	4	8
IMPROVE Refl	5	5	10
NIOSH Refl	6	6	12
OC	**Between laboratory**	**Internal laboratory**	**Combined Rank**
NIOSH Trans	0.75	0.75	1.5
EUSAAR2 Trans	2	4	6
IMPROVE Trans	4	3	7
NIOSH Refl	6	2	8
EUSAAR2 Refl	3	6	9
IMPROVE Refl	5	5	10
TC	**Between laboratory**	**Internal laboratory**	**Combined Rank**
NIOSH Refl	3	0.75	3.75
NIOSH Trans	4	2	6
EUSAAR2 Trans	0.75	6	6.75
EUSAAR2 Refl	2	5	7
IMPROVE Trans	5	4	9
IMPROVE Refl	6	3	9

Combined between laboratory and internal laboratory variability protocol ranking

3.2 DATA SET 2 – BETWEEN SAMPLER VARIABILITY

The following summarises the results of the between sampler variability:

- No significant between sampler variability was found for TC.
- One protocol gave a possibly significant between sampler variability for OC. IMPROVE Trans, 5.5% level, resulting in an inter-sampler variability of 1.94% (2σ, 95%).
- Three protocols showed a significant to very significant between sampler variability for EC. EUSAAR2 Trans, 3.2% level, IMPROVE Trans, 0.3% level & NIOSH Trans 0.5% level, resulting in a between sampler variability of 5.8, 6.0 and 8.8% (2σ, 95%) respectively. This significant between sampler variability may have only been detected due to the lower repeatability of these 3 protocols, 18%, 22% & 32% (2σ, 95%).
- The other 3 protocols, EUSAAR2 Refl, IMPROVE Refl & NIOSH Refl had internal repeatability's of 112%, 800% and 7800% (2σ, 95%) respectively making the determination of between sampler repeatability impossible.
- There was no significant between sampler variability detected for most components and most protocols. Where it was detected it was insignificant compared to the internal repeatability.

Between sampler variability was not included in the overall uncertainty calculations.

3.3 DATA SET 3A – SITE SPECIFIC RANKING

Combined variability was calculated from the between laboratory variability and internal laboratory variability and the results are shown below for EC, OC and TC:

Score	Analysis Protocol	Component	Site	Combined variability, %
0.75	IMPROVE Trans	EC	CAB	13.6
2	EUSAAR2 Trans	EC	CAB	19.0
3	NIOSH Trans	EC	CAB	23.5
4	IMPROVE Refl	EC	CAB	27.3
5	EUSAAR2 Refl	EC	CAB	28.7
6	NIOSH Refl	EC	CAB	34.2
0.75	IMPROVE Refl	EC	IPR	10.8
2	IMPROVE Trans	EC	IPR	11.0
3	NIOSH Refl	EC	IPR	11.4
4	EUSAAR2 Refl	EC	IPR	15.8
5	EUSAAR2 Trans	EC	IPR	15.9
6	NIOSH Trans	EC	IPR	16.3
0.75	EUSAAR2 Trans	EC	WAL	15.3
2	IMPROVE Trans	EC	WAL	19.7
3	NIOSH Trans	EC	WAL	30.1
4	EUSAAR2 Refl	EC	WAL	117.7
5	IMPROVE Refl	EC	WAL	880.0
6	NIOSH Refl	EC	WAL	8573.5
0.75	IMPROVE Trans	EC	BCN	4.8
2	EUSAAR2 Trans	EC	BCN	6.6
3	NIOSH Trans	EC	BCN	12.3
4	EUSAAR2 Refl	EC	BCN	16.3
5	IMPROVE Refl	EC	BCN	19.1
6	NIOSH Refl	EC	BCN	30.1
0.75	EUSAAR2 Trans	EC	DUI	5.2
2	NIOSH Refl	EC	DUI	6.6
3	IMPROVE Trans	EC	DUI	8.9
4	EUSAAR2 Refl	EC	DUI	10.1
5	IMPROVE Refl	EC	DUI	11.3
6	NIOSH Trans	EC	DUI	15.0
0.75	EUSAAR2 Trans	EC	AMS	9.3
2	IMPROVE Trans	EC	AMS	10.1
3	EUSAAR2 Refl	EC	AMS	11.9
4	NIOSH Trans	EC	AMS	13.0
5	NIOSH Refl	EC	AMS	17.1
6	IMPROVE Refl	EC	AMS	17.3

Score	Analysis Protocol	Component	Site	Combined variability, %
0.75	EUSAAR2 Trans	OC	CAB	7.1
2	IMPROVE Trans	OC	CAB	7.4
3	NIOSH Trans	OC	CAB	9.2
4	NIOSH Refl	OC	CAB	11.9
5	EUSAAR2 Refl	OC	CAB	12.5
6	IMPROVE Refl	OC	CAB	14.3
0.75	NIOSH Trans	OC	IPR	5.1
2	IMPROVE Trans	OC	IPR	5.4
3	NIOSH Refl	OC	IPR	5.7
4	IMPROVE Refl	OC	IPR	7.2
5	EUSAAR2 Trans	OC	IPR	11.3
6	EUSAAR2 Refl	OC	IPR	11.5
0.75	NIOSH Trans	OC	WAL	5.0
2	NIOSH Refl	OC	WAL	5.5
3	EUSAAR2 Refl	OC	WAL	9.1
4	EUSAAR2 Trans	OC	WAL	9.6
5	IMPROVE Refl	OC	WAL	11.3
6	IMPROVE Trans	OC	WAL	11.6
0.75	NIOSH Trans	OC	BCN	3.3
2	IMPROVE Trans	OC	BCN	4.0
3	EUSAAR2 Trans	OC	BCN	5.5
4	EUSAAR2 Refl	OC	BCN	6.9
5	IMPROVE Refl	OC	BCN	7.1
6	NIOSH Refl	OC	BCN	9.4
0.75	EUSAAR2 Trans	OC	DUI	2.9
2	NIOSH Trans	OC	DUI	3.5
3	NIOSH Refl	OC	DUI	3.6
4	IMPROVE Trans	OC	DUI	4.4
5	EUSAAR2 Refl	OC	DUI	4.7
6	IMPROVE Refl	OC	DUI	5.3
0.75	IMPROVE Refl	OC	AMS	5.0
2	IMPROVE Trans	OC	AMS	5.0
3	NIOSH Trans	OC	AMS	5.5
4	NIOSH Refl	OC	AMS	5.8
5	EUSAAR2 Trans	OC	AMS	8.2
6	EUSAAR2 Refl	OC	AMS	8.3

Score	Analysis Protocol	Component	Site	Combined variability, %
0.75	EUSAAR2 Refl	TC	CAB	6.0
2	EUSAAR2 Trans	TC	CAB	6.0
3	IMPROVE Refl	TC	CAB	6.5
4	IMPROVE Trans	TC	CAB	6.5
5	NIOSH Refl	TC	CAB	8.4
6	NIOSH Trans	TC	CAB	8.4
0.75	IMPROVE Trans	TC	IPR	4.3
2	IMPROVE Refl	TC	IPR	4.3
3	NIOSH Refl	TC	IPR	4.6
4	NIOSH Trans	TC	IPR	4.6
5	EUSAAR2 Refl	TC	IPR	11.3
6	EUSAAR2 Trans	TC	IPR	11.3
0.75	NIOSH Refl	TC	WAL	5.2
2	NIOSH Trans	TC	WAL	5.2
3	EUSAAR2 Refl	TC	WAL	8.9
4	EUSAAR2 Trans	TC	WAL	8.9
5	IMPROVE Refl	TC	WAL	11.0
6	IMPROVE Trans	TC	WAL	11.0
0.75	NIOSH Refl	TC	BCN	3.0
2	NIOSH Trans	TC	BCN	3.0
3	IMPROVE Refl	TC	BCN	3.3
4	IMPROVE Trans	TC	BCN	3.3
5	EUSAAR2 Trans	TC	BCN	4.2
6	EUSAAR2 Refl	TC	BCN	4.2
0.75	EUSAAR2 Trans	TC	DUI	2.7
2	EUSAAR2 Refl	TC	DUI	2.7
3	NIOSH Refl	TC	DUI	3.2
4	NIOSH Trans	TC	DUI	3.2
5	IMPROVE Trans	TC	DUI	4.1
6	IMPROVE Refl	TC	DUI	4.1
0.75	IMPROVE Refl	TC	AMS	3.4
2	IMPROVE Trans	TC	AMS	3.4
3	NIOSH Refl	TC	AMS	4.2
4	NIOSH Trans	TC	AMS	4.2
5	EUSAAR2 Refl	TC	AMS	6.8
6	EUSAAR2 Trans	TC	AMS	6.8

The results for EC, OC and TC were combined by site classification to give an overall ranking per site classification as shown below:

Rural Background

EC		OC		TC	
Total score	**Protocol**	**Total score**	**Protocol**	**Total score**	**Protocol**
4.75	IMPROVE Trans	4.5	NIOSH Trans	8.75	EUSAAR2 Refl
7.75	EUSAAR2 Trans	9	NIOSH Refl	8.75	NIOSH Refl
9.75	IMPROVE Refl	9.75	EUSAAR2 Trans	10	IMPROVE Refl
12	NIOSH Trans	10	IMPROVE Trans	10.75	IMPROVE Trans
13	EUSAAR2 Refl	14	EUSAAR2 Refl	12	EUSAAR2 Trans
15	NIOSH Refl	15	IMPROVE Refl	12	NIOSH Trans

Urban Background

EC		OC		TC	
Total score	**Protocol**	**Total score**	**Protocol**	**Total score**	**Protocol**
2.75	EUSAAR2 Trans	2.75	NIOSH Trans	3.75	NIOSH Refl
3.75	IMPROVE Trans	3.75	EUSAAR2 Trans	5.75	EUSAAR2 Trans
8	EUSAAR2 Refl	6	IMPROVE Trans	6	NIOSH Trans
8	NIOSH Refl	9	EUSAAR2 Refl	8	EUSAAR2 Refl
9	NIOSH Trans	9	NIOSH Refl	9	IMPROVE Refl
10	IMPROVE Refl	11	IMPROVE Refl	9	IMPROVE Trans

Roadside

EC		OC		TC	
Total score	**Protocol**	**Total score**	**Protocol**	**Total score**	**Protocol**
0.75	EUSAAR2 Trans	0.75	IMPROVE Refl	0.75	IMPROVE Refl
2	IMPROVE Trans	2	IMPROVE Trans	2	IMPROVE Trans
3	EUSAAR2 Refl	3	NIOSH Trans	3	NIOSH Refl
4	NIOSH Trans	4	NIOSH Refl	4	NIOSH Trans
5	NIOSH Refl	5	EUSAAR2 Trans	5	EUSAAR2 Refl
6	IMPROVE Refl	6	EUSAAR2 Refl	6	EUSAAR2 Trans

This ranking was repeated just taking internal laboratory variability into account to try and remove any between laboratory dependence. The results are shown below:

Rural Background

EC		OC		TC	
Total score	**Protocol**	**Total score**	**Protocol**	**Total score**	**Protocol**
4.75	IMPROVE Trans	7.5	NIOSH Trans	6.5	IMPROVE Refl
7.75	EUSAAR2 Trans	8.75	IMPROVE Trans	9.75	NIOSH Refl
8.75	IMPROVE Refl	9	NIOSH Refl	10	IMPROVE Trans
11	NIOSH Trans	11	EUSAAR2 Refl	11	EUSAAR2 Refl
15	EUSAAR2 Refl	12	EUSAAR2 Trans	11	NIOSH Trans
15	NIOSH Refl	14	IMPROVE Refl	14	EUSAAR2 Trans

Urban Background

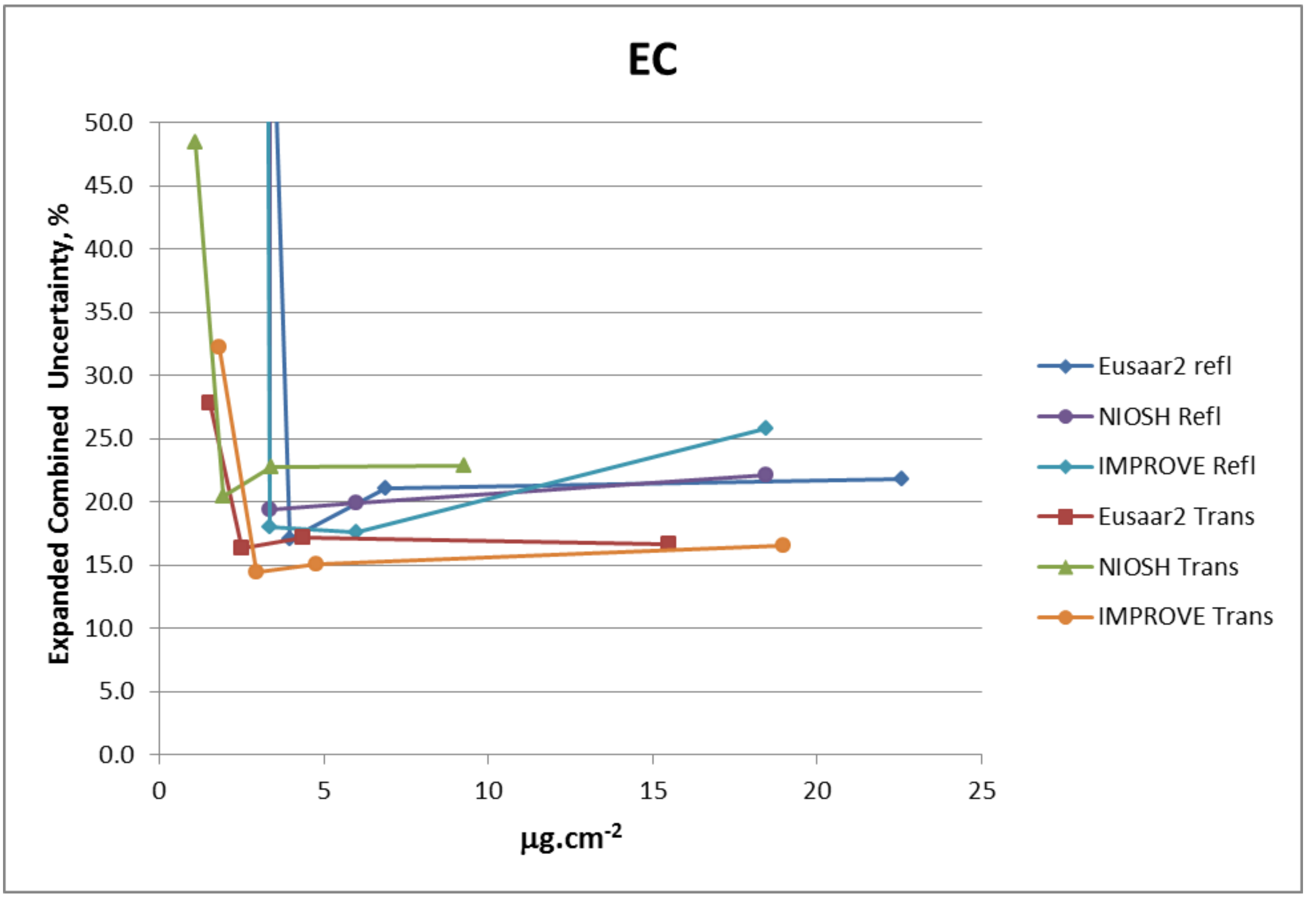
EC		OC		TC	
Total score	**Protocol**	**Total score**	**Protocol**	**Total score**	**Protocol**
3.75	IMPROVE Trans	3.75	NIOSH Trans	3.75	IMPROVE Refl
3.75	EUSAAR2 Trans	4	IMPROVE Trans	5.75	NIOSH Refl
4	NIOSH Refl	4.75	EUSAAR2 Trans	6	IMPROVE Trans
9	EUSAAR2 Refl	7	NIOSH Refl	8	NIOSH Trans
10	IMPROVE Refl	11	IMPROVE Refl	9	EUSAAR2 Refl
11	NIOSH Trans	11	EUSAAR2 Refl	9	EUSAAR2 Trans

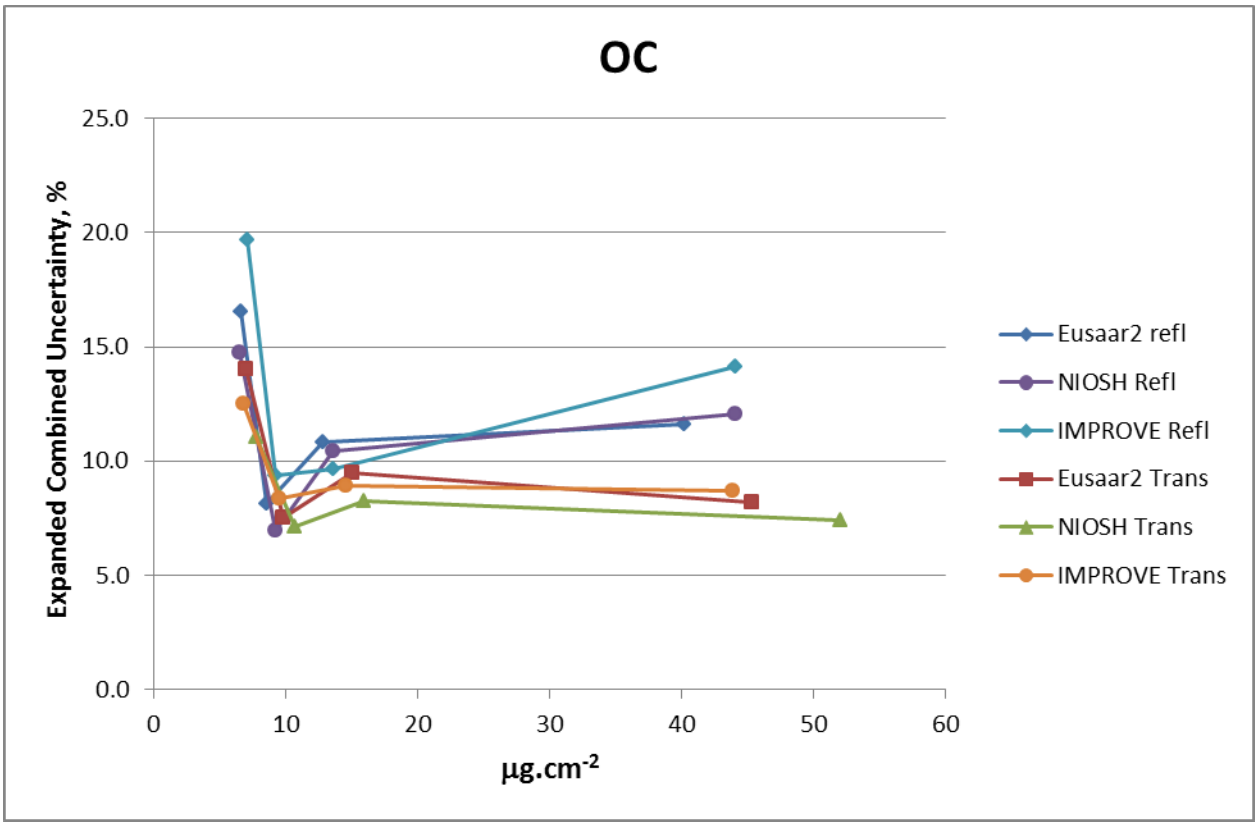
Roadside

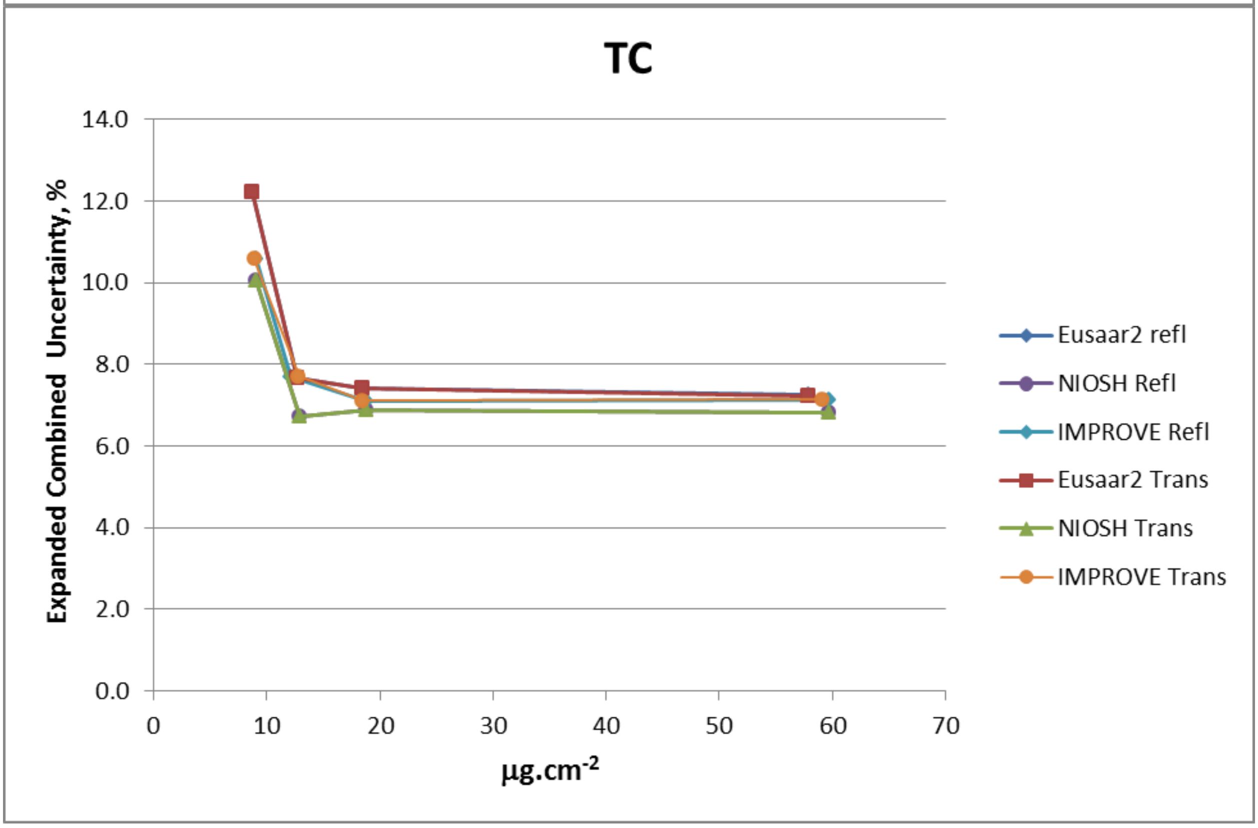
EC		OC		TC	
Total score	**Protocol**	**Total score**	**Protocol**	**Total score**	**Protocol**
0.75	IMPROVE Trans	0.75	IMPROVE Trans	0.75	IMPROVE Refl
2	EUSAAR2 Trans	2	IMPROVE Refl	2	IMPROVE Trans
3	NIOSH Trans	3	NIOSH Trans	3	NIOSH Refl
4	EUSAAR2 Refl	4	NIOSH Refl	4	NIOSH Trans
5	NIOSH Refl	5	EUSAAR2 Trans	5	EUSAAR2 Refl
6	IMPROVE Refl	6	EUSAAR2 Refl	6	EUSAAR2 Trans

3.4 DATA SET 3B - UNCERTAINTY OVER THE MEASURED CONCENTRATION RANGE

Results for each thermal / optical protocol from the complete data set were ordered by concentration and then split into 4 concentration bins: 0% - 25%, 25% - 50%, 50% - 75% & 75% - 100% with equal number of measurements in each concentration bin. The combined expanded uncertainty (2σ, 95%) due to between laboratory variability and internal laboratory variability were calculated for each concentration bin, the results of which are shown below:







The following tables give the full results:

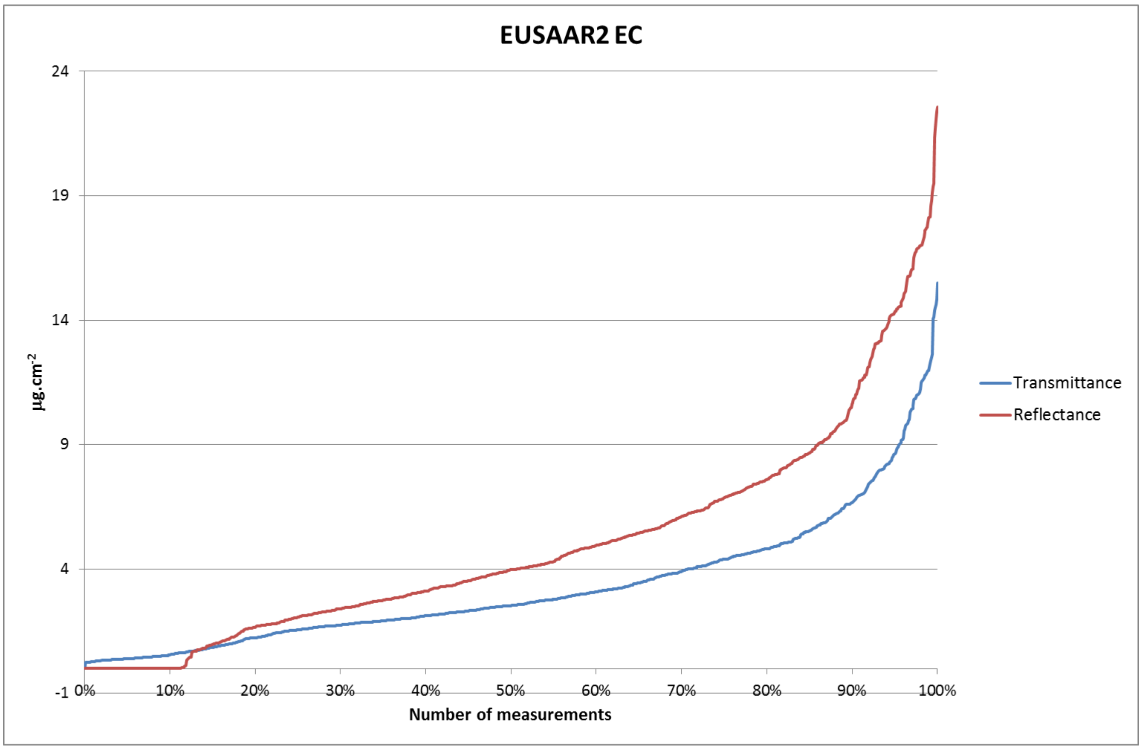
Analysis Protocol	Component	Concentration quarter	Between laboratory repeatability, %	Internal laboratory repeatability, %	Expanded combined Uncertainty, %	Minimum, μg.cm^{-2}	Maximum, μg.cm^{-2}	Mid-range, μg.cm^{-2}
EUSAAR2 Refl	EC	Q1	16.2	86.5	176.0	0.00	2.05	1.03
EUSAAR2 Refl	EC	Q2	2.1	8.3	17.1	2.08	3.97	3.03
EUSAAR2 Refl	EC	Q3	4.3	9.6	21.1	3.97	6.86	5.42
EUSAAR2 Refl	EC	Q4	6.6	8.7	21.8	6.87	22.57	14.72
EUSAAR2 Trans	EC	Q1	2.6	13.7	27.8	0.00	1.54	0.77
EUSAAR2 Trans	EC	Q2	4.5	6.8	16.4	1.55	2.52	2.04
EUSAAR2 Trans	EC	Q3	4.0	7.6	17.2	2.53	4.38	3.46
EUSAAR2 Trans	EC	Q4	4.2	7.1	16.6	4.39	15.49	9.94
IMPROVE Refl	EC	Q1	98.0	619.0	1253.0	0.00	1.62	0.81
IMPROVE Refl	EC	Q2	4.5	7.8	18.1	1.63	3.37	2.50
IMPROVE Refl	EC	Q3	4.3	7.7	17.6	3.38	5.98	4.68
IMPROVE Refl	EC	Q4	9.2	9.1	25.8	5.98	18.43	12.21
IMPROVE Trans	EC	Q1	1.9	16.0	32.3	0.00	1.82	0.91
IMPROVE Trans	EC	Q2	3.2	6.5	14.5	1.82	2.95	2.39
IMPROVE Trans	EC	Q3	4.0	6.4	15.1	2.95	4.76	3.86
IMPROVE Trans	EC	Q4	3.9	7.3	16.5	4.78	18.96	11.87
NIOSH Refl	EC	Q1	741.0	6064.0	12218.0	0.00	1.62	0.81
NIOSH Refl	EC	Q2	2.7	9.3	19.4	1.63	3.37	2.50
NIOSH Refl	EC	Q3	4.2	9.0	19.9	3.38	5.98	4.68
NIOSH Refl	EC	Q4	5.7	9.5	22.2	5.98	18.43	12.21
NIOSH Trans	EC	Q1	7.2	23.1	48.4	0.00	1.11	0.56
NIOSH Trans	EC	Q2	5.0	8.9	20.4	1.11	1.95	1.53
NIOSH Trans	EC	Q3	5.7	9.8	22.7	1.96	3.38	2.67
NIOSH Trans	EC	Q4	6.6	9.4	22.9	3.38	9.28	6.33

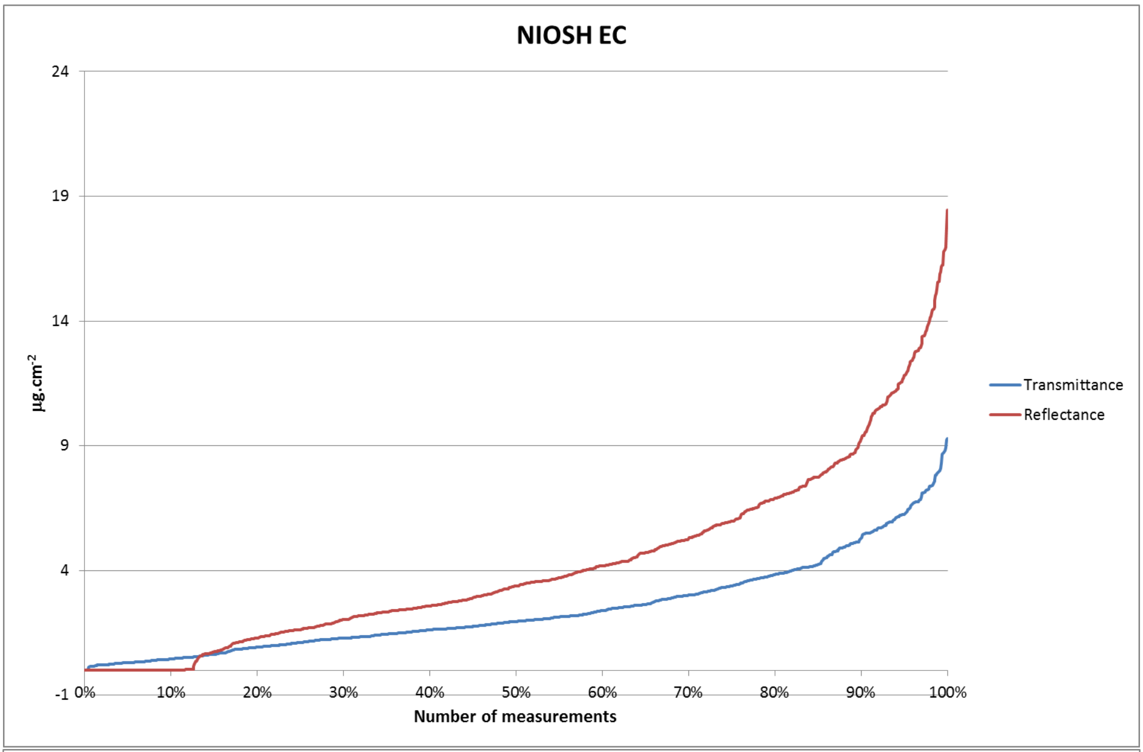
Analysis Protocol	Component	Concentration quarter	Between laboratory repeatability, %	Internal laboratory repeatability, %	Expanded combined Uncertainty, %	Minimum, μg.cm^{-2}	Maximum, μg.cm^{-2}	Mid-range, μg.cm^{-2}
EUSAAR2 Refl	OC	Q1	2.4	7.9	16.6	2.46	6.62	4.54
EUSAAR2 Refl	OC	Q2	0.7	4.0	8.1	6.62	8.57	7.60
EUSAAR2 Refl	OC	Q3	1.3	5.3	10.8	8.59	12.79	10.69
EUSAAR2 Refl	OC	Q4	2.4	5.3	11.6	12.82	40.24	26.53
EUSAAR2 Trans	OC	Q1	1.8	6.8	14.0	2.62	7.03	4.83
EUSAAR2 Trans	OC	Q2	0.9	3.6	7.5	7.04	9.81	8.43
EUSAAR2 Trans	OC	Q3	1.3	4.6	9.5	9.81	15.05	12.43
EUSAAR2 Trans	OC	Q4	0.9	4.0	8.2	15.09	45.33	30.21
IMPROVE Refl	OC	Q1	4.4	8.8	19.7	2.91	7.13	5.02
IMPROVE Refl	OC	Q2	0.9	4.6	9.4	7.47	9.23	8.35
IMPROVE Refl	OC	Q3	1.0	4.7	9.7	9.24	13.63	11.44
IMPROVE Refl	OC	Q4	4.0	5.9	14.2	13.63	44.10	28.87
IMPROVE Trans	OC	Q1	2.6	5.7	12.5	2.46	6.83	4.65
IMPROVE Trans	OC	Q2	1.7	3.8	8.4	6.83	9.51	8.17
IMPROVE Trans	OC	Q3	2.0	4.0	8.9	9.51	14.56	12.04
IMPROVE Trans	OC	Q4	1.1	4.2	8.7	14.57	43.88	29.23
NIOSH Refl	OC	Q1	2.6	6.9	14.7	2.91	6.54	4.73
NIOSH Refl	OC	Q2	0.5	3.4	6.9	7.47	9.23	8.35
NIOSH Refl	OC	Q3	0.7	5.2	10.4	9.24	13.63	11.44
NIOSH Refl	OC	Q4	2.2	5.6	12.0	13.64	44.10	28.87
NIOSH Trans	OC	Q1	1.5	5.3	11.1	2.75	7.74	5.25
NIOSH Trans	OC	Q2	0.7	3.5	7.1	7.75	10.69	9.22
NIOSH Trans	OC	Q3	1.3	3.9	8.3	10.69	15.97	13.33
NIOSH Trans	OC	Q4	1.0	3.6	7.4	15.99	52.09	34.04

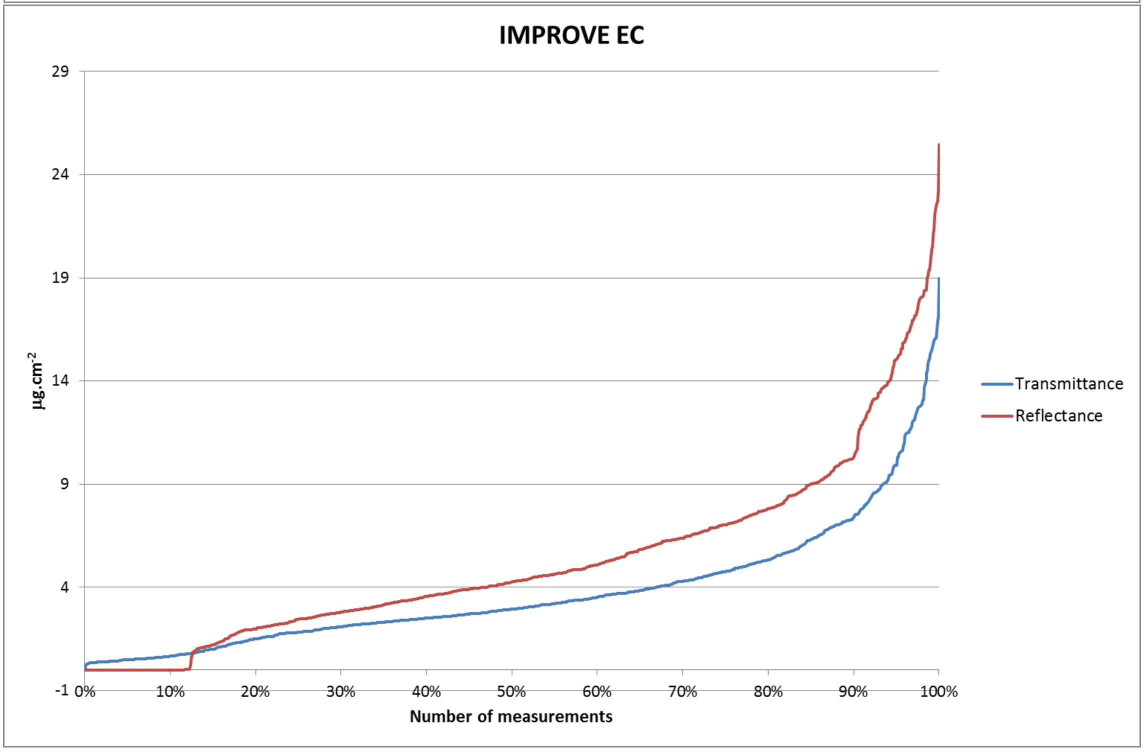
Analysis Protocol	Component	Concentration quarter	Between laboratory repeatability, %	Internal laboratory repeatability, %	Expanded combined Uncertainty, %	Minimum, µg.cm^{-2}	Maximum, µg.cm^{-2}	Mid-range, µg.cm^{-2}
EUSAAR2 Refl	TC	Q1	2.2	5.7	12.2	3.01	8.74	5.88
EUSAAR2 Refl	TC	Q2	1.2	3.6	7.7	8.76	12.67	10.72
EUSAAR2 Refl	TC	Q3	1.2	3.5	7.4	12.68	18.44	15.56
EUSAAR2 Refl	TC	Q4	1.5	3.3	7.2	18.45	57.90	38.18
EUSAAR2 Trans	TC	Q1	2.2	5.7	12.2	3.01	8.74	5.88
EUSAAR2 Trans	TC	Q2	1.2	3.6	7.7	8.76	12.67	10.72
EUSAAR2 Trans	TC	Q3	1.2	3.5	7.4	12.38	18.44	15.41
EUSAAR2 Trans	TC	Q4	1.5	3.3	7.2	18.45	57.90	38.18
IMPROVE Refl	TC	Q1	2.3	4.7	10.6	3.14	9.09	6.12
IMPROVE Refl	TC	Q2	1.9	3.4	7.7	9.10	12.16	10.63
IMPROVE Refl	TC	Q3	1.9	3.0	7.1	12.92	18.80	15.86
IMPROVE Refl	TC	Q4	1.6	3.2	7.1	18.82	59.68	39.25
IMPROVE Trans	TC	Q1	2.4	4.7	10.6	3.10	8.92	6.01
IMPROVE Trans	TC	Q2	1.8	3.4	7.7	8.92	12.81	10.86
IMPROVE Trans	TC	Q3	1.9	3.0	7.1	12.82	18.48	15.65
IMPROVE Trans	TC	Q4	1.6	3.2	7.1	18.51	59.13	38.82
NIOSH Refl	TC	Q1	1.4	4.8	10.0	3.14	9.09	6.12
NIOSH Refl	TC	Q2	1.5	3.0	6.7	9.10	12.91	11.01
NIOSH Refl	TC	Q3	1.4	3.2	6.9	12.92	18.80	15.86
NIOSH Refl	TC	Q4	1.5	3.1	6.8	18.82	59.68	39.25
NIOSH Trans	TC	Q1	1.4	4.8	10.0	3.14	9.09	6.12
NIOSH Trans	TC	Q2	1.5	3.0	6.7	9.10	12.91	11.01
NIOSH Trans	TC	Q3	1.4	3.2	6.9	11.04	18.80	14.92
NIOSH Trans	TC	Q4	1.5	3.1	6.8	18.82	59.68	39.25

As the above uncertainties are calculated on a single measurement result, it shows that repeat analysis is not required to deliver an overall uncertainty of less than 25% for concentrations above 2 $\mu g.cm^{-2}$. For concentrations below this the relative uncertainty is greater than 25%, but probably limited by the detection limit.

The above results show that the combined uncertainty for the reflectance optical correction increases dramatically at low concentrations due to very large internal repeatabilities. This is due to the reflectance method being unable to detect small EC concentrations. This is highlighted by the charts below:







3.4.1 Internal repeatability by individual laboratories

In addition to analysing sub samples each analysis laboratory performed repeated measurements from a single filter to get a separate measure of internal repeatability. The results are presented in the following table:

Protocol	**Site**	**OC Repeatability, %**	**EC Repeatability, %**	**TC Repeatability, %**
ERL				
No protocol Trans	IPR	7.3	17.6	5.7
No protocol Refl	IPR	8.1	11.3	5.7
GGD				
No protocol Trans	IPR	4.1	12.9	5.7
IUTA				
EUSAAR2 Trans	AMS	6.9	10.9	6.4
IMPROVE Trans	AMS	6.9	12.9	5.4
NIOSH Trans	AMS	8.2	25.7	4.9
EUSAAR2 Trans	CAB	12.3	28.9	3.2
IMPROVE Trans	CAB	8.1	18.7	8.4
NIOSH Trans	CAB	7.7	12.5	7.8
EUSAAR2 Trans	IPR	7.3	10.8	6.9

The above results are similar to the overall uncertainties calculated in Section 3.4.

3.5 DETECTION LIMITS

Laboratory blank filters were repeatedly analysed by each laboratory and the results pooled to determine the method detection limit in µg.cm^{-2}, for each protocol according to the following equation:

$$Detection\ Limit = SD * t_{99,n-1}$$

Where:

SD = the standard deviation of the repeated measurements, µg.cm^{-2}
$T_{99,\ n-1}$ = the student t factor with a level of confidence of 99% for *n-1* degrees of freedom
n = the number of repeat measurements

The following tables give the calculated method detection limits for OC, EC and TC for each protocol:

		n	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**
EUSAAR2	Refl	14	0.731	1.852	1.364
	Trans	14	0.691	1.750	1.326
IMPROVE	Refl	14	0.878	2.224	1.455
	Trans	14	0.843	2.136	1.388
NIOSH	Refl	12	1.087	2.818	2.162
	Trans	12	0.902	2.338	2.040

OC Detection Limit

The proposed standard specifies that the maximum OC content of a laboratory blank filter shall be <= 2.0 µg.cm^{-2}. It appears that the NIOSH protocols are over reporting OC as the same filters were analysed by the other 2 protocols. This OC level is generally higher than that seen in other measurement studies.

		n	SD, µg.cm^{-2}	DL, µg.cm^{-2}	Mean, µg.cm^{-2}
EUSAAR2	Refl	14	0.007	0.017	-0.002
	Trans	14	0.071	0.179	0.036
IMPROVE	Refl	14	0.000	0.000	0.000
	Trans	14	0.093	0.237	0.066
NIOSH	Refl	12	0.001	0.002	0.000
	Trans	12	0.256	0.663	0.122

EC Detection Limit

The mean detection limit for reflectance protocols is <0.1 µg.cm^{-2}, while the mean detection limit for transmittance protocols was ~0.4 µg.cm^{-2}. This was above the proposals for the draft standard and is higher than that seen in other measurement studies.

		n	SD, µg.cm^{-2}	DL, µg.cm^{-2}	Mean, µg.cm^{-2}
EUSAAR2	Refl	14	0.734	1.858	1.362
	Trans	14	0.734	1.858	1.362
IMPROVE	Refl	14	0.878	2.224	1.455
	Trans	14	0.878	2.224	1.455
NIOSH	Refl	12	1.087	2.818	2.162
	Trans	12	1.087	2.818	2.162

TC Detection Limit

3.5.1 Detection limit calculated from sampled filters with low concentrations

The detection limit was also calculated using the same equation as in Section 3.5 from sampled filters with low concentrations. Filters with a negative or zero content were removed from the data set before calculation. There were no sampled filters with an OC or TC content <2.0 µg.cm^{-2}, therefore detection limits for OC and TC have not been calculated.

For filters with low EC content a cut-off threshold of 0.4 µg.cm^{-2} was chosen as this represents twice the acceptable laboratory filter blank limit. The resulting detection limits for each protocol are shown in the following table:

		n	SD, µg.cm^{-2}	DL, µg.cm^{-2}	Mean, µg.cm^{-2}	No. of filters excluded
EUSAAR2	Refl	21	0.101	0.245	0.053	110
	Trans	59	0.044	0.102	0.331	2
IMPROVE	Refl	39	0.045	0.105	0.012	95
	Trans	29	0.040	0.096	0.355	2
NIOSH	Refl	42	0.097	0.225	0.044	99
	Trans	82	0.074	0.168	0.269	5

The difference between the reflectance and transmittance protocols in measuring low levels of EC is best demonstrated by ranked frequency charts as shown in Section 3.4. The validity of the detection limit results for the transmittance protocols is limited due to the low number of samples below the cut-off threshold.

3.6 FIELD BLANKS

Field blanks were analysed by each laboratory using the 6 protocols. Field blank OC content was similar to the laboratory blank content for all sites for all protocols. Field blank EC content was at or below the detection limit results calculated from the laboratory blanks.

The following tables provide the results in detail, blank levels above 2 µg.cm^{-2} have been highlighted in red:

		OC			EC			TC		
Site	**Count**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**
AMS	31	0.942	2.224	2.160	0.000	0.000	0.000	0.942	2.224	2.160
BCN	8	0.204	0.579	1.591	0.056	0.159	0.024	0.224	0.637	1.615
CAB	45	0.604	1.402	1.932	0.023	0.053	0.002	0.607	1.409	1.934
DUI	16	0.695	1.730	2.766	0.010	0.024	0.004	0.694	1.729	2.770
IPR	10	0.514	1.380	1.827	0.006	0.017	0.002	0.511	1.372	1.829
WAL	16	0.533	1.327	1.583	0.000	0.001	0.000	0.533	1.328	1.583
combined	126	0.757	1.717	2.020	0.020	0.046	0.003	0.757	1.719	2.023

Eusaar2 Reflectance

		OC			EC			TC		
Site	**Count**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**
AMS	32	0.923	2.175	2.060	0.120	0.282	0.083	0.932	2.195	2.144
BCN	16	0.212	0.529	1.626	0.014	0.036	0.005	0.215	0.536	1.631
CAB	45	0.613	1.423	1.926	0.051	0.117	0.012	0.608	1.411	1.938
DUI	16	0.694	1.729	2.770	0.000	0.000	0.000	0.694	1.729	2.770
IPR	14	0.473	1.198	1.830	0.038	0.097	0.025	0.473	1.198	1.855
WAL	16	0.488	1.216	1.558	0.065	0.162	0.025	0.533	1.328	1.583
combined	139	0.726	1.644	1.969	0.075	0.170	0.029	0.730	1.655	1.998

Eusaar2 Transmittance

		OC			EC			TC		
Site	**Count**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**
AMS	8	0.449	1.276	1.973	0.000	0.000	0.000	0.449	1.276	1.973
BCN	8	0.365	1.038	1.402	0.429	1.220	0.253	0.203	0.577	1.655
CAB	43	0.459	1.068	1.890	0.140	0.325	0.042	0.466	1.083	1.932
DUI	16	0.774	1.927	2.748	0.207	0.515	0.128	0.756	1.883	2.876
IPR	10	0.542	1.454	1.501	0.020	0.053	-0.005	0.545	1.463	1.496
WAL	16	0.696	1.733	1.669	0.000	0.000	0.000	0.696	1.733	1.669
combined	101	0.679	1.544	1.920	0.181	0.411	0.058	0.686	1.561	1.978

IMPROVE Reflectance

		OC			EC			TC		
Site	**Count**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**
AMS	8	0.449	1.276	1.973	0.000	0.000	0.000	0.449	1.276	1.973
BCN	16	0.179	0.445	1.673	0.000	0.001	0.000	0.179	0.445	1.673
CAB	43	0.469	1.090	1.910	0.061	0.141	0.022	0.466	1.083	1.932
DUI	16	0.750	1.866	2.856	0.003	0.007	0.101	0.038	0.094	0.344
IPR	14	0.650	1.647	1.643	0.134	0.338	0.090	0.692	1.751	1.733
WAL	16	0.678	1.688	1.611	0.090	0.224	0.058	0.696	1.733	1.669
combined	113	0.665	1.511	1.939	0.076	0.173	0.031	0.668	1.517	1.970

IMPROVE Transmittance

		OC			EC			TC		
Site	**Count**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**
AMS	9	0.345	0.950	1.679	0.000	0.000	0.000	0.345	0.950	1.679
BCN	8	0.812	2.306	2.024	0.031	0.089	0.003	0.820	2.331	2.026
CAB	33	0.593	1.394	2.116	0.017	0.040	-0.009	0.593	1.395	2.107
DUI	8	0.577	1.639	2.810	0.031	0.087	0.009	0.558	1.585	2.820
IPR	8	1.050	2.983	2.199	0.000	0.000	0.000	1.050	2.983	2.199
WAL	16	0.856	2.133	1.772	0.000	0.000	0.000	0.856	2.133	1.772
combined	82	0.747	1.707	2.068	0.018	0.041	-0.003	0.748	1.708	2.065

NIOSH Reflectance

		OC			EC			TC		
Site	**Count**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**	**SD, µg.cm^{-2}**	**DL, µg.cm^{-2}**	**Mean, µg.cm^{-2}**
AMS	8	0.369	1.048	1.684	0.000	0.000	0.000	0.369	1.048	1.684
BCN	16	0.592	1.474	1.863	0.000	0.000	0.000	0.592	1.474	1.863
CAB	33	0.594	1.396	2.108	0.014	0.034	-0.001	0.593	1.395	2.107
DUI	8	0.556	1.581	2.823	0.005	0.014	-0.003	0.558	1.585	2.820
IPR	12	0.876	2.271	2.045	0.028	0.073	0.004	0.875	2.270	2.048
WAL	15	0.747	1.875	1.765	0.188	0.472	0.056	0.862	2.164	1.822
combined	92	0.692	1.577	2.026	0.078	0.177	0.009	0.709	1.615	2.035

NIOSH Transmittance

4. CONCLUSIONS

The analysis shows that the reflectance protocols have problems detecting very low levels of elemental carbon and are unable to deliver the detection limits required.

The results from the transmittance protocols show no protocol clearly performing better than the others across all of the site types and concentrations encountered during the field validation tests. EUSAAR2 performs best for EC at urban background and roadside locations and second best at rural locations.

There was no significant between sampler variability detected for most components and most protocols. Where it was detected it was insignificant compared to the internal repeatability.

The uncertainty of a single measurement result (95%, 2σ) for the transmittance protocols is less than 25% above concentrations of 2 $\mu g.cm^{-2}$. For concentrations below this the relative uncertainty is greater than 25%, but probably limited by the detection limit. When performing repeat measurements of a single sampled filter the repeatability was similar to the calculated uncertainty of a single measurement result.

The OC detection limit measured from laboratory blank filters was close to or exceeded the requirements of the draft standard, with the NIOSH protocols over reporting OC levels compared to the other protocols. The mean EC detection limit for reflectance protocols is <0.1 $\mu g.cm^{-2}$, while the mean detection limit for transmittance protocols was ~0.4 $\mu g.cm^{-2}$. This was above the proposals for the draft standard and is higher than that seen in other measurement studies.

The EC detection limit measured from sampled filters with low EC content was similar for both reflectance and transmittance protocols with mean EC detection limits of 0.192 $\mu g.cm^{-2}$ and 0.122 μg.cm-2 for reflectance and transmittance protocols, respectively.

Field blank OC and EC content was at or below the detection limit results calculated from the laboratory blanks.

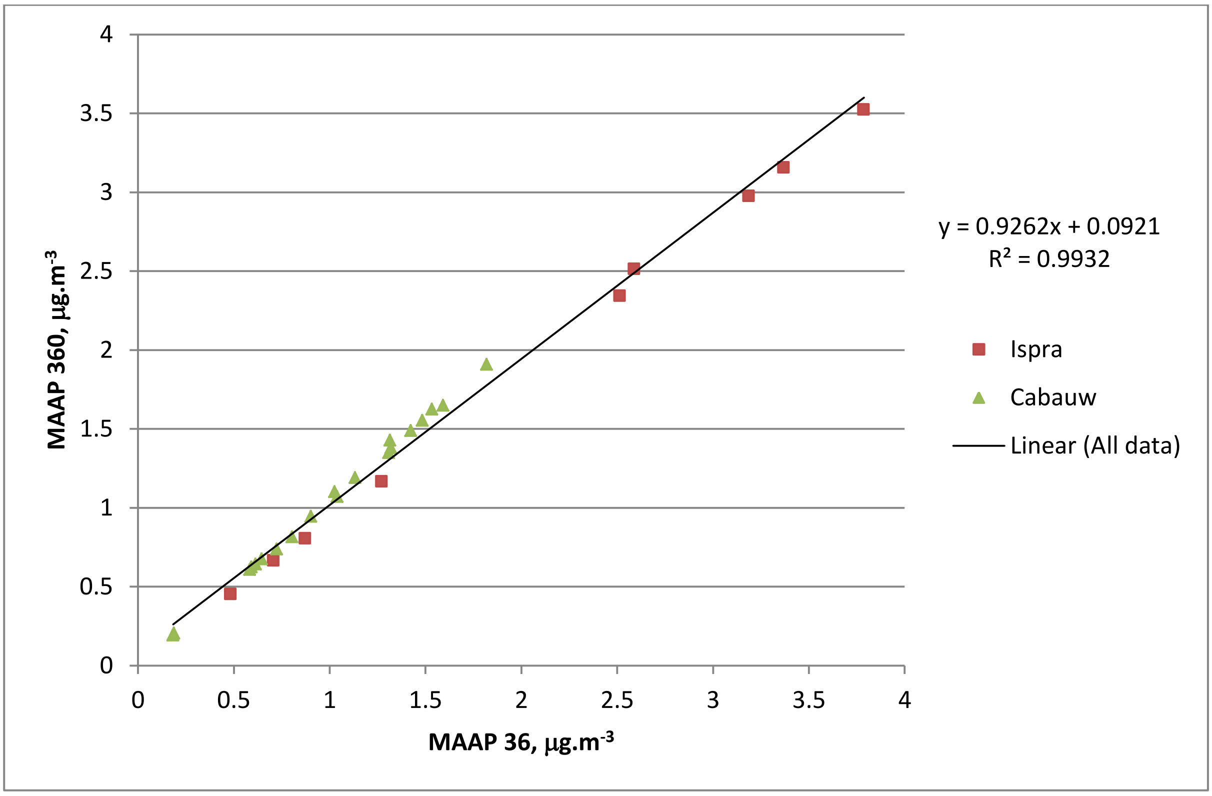
ANNEX 1 EQUIVALENCE CALCULATIONS FOR MULTI ANGLE ABSORPTION PHOTOMETER (MAAP)

Two MAPP analysers also took part in the field campaigns and were run alongside the filter samplers.

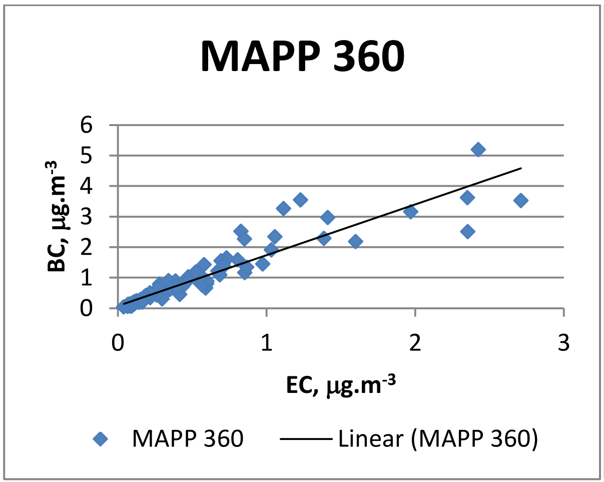
The procedure outlined in the EU Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods and the EU Excel spreadsheet were used to calculate the equivalence of the MAPP compared to filter samples analysed using the EUSAAR2 Transmittance Thermal-Optical Protocol. Details of the monitoring data are shown below:

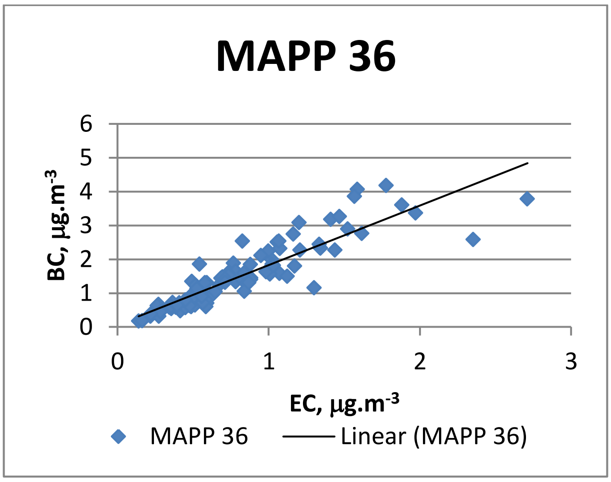
Site	Analyser	Start date	Stop date	Number of data points
Ispra	#36 & #360	12/11/2013	21/11/2013	9
Barcelona	#36	20/02/2014	04/04/2014	38
Amsterdam	#36	12/06/2014	14/07/2014	30
Duisburg	#360	09/02/2014	09/04/2014	38
Waldhof	#360	26/05/2014	13/07/2014	37
Cabauw	#36 & #360	02/09/2014	13/10/2014	20

The following chart shows the comparison of the concentrations measured by the 2 instruments at the Ispra and Cabauw sites. The linear regression is the normal least squares fit calculated by Excel and not the orthogonal regression calculated by the EU spreadsheet.



The following 2 charts show the relationship between the 2 instruments and the filter measurements. Where parallel filter measurements were performed these have been averaged to provide 1 result.





The following table gives the results of the orthogonal regression of the combined data of both analysers versus the filter samples, taking 10 µg.m^3 as the Limit Value for calculating the percentage uncertainty.

Data Set	Un-calibrated Uncertainty, %
Full	190
Ispra	108
Barcelona	287
Duisburg	232
Amsterdam	234
Waldhof	316
Cabauw	232

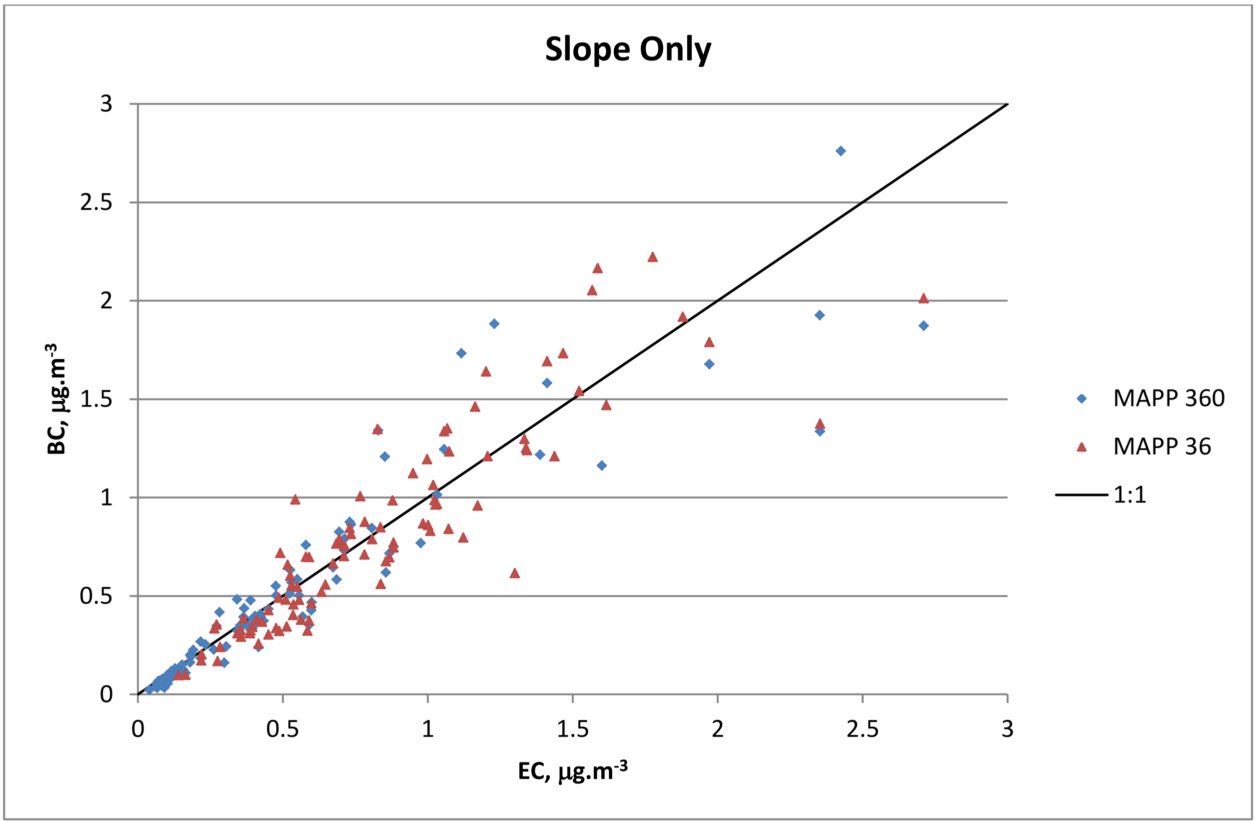
The equivalence uncertainties above are unacceptably high so calibration of the MAAP data is required. The following table gives the calibration slopes and intercept as calculated by the EU spreadsheet.

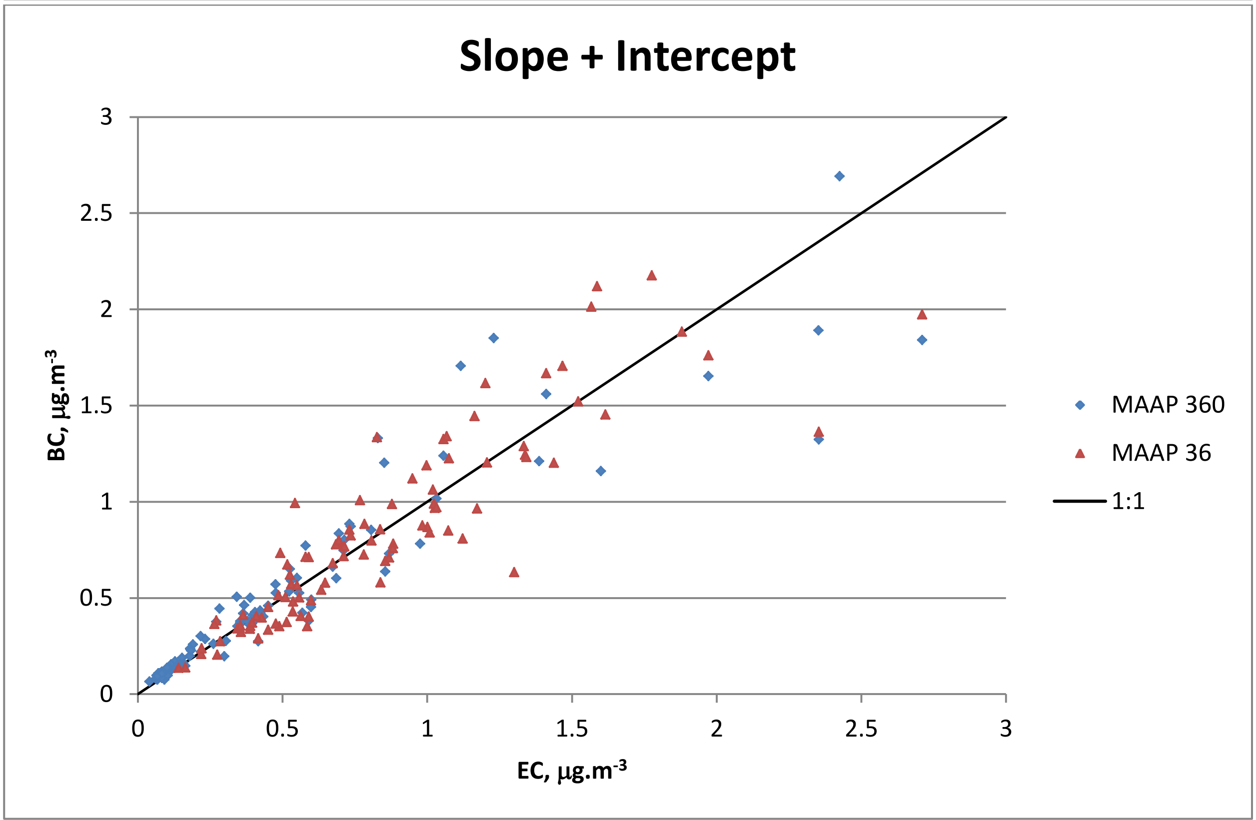
Data Set	Slope	Intercept
Full	1.882	N/A
Full	1.961	-0.083

Applying these calibrations to the MAAP data provides the following relative uncertainties to the filter method:

Data Set	Slope Only, %	Slope + Intercept, %
All	1.7	9.5
Ispra	47.5	53.5
Barcelona	49.6	39.7
Duisburg	20.1	11.4
Amsterdam	16.6	7.7
Waldhof	69.1	58.7
Cabauw	23.6	15.0

Although the relative uncertainty of the full data set using both calibration methods is low, the relative uncertainty at most monitoring sites is large. The following charts show the relationship between the calibrated MAAP data and the filter method:





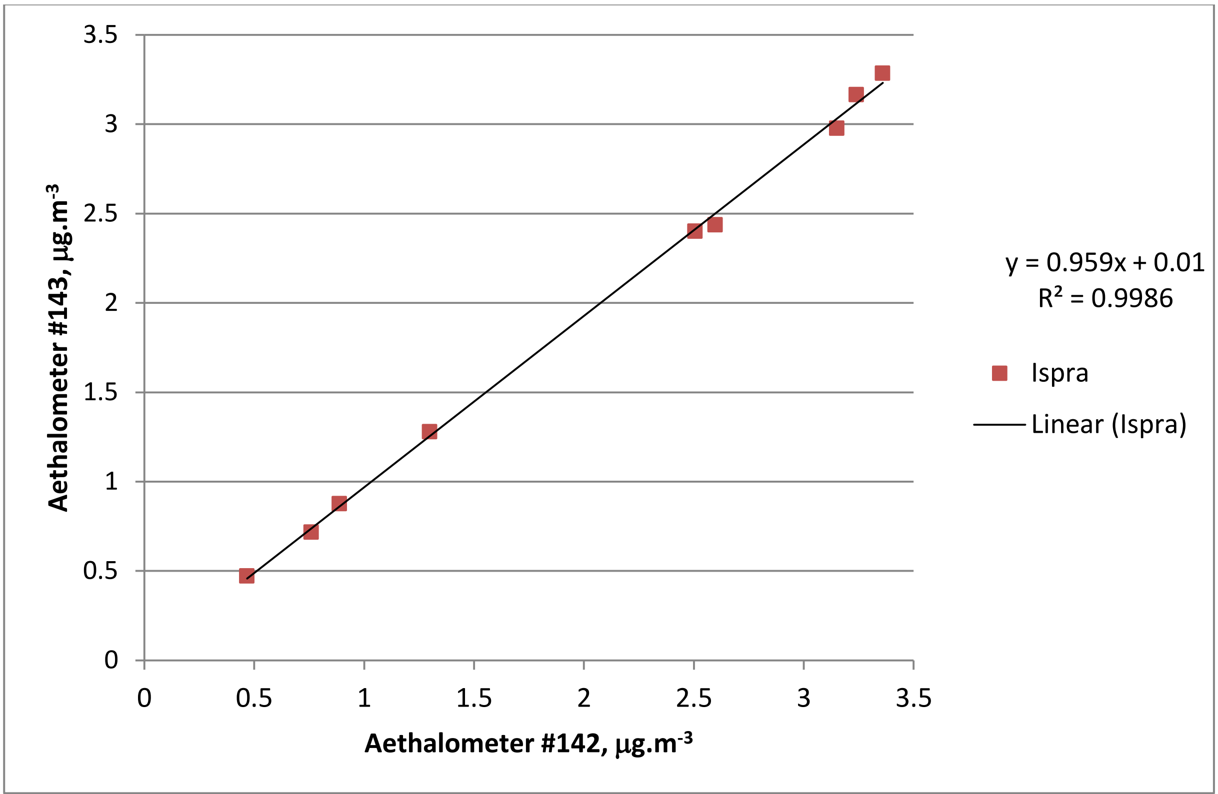
ANNEX 2 EQUIVALENCE CALCULATIONS FOR SEVEN WAVELENGTH AETHALOMETER

Three 7 wavelength Aethalometer analysers also took part in the field campaigns and were run alongside the filter samplers. Analyser # 142 failed at the start of the Amsterdam field measurements and was replaced by analyser #197. Analyser #143 did not record data correctly during the Cabauw field measurements so these results have not been included.

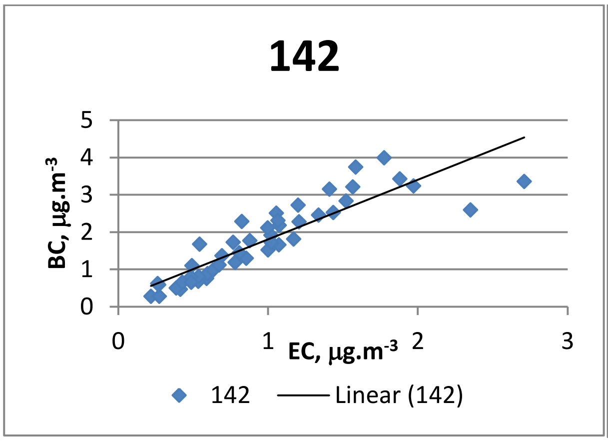
The procedure outlined in the EU Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods and the EU Excel spreadsheet were used to calculate the equivalence of the Aethalometer compared to filter samples analysed using the EUSAAR2 Transmittance Thermal-Optical Protocol. Details of the monitoring data are shown below:

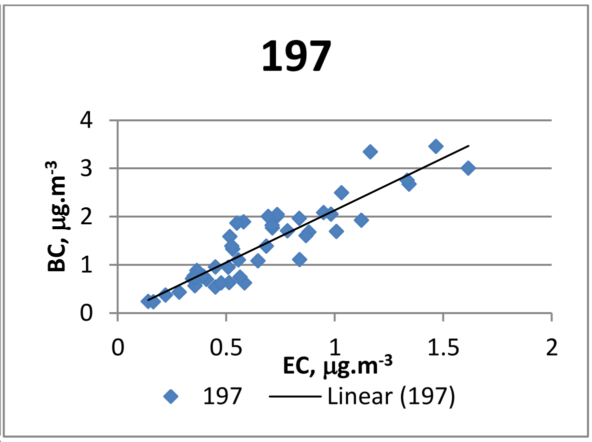
Site	Analyser	Start date	Stop date	Number of data points
Ispra	#142 & #143	12/11/2013	21/11/2013	9
Barcelona	#142	20/02/2014	04/04/2014	38
Amsterdam	#197	14/06/2014	14/07/2014	27
Duisburg	#143	09/02/2014	09/04/2014	38
Waldhof	#143	26/05/2014	13/07/2014	37
Cabauw	#197	02/09/2014	13/10/2014	20

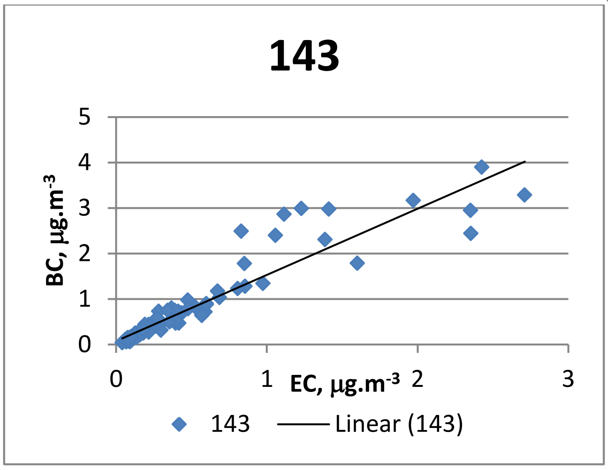
The following chart shows the comparison of the concentrations measured by the 2 instruments at the Ispra site. The linear regression is the normal least squares fit calculated by Excel and not the orthogonal regression calculated by the EU spreadsheet.



The following 3 charts show the relationship between the 2 instruments and the filter measurements. Where parallel filter measurements were performed these have been averaged to provide 1 result.







The following table gives the results of the orthogonal regression of the combined data of all analysers versus the filter samples, taking 10 µg.m^3 as the Limit Value for calculating the percentage uncertainty.

Data Set	Un-calibrated Uncertainty, %
Full	177
Ispra	90
Barcelona	245
Duisburg	150
Amsterdam	305
Waldhof	283
Cabauw	403

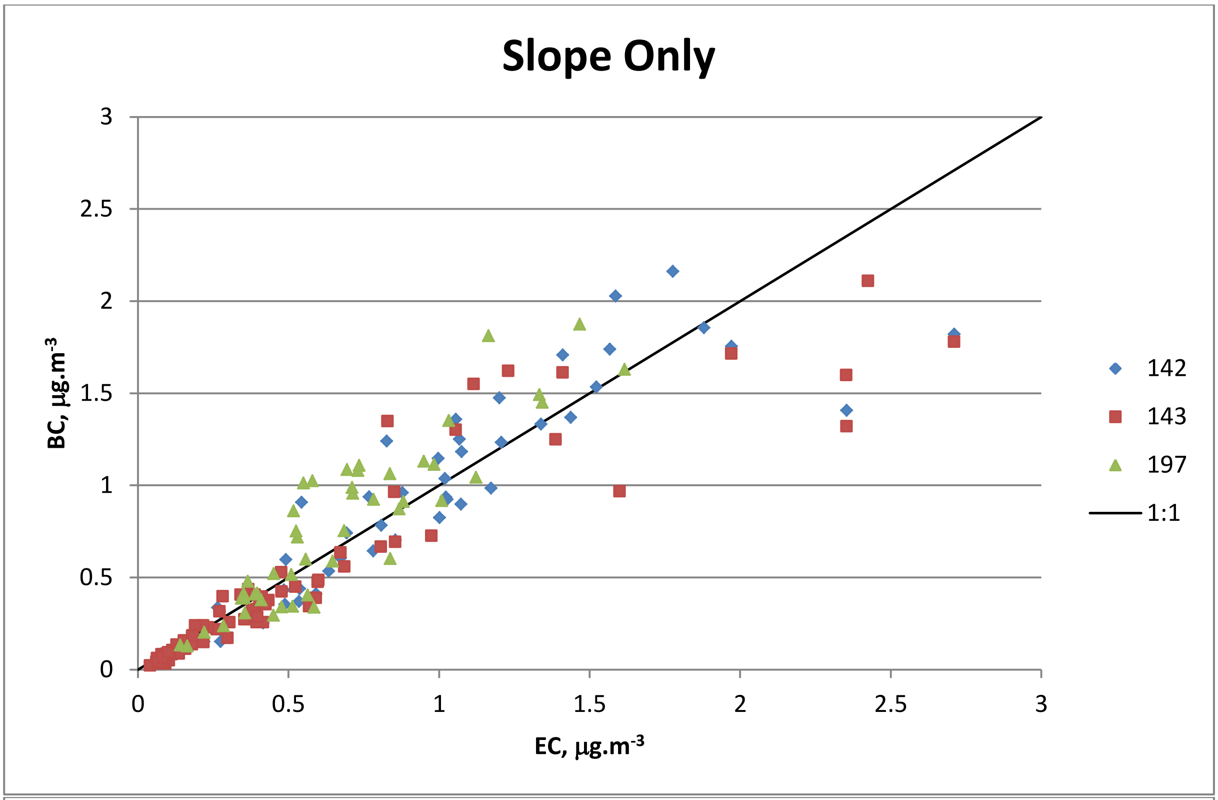
The equivalence uncertainties above are unacceptably high so calibration of the Aethalometer data is required. The following table gives the calibration slopes and intercept as calculated by the EU spreadsheet.

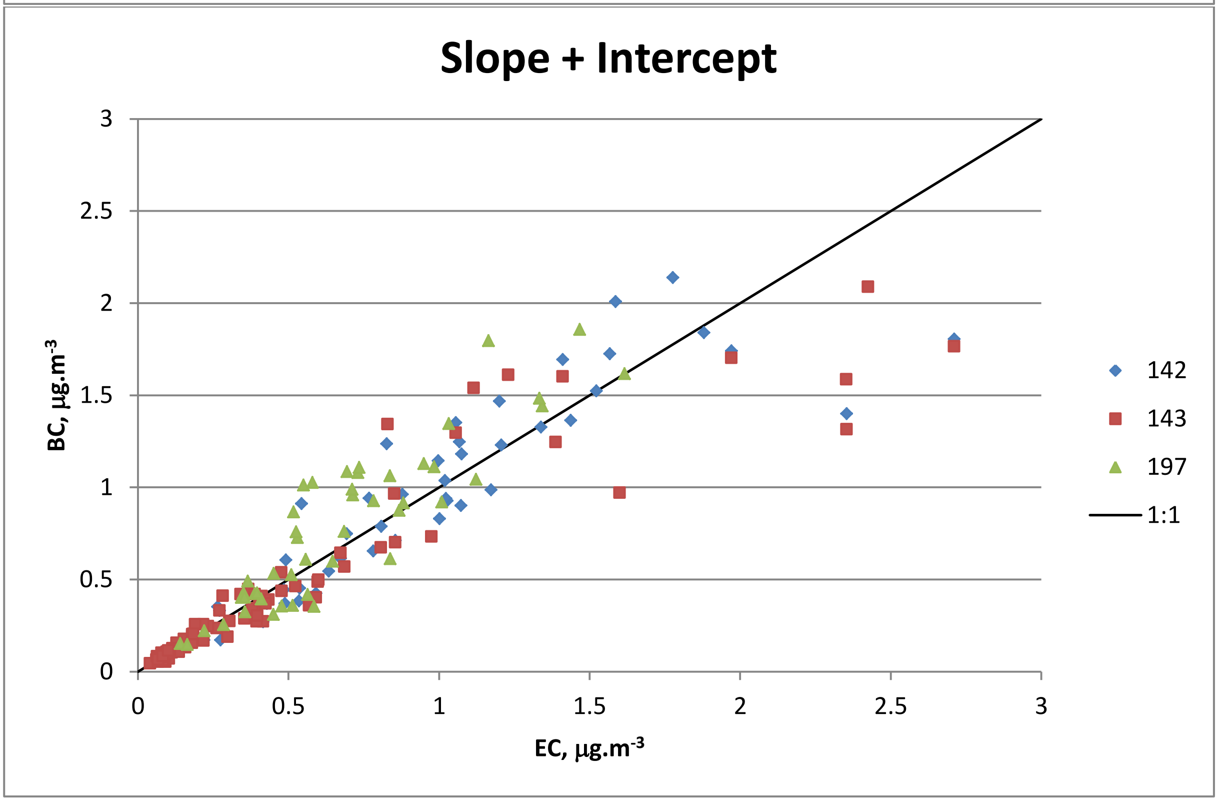
Data Set	Slope	Intercept
Full	1.846	N/A
Full	1.885	-0.042

Applying these calibrations to the Aethalometer data provides the following relative uncertainties to the filter method:

Data Set	Slope Only, %	Slope + Intercept, %
All	6.2	10.1
Ispra	55.6	58.5
Barcelona	35.6	31.0
Duisburg	20.4	24.1
Amsterdam	65.8	60.4
Waldhof	53.3	48.1
Cabauw	118.0	111.5

Although the relative uncertainty of the full data set using both calibration methods is low, the relative uncertainty at most monitoring sites is large. The following charts show the relationship between the calibrated Aethalometer data and the filter method:


Slope Only
BC, µg.m-3
EC, µg.m-3
0
0.5
1
1.5
2
2.5
3
142
143
197
1:1


Slope + Intercept
BC, µg.m-3
EC, µg.m-3
0
0.5
1
1.5
2
2.5
3
142
143
197
1:1

ANNEX 3 FILTER CONCENTRATION DATA AND RESULTS OF CALCULATIONS

Filter concentration data and uncertainty calculation results are supplied as separate Excel spreadsheets.

Results of filter concentration data used for uncertainty calculations

OCEC Filters.xlsx

Results of calculations

Matlab Results.xlsx