UK Equivalence Programme for Monitoring of Particulate Matter.

Final Report for:

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EXECUTIVE SUMMARY

European Directive 96/62/EC sets out the current framework for the assessment of twelve different pollutant species across the EU. In order to achieve harmonisation of measurements across Member States, the Directive provides for the setting of European standards for monitoring and analysis. These standards are set by the Comité Européen de Normalisation (CEN).

The First Daughter Directive 1999/30/EC (DD1) sets Limit Values for particles within the PM_{10} fraction, based on measurements made using the reference method EN12341 – a filter-based gravimetric measurement method. In the UK, measurements of PM_{10} are largely founded on the use of the Tapered Element Oscillating Microbalance. More recently, the EU Commission has proposed Concentration caps and Exposure Reduction Targets for particles less than 2.5µm in diameter and CEN has published the standard method in EN14907.

Where a Member State chooses to employ monitoring methods outside of the reference method, a programme of 'equivalence' must be undertaken. In recognising the need for further guidance on such programmes – the approach to be taken, the assessment criteria and the methods of reporting - the European Commission has produced the Guidance for the Demonstration of Equivalence of Ambient Air Monitoring Methods (herein referred to as The Guidance), which sets out whether a candidate method can be considered equivalent to the EU reference method.

For particulate monitors 'equivalence' is defined in terms of whether the candidate method is capable of fulfilling the Data Quality Objectives as specified in the First Daughter Directive, and strict equivalence criteria are set out. This report summarises the results of the UK Particulate Monitoring Programme, which has included the operation of seven candidate instruments collocated with the EU reference method (Low Volume Samplers for PM_{10} and $PM_{2.5}$). Instruments included in the programme are: Tapered Element Oscillating Micro-balance (TEOM); TEOM retrofitted with Filter Dynamics Measurement System (FDMS); Partisol 2025 Sequential Sampler; OPSIS SM200 (Beta and Mass configurations); Met-One Beta Attenuation Monitor (BAM), and Met-One BAM retrofitted with a heater (herein referred to as a "Smart BAM").

The programme has included operation of the monitoring equipment across eight studies that collectively represent particulate conditions typically encountered across the United Kingdom. Field campaigns have been undertaken during summer and winter periods at Teddington (SE England); Birmingham (Midlands); East Kilbride (Scotland) and Bristol (SW England). All instruments were operated in duplicate in order to determine the 'between-sampler' uncertainty.

Experience gained in undertaking the current programme highlights a number of issues related to The Guidance, which the UK proposes to feedback to the Commission. In applying

the criteria contained within The Guidance, it has been necessary for the investigators in the current study to make some interpretation of the current criteria set down in The Guidance. The following interpretation of The Guidance has been made regarding the application of the criteria in the current study, and a more thorough discussion of these is given in Appendix E:

- Corrections are applied where the slopes of all data sets are either all greater or all less than 1 and/or where the intercepts of all the data sets are either all greater or all less than zero;
- If a candidate instrument fails on W_{CM} for the <50% LV dataset alone (either before or after slope and/or intercept correction), this has not been considered sufficient evidence for a candidate instrument to be excluded.

Gravimetric analysis of particulates in the current study has employed the use of Emfab (Teflon coated glass fibre) filters. These were found to have many advantages in robustness and inertness over the other more commonly used media allowed in EN14907 of Teflon; quartz; and glass-fibre filters. However, sampling in highly humid conditions was shown to result in the interruption of sampling of the reference samplers, and it is thought that moisture collecting on the filter was blocking the passage of air through the filter. Closer investigation of the reference methods in the current study suggests that the design of the reference inlets may have the effect of directing water droplets in the air onto the filter (not just those smaller than 2.5 µm or 10 µm). Moreover, repeatedly using Emfab filters as a "tare" for gravimetric measurements of particulate mass was shown to result in a small (approximately 20 µg) loss in filter mass. This could be minimised by using metal check-weights as a tare for sample filters. Previous studies have indicated that both Teflon and quartz filter media lose volatile species during the summer; however, this seasonal effect was not observed with Emfab filters in the current study.

Results for other instruments show that the following meet the equivalence criteria set out in this study: Partisol 2025 Sequential Sampler; TEOM retrofitted with FDMS (for PM_{10} and $PM_{2.5}$); and the OPSIS SM200 (by Beta). All these units meet the equivalence criteria set down in this study without the application of correction for slope and/or intercept. The following instruments meet the equivalence criteria set down in this study only after application of correction factors for slope and/or intercept: OPSIS SM200 (by Mass) and Met-One BAM. The Met-One Smart BAM has been excluded from any statistical consideration of the equivalence criteria set down in this study due to incorrect configuration during installation and set-up.

The results of the investigations show that the current TEOM monitoring method used in the UK fails to meet the criteria for equivalence set out in this study. This result is consistent with previous investigations reported by Defra and the devolved administrations. The UK currently reports TEOM measurements using the inbuilt 3 and 1.03 correction factors with the application of an additional 1.3 correction factor (herein referred to as TEOM (3,1.03,1.3)).

Analysis of TEOM datasets shows that the use of the 1.3 factor (in addition to those already contained within the TEOM units) does not lead to any adherence to the equivalence criteria set out in this study. Further, were the TEOM units to be replaced with any of the instruments that are deemed to meet the equivalence criteria (either with or without correction) there would likely be an increase in daily LV exceedences reported at locations with a significant volatile mass fraction. It would not be known whether this was due to the change in monitoring method or an actual change in ambient concentrations.

The following table provides an overall summary of the results of the current study for each instrument included. The operation of candidate instruments in configurations different from those employed in this study may constitute a different method, and it cannot be assumed that the conclusions are transferred.

Candidate Instrument	PM Size Fraction	Manufacturer	Equivalence Criteria Met?	Correction Required
Partisol 2025	PM_{10}	Thermo Electron Corporation	Meets equivalence criteria.	No correction required.
TEOM	PM_{10}	Thermo Electron Corporation	Does not meet equivalence criteria.	Correction does not aid the adherence of equivalence criteria.
PM_{10} FDMS	PM_{10}	Thermo Electron Corporation	Meets equivalence criteria.	No correction required.
$PM_{2.5}$ FDMS	$PM_{2.5}$	Thermo Electron Corporation	Meets equivalence criteria.	No correction required.
SM200 by Beta	PM_{10}	Opsis AB	Meets equivalence criteria.	No correction required.
SM200 by Mass	PM_{10}	Opsis AB	Meets equivalence criteria after application of slope and intercept correction factors.	$SM200Mass_{Corrected} = \frac{(SM200Mass - 1.286)}{0.819}$
BAM†	PM_{10}	Met-One	Meets equivalence criteria after application of a slope correction factor.	If flow reported at standard conditions: $BAM_{Corrected} = \frac{BAM}{1.211}$ If flow corrected to ambient conditions: $BAM_{Ambient\ Corrected} = \frac{BAM_{Ambient}}{1.273}$

† The Met-One Smart heated BAM was also included in this study, however upon analysis of the data it was discovered that the instrument had been supplied with an incorrect configuration, and the instrument has been excluded from statistical analysis.

The PM_{10} FDMS provides a measurement of the non-volatile mass fraction (herein referred to as PM_{10} $FDMS_{Base}$), and this is a comparable (though not identical) parameter to the TEOM. A comparison of PM_{10} $FDMS_{Base}$ and TEOM data without any inbuilt or subsequent correction factors (herein referred to as TEOM (0,1,1)) yields the following relationship:

$$TEOM\,(0,1,1) = \left(\frac{\left(PM_{10} FDMS_{Base} + 2.061 \right)}{1.360} \right)$$

A comparison of the TEOM and PM_{10} $FDMS_{Base}$ in London by KCL-ERG showed that PM_{10} $FDMS_{Base}$ plotted against TEOM (0,1,1) resulted in a regression analysis of slope = 1.08; intercept = –2.1 µg m^{-3}; and R = 0.92 (with the FDMS on the Y axis). These results are clearly different from those shown in the current study.

A comparison of PM_{10} $FDMS_{Base}$ and TEOM (3,1.03,1.3) data yields the following relationship:

$$TEOM\,(3,1.03,1.3) = \left(PM_{10} FDMS_{Base} + 5.826 \right)$$

1. INTRODUCTION

European Directive 96/62/EC "Ambient Air Quality Assessment and Management" (the "Framework Directive") sets out the current framework for the assessment of twelve different pollutant species across EU (European Union) Member States [1]. For each pollutant a statutory Limit or Target Value is set through the promulgation of a sub-set of Directives (known as Daughter Directives).

In order to achieve harmonisation of measurements across Member States the Framework Directive provides for the setting of European standards for monitoring and analysis. These standards are set by CEN (Comité Européen de Normalisation) through Working Groups (WGs) comprised of relevant experts within their fields and cover all aspects of monitoring for the reporting of compliance measurements. Once set, such methods become adopted as a European reference method and take into account the inherent uncertainty of the measurements made, in order to comply with the Data Quality Objectives (DQOs) of the relevant Limit Value (LV) for each of the pollutants within the Daughter Directives. Member States are not obliged to employ the reference method as standard across their networks. However, where a Member State decides to employ other methods of sampling and analysis, such methods should be shown to be 'equivalent' with the reference method and pass the test criteria set out in the EC Guidance for the Demonstration of Equivalence of Ambient Air Monitoring Methods (hereafter referred to as The Guidance) [2].

The First Daughter Directive 1999/30/EC (DD1) [3] sets LVs for PM_{10} based on measurements performed using the reference method or equivalent. The reference method is defined in the CEN standard EN12341 [4], and is a filter-based gravimetric sampler, which relies on determining the mass of particles collected on a filter after a known volume of air has been drawn through it.

Within the UK networks, PM_{10} monitoring is largely founded on the Tapered Element Oscillating Microbalance (TEOM) analyser. EN12341 sets out procedures for determining whether non-reference samplers are equivalent to the reference method. However, the procedure is not suitable for determining the equivalence of automatic analysers (such as the TEOM), and the criteria are not directly comparable with the Data Quality Objectives. More recently, the "CAFE Directive" has proposed a concentration cap and an Exposure Reduction Target for particles less than 2.5 µm in diameter ($PM_{2.5}$) [5]. A standard method for $PM_{2.5}$ (EN14907) has been published by CEN [6].

This report provides the results of eight inter-comparison studies undertaken by the UK in respect of PM_{10} and $PM_{2.5}$. It is the aim of this report to summarise the results of the inter-comparison exercise only. It is not within the scope of this document to draw any conclusions from the data with respect to the operation of the UK network, nor to identify scientific reasons for equivalence not being met. Other Member States are proceeding with analogous instrument comparisons, though results are not available at time of writing.

2. SCOPE OF STUDY

2.1 Equivalence Guidance

The Guidance has the general aim of determining whether a candidate method (including automatic analysers) can be considered equivalent to the reference method. This is broadly defined in terms of whether the candidate method is capable of fulfilling the Data Quality Objectives as specified in the relevant Daughter Directive.

An inter-comparison exercise using collocated reference samplers and a number of candidate samplers has been undertaken in line with The Guidance. It is emphasised that the application of the precise methodology set out within The Guidance is not mandatory, and that other approaches that are in broad compliance with the principles of ENV 13005 [7] may be used, provided that the validity of the approach is adequately justified. During the course of the study, interpretation of The Guidance has been undertaken to meet the UK requirements for the programme. Where modifications to the approach have been applied the details are described, and the implications of these modifications to future possible revisions of The Guidance are discussed in **Appendix E**.

The following key aspects of The Guidance have been followed in the UK programme:

- Test sites shall be representative for typical conditions for which equivalence will be claimed including possible episodes of high concentrations.
- A minimum of four comparisons shall be performed with particular emphasis on the following variables, if appropriate:
    - Composition of the PM fraction, notably high and low fractions of semi-volatile particles, to cover the maximum impact of losses of semi-volatiles.
    - Air humidity and temperature (high and low) to cover any conditioning losses of semi-volatiles during the sampling process.
    - Wind speed (high and low) to cover any dependency of inlet performance due to deviations from ideal behaviour as dictated by mechanical design, or deviations from the designated sampling flow rate.
- A minimum of 40 measurement results each averaged over at least 24-hour per comparison shall be collected.
- Samplers and instruments shall be positioned in such a way that the effect of spatial inhomogeneities of the compound concentration in the sampled air are negligible in comparison with other uncertainty contributions
- Between-sampler uncertainty of both reference and candidate samplers should be determined.

A programme of study at four UK sites over both summer and winter periods (giving a total of eight field campaigns) was undertaken from late 2004 through to early 2006.

2.2 Reference and Candidate Samplers

The choice of reference Low Volume Samplers (LVS) and candidate instruments to be included in the study was determined through discussions with Defra and the devolved administrations and is based upon the current understanding and setup of both the reference methods and the National Network infrastructure for particulate monitoring. All instruments were operated in duplicate, and so there were a total of eighteen instruments at each site. Details of the specific operating procedures involved for each instrument are summarised in the Sections listed below.

The following EN12431 compliant **PM_{10} reference method** was employed in the study:

- Klein Filtergerat. Herein referred to as PM_{10} KFG (Section 5.1).

The following **PM_{10} candidate methods** were employed in the study:

- Partisol 2025 (Section 5.3);
- TEOM (Section 5.4);
- TEOM retrofitted with a Filter Dynamics Measurement System (FDMS). Herein referred to as PM_{10} FDMS (Section 5.5);
- OPSIS SM200, which has 2 measurements herein referred to as SM200 Beta and SM200 Mass (both Section 5.6);
- Met-One Beta Attenuation Monitor (BAM) (Section 5.7);
- Met-One BAM retrofitted with a heater herein referred to as Smart BAM (Section 5.8).

The following EN14907 compliant **$PM_{2.5}$ reference method** was employed in the study:

- $PM_{2.5}$ Leckel (Section 5.2).

The following **$PM_{2.5}$ candidate method** was employed in the study:

- TEOM retrofitted with an FDMS. Herein referred to as $PM_{2.5}$ FDMS (Section 5.5).

All instruments report concentrations to ambient conditions with the exception of the BAM, which reports to standard temperature and pressure. BAM concentrations were corrected to ambient conditions and the results of the equivalence tests are reported for both the ambient and standard condition datasets.

2.3 Roles and Organisations

The following organisations were appointed to undertake the work:

- Bureau Veritas – Air Quality (formerly Casella Stanger): the ambient air quality team currently hold the contract for the Central Management and Co-ordination Unit (CMCU) of the Automatic Urban and Rural Network (AURN). Bureau Veritas – Air Quality were responsible for the overall project management of the study and report directly to Defra and the devolved administrations;
- National Physical Laboratory (NPL): were appointed as sub-contractors to the project

management team for the determination of weighing protocols for delivery of accurate and quality assured mass measurement data (gravimetric analysis only);

- Air Quality Consultants: Steve Moorcroft (formerly of Casella Stanger) has provided technical support to the project management team.

The following organisations provided local technical support through undertaking the necessary Local Site Operator (LSO) procedures:

- NPL;
- The University of Birmingham;
- Bristol City Council;
- AEA Technology netcen

The following companies were sub-contracted to act as Equipment Support Units (ESUs):

- Enviro Technology (PM_{10} KFG, $PM_{2.5}$ Leckel, BAM, Smart BAM, Opsis SM200);
- Air Monitors UK (Partisol 2025, TEOM, PM_{10} FDMS, $PM_{2.5}$ FDMS)

The instrument manufacturers were in some instances directly involved in the set up and maintenance of instruments, and were consulted in the event of technical difficulties, however, they were not subcontracted directly.

- Sven Leckel GmbH (PM_{10} KFG, $PM_{2.5}$ Leckel);
- Opsis AB (Opsis SM200);
- Met-One (BAM, Smart BAM);
- Thermo Electron Corporation (Formerly known as Rupprecht & Patashnick (R&P)) (Partisol 2025, TEOM, PM_{10} FDMS, $PM_{2.5}$ FDMS);

In addition, AEA Technology netcen were sub-contracted to provide independent audits on each instrument. Netcen have UKAS (United Kingdom Accreditation Service) accreditation for measuring the flows of instruments in the range 1 to 18 l min^{-1}, and also measuring the spring calibration constant K_0 for TEOM and FDMS units. Analogous auditing methods were used in this study as are used by netcen when they audit the UK National Networks. Flow rates of TEOMs; FDMSs; Partisol 2025s; BAMs; Opsis SM200s; and Smart BAMs were measured using a BIOS DryCal DCLite MH (working range 200 ml min^{-1} to 20 l min^{-1}), and were corrected from ambient to standard (298 K and 1013 mbar) conditions by netcen. The PM_{10} KFG and $PM_{2.5}$ Leckel were outside the range of the BIOS, and so were measured using an AGL SK25 gas meter averaged across 2 minutes of sampling. There were three audits for each of the four sites; one each at the beginning, middle and end of each sampling period.

2.4 Macro and Micro Scale Instrument Location

Sites were selected to represent both urban background and roadside locations, and the particulate matter pollution climate in different geographical regions of the UK Current knowledge of PM concentrations across the UK shows that episodes of volatile ammonium

nitrate aerosol occurs predominantly in the Southeast of the UK. **Table 2.1** and **Figure 2.1** summarise the sites, their location [8], the appointed LSO, and the dates of the summer and winter campaigns at that location.

Particular attention was paid to any influences of aligning the sampling trailer relative to the dominant local emission source. The micro-scale set up of samplers installed in the monitoring trailer is shown in **Figure 2.2**. Instruments were positioned in a trailer at distances of around 70 cm to 1 m between sample inlets (which was found to be the optimal distance allowable within the constraints of the trailer). This is less than the 2 m separation distance recommended by the United States Environmental Protection Agency (USEPA) [9], however, close spacing was particularly important at the Bristol site, where the instruments were situated 10-12 m from a busy road. Roadside sites are defined within the UK National Networks and within Local Air Quality Management Technical Guidance [10]. A roadside site is defined as one "sampling between 1 m of the kerbside of a busy road and the back of the pavement. Typically this will be within 5 m of the road, but could be up to 15 m". It was considered that placing the instruments any closer to the road, could have led to the introduction of unnecessary artefacts associated with sample inlet orientation relative to the emission source (due to the strong concentration gradient close to the carriageway), and so compromise the validity of the comparison study. The reproducibility of samplers (*i.e.* the between-sampler uncertainty) provides for a measure of the potential influences of trailer alignment. Analysis of the TEOM data (the most reproducible instrument) showed a between-sampler uncertainty of 1.15 µg m^{-3} for all 1-hour data (16644 data-pairs), and this is indicative that there were no negative effects due to cross-sampling between the instruments. The Opsis SM200s were located in a separate trailer, and the Partisol 2025s stood outside or in a lockable cage depending on local site security. Both sets of trailers were built by Enviro Technology (Stroud, UK). **Figure 2.3** shows external and internal views of the trailers *in-situ* at the Bristol and East Kilbride sites.

Table 2.1: Site Locations, Classifications and Campaign Details

Site Name	Location	Site Classification	Local Site Operator	Winter Dates	Summer Dates
Teddington	52° 25' 28.32" N 0° 20' 43.66" W 13 m ASL	Suburban	NPL	14th November 2004 to 21st March 2005	22nd March 2005 to 25th July 2005
Birmingham	52° 27' 19.60" N 1° 55' 44.07" W 144 m ASL	Urban Background	University of Birmingham	28th November 2004 to 22nd March 2005	23rd March 2005 to 22nd July 2005
East Kilbride	55° 45' 19.50" N 4° 10' 08.50" W 180 m ASL	Suburban	netcen	13th October 2005 to 12th January 2006	1st August 2005 to 12th October 2005
Bristol	51° 26' 57.63" N 2° 35' 04.66" W 10 m ASL	Roadside	Bristol City Council	13th October 2005 to 19th January 2006	10th August 2005 to 12th October 2005

Figure 2.1 Map of the UK showing site locations.

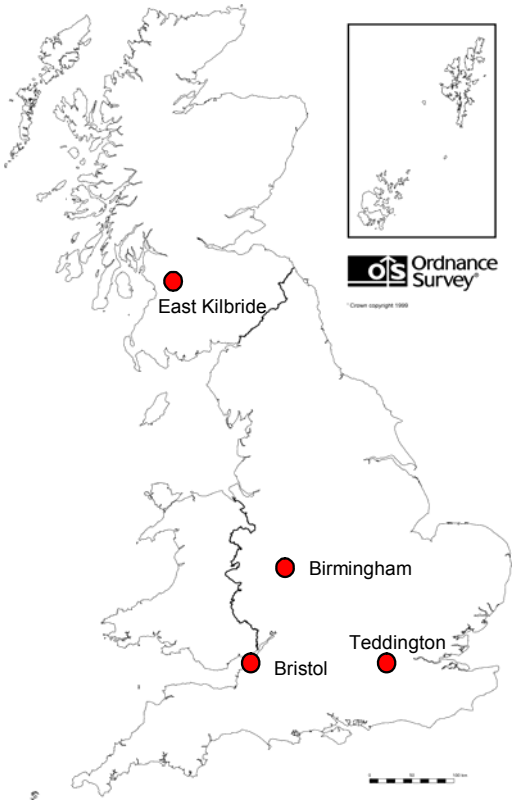


Figure 2.2 The micro-scale set up of samplers installed in the main monitoring trailer. The SM200s were located in a separate trailer, and the Partisol 2025s were located outside.

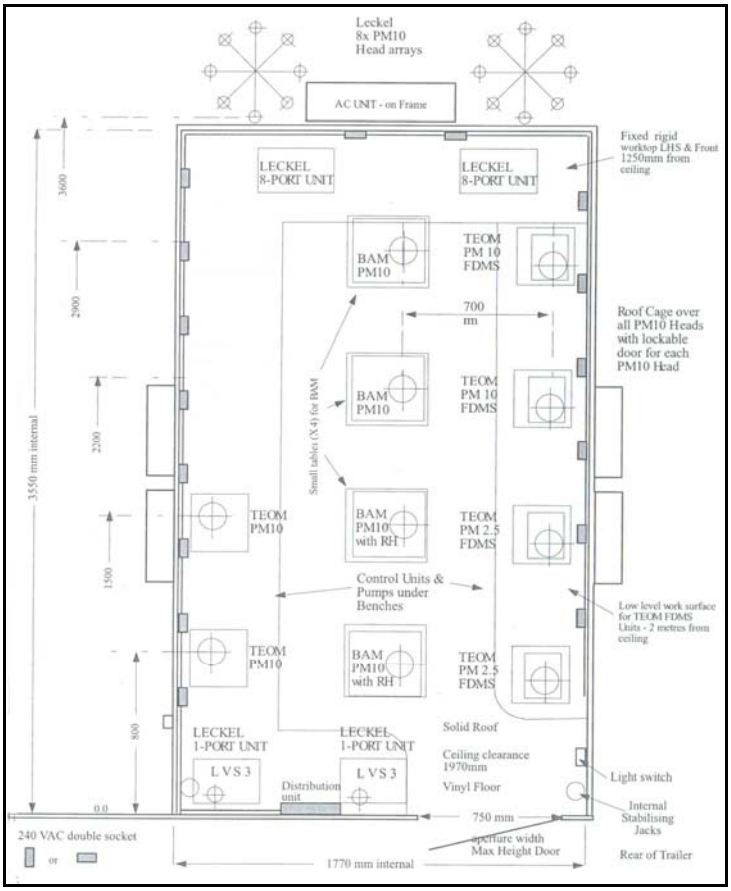
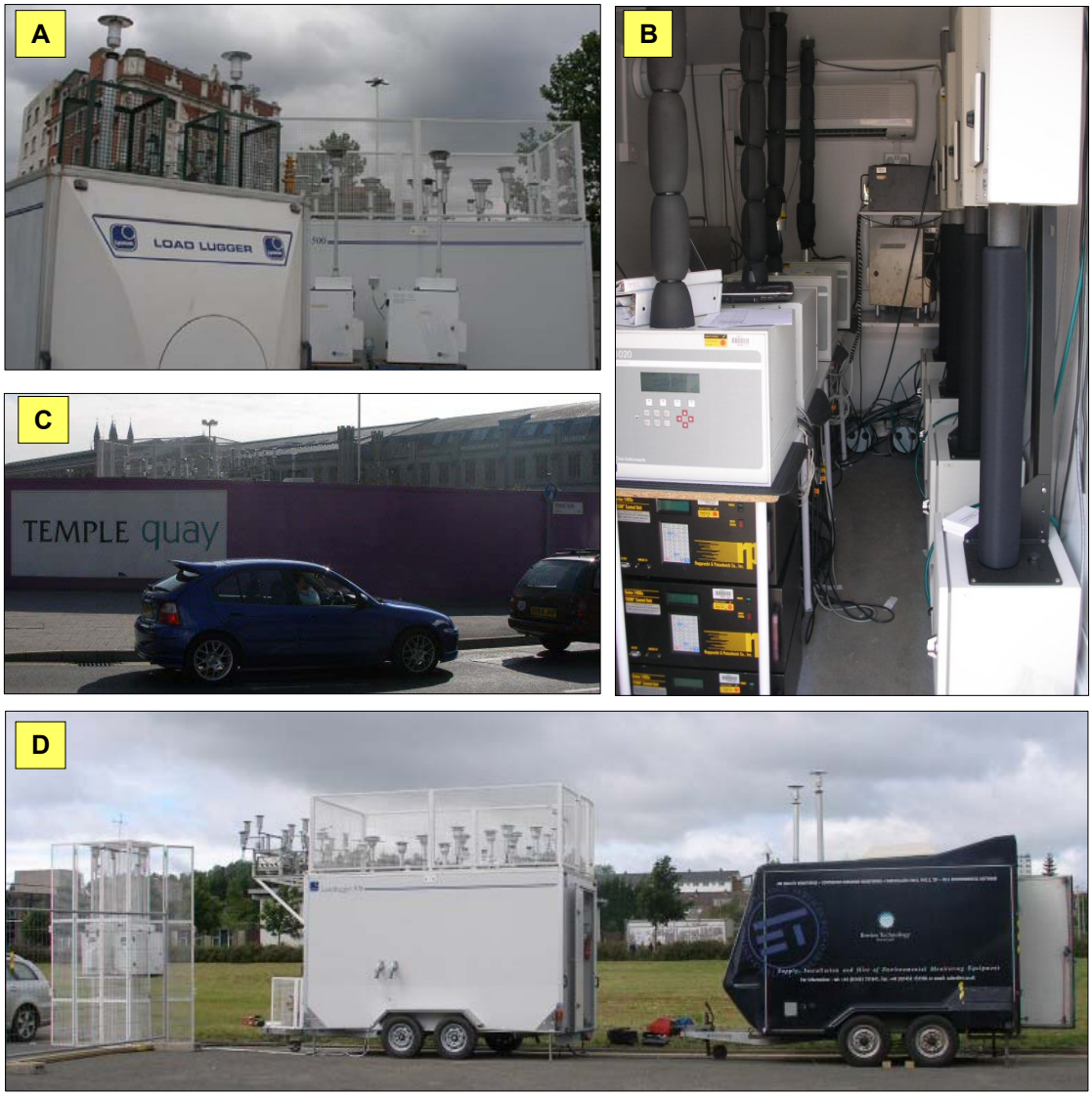


Figure 2.3: **A.** External view of the trailers and Partisol 2025s at Bristol. **B.** Internal view of the main trailer at Bristol. **C.** External view of the Bristol site from the road. **D.** External view of the trailers and Partisol 2025s at East Kilbride.



3. EXPERIMENTAL OVERVIEW

For each of the four sites incorporated in this study, **Figure 3.1** shows the flow of data between the sites, Bureau Veritas and NPL. Initial work was undertaken by NPL to produce an optimised weighing protocol (based on future $PM_{2.5}$ guidelines [6]) and to quantify the major sources of error in the gravimetric technique [11]. Emfab (Teflon coated glass fibre) was chosen as the filter medium for the PM_{10} KFG, $PM_{2.5}$ Leckel and Partisol 2025 samplers, as it is both inert and can operate to high masses of PM. Opsis SM200 instruments use stretched 2µm Teflon membrane filters, as per the manufacturers' request. Details of the weighing methodology are discussed in **Appendix A**.

The weighing room was maintained at 50 ± 5 % Relative Humidity and 20 ± 1 ºC. Prior to sampling, filters were conditioned for a minimum of 48 hours, before being weighed, conditioned for a further 24 hours and then weighed again. Filters were transported to the sites in Analyslides (Pall Corp., NY, USA). Filters were removed after sampling, placed in Analyslides and stored in a refrigerator. PM_{10} KFG and $PM_{2.5}$ Leckel filters were removed directly after sampling each 24 hour period in accordance with guidelines [4,6]. For the Partisol 2025 and Opsis SM200, the filters were left in the instrument for up to two weeks after sampling as per the manufacturers suggested field operation. Filters were returned from the sites to NPL *via* overnight courier in cool boxes with ice packs. Filters were conditioned for 48 to 72 hours, then weighed, conditioned for a further 24 hours, and weighed again. Filter mass data were then given to Bureau Veritas for further processing.

Semi-continuous data were collated directly by Bureau Veritas. Intra-instrument comparisons were undertaken for all reference and candidate instruments, and data-points only deleted if there was a sound scientific reason to do so. In the case of hourly measurements, these were averaged to 24 hours provided there was at least 90 % data capture (22 1-hour measurements) [5].

Significant outliers were sometimes observed when considering the intra-instrument comparison of filter mass based measurements (PM_{10} KFG; $PM_{2.5}$ Leckel; Partisol 2025; and SM200 Mass). It is thought that these outliers are associated with human error (for example through transporting or weighing filters, or problems related to filter identification), and are therefore representative of the methods employed by the operators and not the instrument itself. Particularly where significant 'human error' outliers occur for the reference sampler, leaving these outliers in will result in the failure of all candidate instruments, and so it was considered necessary to remove these outliers for filter mass based measurements.

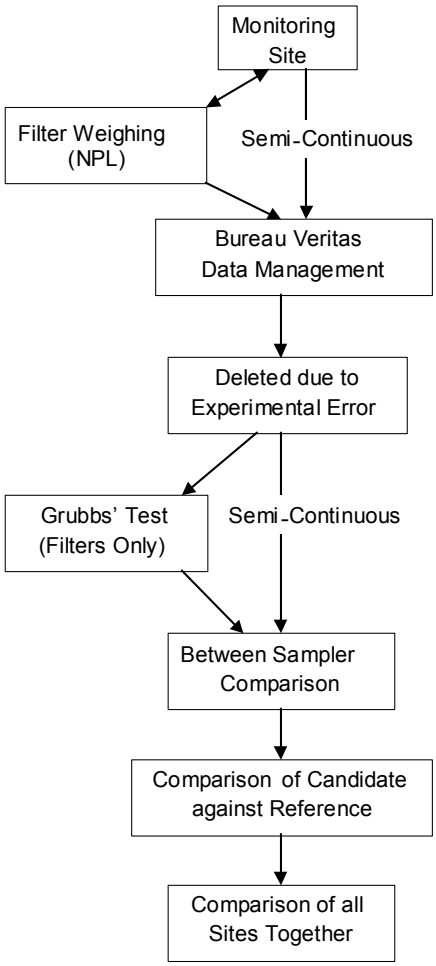
The Guidance states that: "Indications of outlying data (pairs) may be obtained using Grubb's tests on the individual single-period variances. Outlier tests are to be performed at the 99% level". This statement is ambiguous as to whether and to what extent Grubbs' Test should be used, and so the approach followed in the CEN $PM_{2.5}$ study [12] was adopted in the current

study, whereby: "[Grubbs' Test] was repeated until either the critical value was not exceeded, or at most 5% of the data pairs were removed.". In order to standardise this procedure (and so remove any opportunity for bias in data interpretation), all outlying data pairs identified by Grubbs' Test were removed up to a maximum of three pairs in each dataset. Three outliers were chosen as being representative of the maximum 5% of pairs that were deleted in the CEN $PM_{2.5}$ study [12]. Grubbs' Test was applied only to pairs of results from nominally identical instruments. No data were removed because of differences between results from different types of instrument.

The mathematical processes used in the Grubbs' Test and charts identifying which data points were removed are in **Appendix B**. In applying Grubbs' Test, a number of obvious outliers were removed. In addition, a number of less obvious outliers have been removed. It is felt that deleting these points that were not obviously outliers would not compromise the results of the tests for equivalence, so rather than introduce a subjective element into outlier removal; the stated procedure was always followed.

Candidate methods were then compared against the reference method for each field comparison in turn, then for all data together.

Figure 3.1: Flow Diagram showing experimental overview.



4. SUMMARY OF EQUIVALENCE DATA PROCEDURES

4.1 Overview of Guidance Requirements for Particulate Monitors

Equivalence is determined by analysing the correlation between reference measurements and candidate measurements at several field sites. Criteria are set for the measurement uncertainty of the candidate instrument based on the slope and intercept of the regression line, calculated using orthogonal regression, and for the amount of scatter of points around the line.

The Guidance sets out protocols to determine if a candidate method is equivalent to the reference method for three situations:

1. For each of the eight field comparisons separately (though a minimum of four field comparisons is needed to determine equivalence).
2. For all results together.
3. For two datasets obtained by splitting the full dataset into (*i*) greater than or equal to, and (*ii*) below 50 % of the LV. The LVs for PM_{10} are set as: Daily Mean LV 50 µg m^{-3} [3,5] and Annual Mean LV 40 µg m^{-3} [3,5]. For $PM_{2.5}$, the CAFE Directive has recently proposed an Annual Mean LV of 25 µg m^{-3} [5]. There is no proposed Daily Mean LV for $PM_{2.5}$ (though CEN assume an LV of 35 µg m^{-3} in the $PM_{2.5}$ standard that predates the CAFE Directive [6]).

There are therefore a total of 13 datasets (or tests) for PM_{10} candidate methods, but only 11 for the $PM_{2.5}$ FDMS.

For the purposes of this document, datasets have been split according to the average concentration measured by the reference samplers (PM_{10} KFG or $PM_{2.5}$ Leckel). This analysis of high and low PM concentrations was included in The Guidance to prevent the possibility that some automatic instruments might agree with the reference method tolerably well at low concentrations, but may perform poorly at high concentrations, especially in circumstances with a large secondary particulate contribution. The Guidance requires that at least 20 % of the data should be greater than 50% of the LV.

4.2 Explanation of Terms Used in the Uncertainty Analysis

An explanation of the terms used in the uncertainty analysis is as follows. **Appendix C** sets out the equations used for these calculations. The terms defined in this Section are shown in the Charts and Tables in **Section 5** and **Appendix D**.

For each of the eight field comparisons, The Guidance states that 'n' should be at least 40 points for both the between-sampler ($\mathbf{n_{bs}}$) and candidate against reference ($\mathbf{n_{c\_s}}$). However, an 'n' of 30 is normally considered sufficient for statistical analysis. Data are shaded red if there are fewer than 30 data-pairs, orange if there are 30 to 39 data-pairs; and green if there are 40 or greater data-pairs. Both n_{bs} and n_{c_s} are calculated using post Grubbs' Test paired data. For the TEOM, PM_{10} FDMS, $PM_{2.5}$ FDMS, BAM and Smart BAM, n_{bs} is also calculated for the 1-hour data, though there are no associated criteria with this parameter in The Guidance.

To be considered for equivalence, the reference samplers (KFG for PM_{10} and Leckel for $PM_{2.5}$) should have a **24 hour between-sampler uncertainty** ($\mathbf{u_{bs}}$) of less than 2 µg m^{-3} for each individual dataset, and these are shaded red or green accordingly. The candidate methods should have a between-sampler uncertainty of less than 3 µg m^{-3}, and these are shaded red or green accordingly. For the TEOM, PM_{10} FDMS, $PM_{2.5}$ FDMS, BAM and Smart BAM, the 1-hour between-sampler uncertainty is also calculated. This is shaded red if it is greater than 3 µg $m^{-3,}$ though there are no criteria associated with this parameter in The Guidance.

For 24-hour filter-based measurements (PM_{10} KFG, $PM_{2.5}$ Leckel, Partisol 2025 and SM200 Mass), the number of data-pairs deleted by Grubbs' Test ($\mathbf{n_G}$) is calculated, as is $\mathbf{n_{Gmax}}$ (the number of data-pairs that would need to be deleted in order for there to be no more outliers). n_{Gmax} is shaded red if it is greater than 3.

$\mathbf{r^2}$ is a measure of the goodness of the fit of the linear regression (a value closer to 1 signifying less scatter). r^2 has no associated criterion in The Guidance and is not used in the uncertainty calculation.

The **slope b** and **intercept a** are calculated by orthogonal regression. The **uncertainty in the slope** ($\mathbf{u_b}$) is shaded red if it is significantly different from 1, using the criterion: $|b-1| > 2.u_b$. The **uncertainty in the intercept** ($\mathbf{u_a}$) is shaded red if it is significantly different from 0, using the criterion: $|a| > 2.u_a$.

For each test described above, for a candidate instrument to be considered equivalent, $\mathbf{W_{CM}}$ the **expanded uncertainty at limit value** should be less than or equal to the Data Quality Objective (DQO), which is 25 % for PM_{10} and $PM_{2.5}$ field measurements [5]. These are considered for both Daily and Annual Mean LVs, and are shaded red if they exceed the criterion. It is important to note that for lower LVs, a non-zero intercept becomes statistically

more significant to the calculation of W_{CM}. This is of particular relevance for $PM_{2.5}$, where the LV is lower than that for PM_{10}, and has not yet been finalised.

The **percentage of samples greater than 50 % of the limit value (% > 50 % LV)** is listed for the reference method and is calculated for paired data only.

Exceedences (n_{ES},n_{EC}) are in order:

- The number of times the Reference Method exceeds the daily LV for paired data only. This parameter is not calculated for the annual LV.
- The number of times the Candidate Method exceeds the daily LV for paired data only. This parameter is not calculated for the annual LV.

4.3 Equivalence Criteria Used in this Report

The Guidance states that a precondition for acceptance of a dataset is that the slope or intercept should be 'insignificantly different' from 1 and zero respectively for any of the individual or combined datasets. In practice it was considered that these criteria favoured instruments with greater scatter, and their inclusion leads to all candidate instruments requiring correction. An alternative approach was applied in which data were corrected only if the slopes of all datasets were all greater or all less than 1, and/or the intercepts of all datasets were all greater or all less than zero. A discussion of the implications of using this modified approach is given in **Appendix E**.

For the purpose of this study, where a candidate instrument was found to fail on W_{CM} for the <50 % LV dataset alone (either before or after slope and/or intercept correction), this was not considered sufficient evidence for a candidate instrument to be excluded. Rather, it reflects the problems associated with regression calculations where there is significant scatter on data that are restricted to within a narrow range.

This approach has also been followed at East Kilbride, where measured concentrations (particularly for $PM_{2.5}$) were very low. Whilst these data have been included in the tests applied to the combined datasets, the individual East Kilbride datasets have been treated with caution. Failure of a candidate instrument to meet the W_{CM} criterion for this site alone was not considered suitable justification for rejection. The Guidance states that a minimum of four datasets are required to declare that the equivalence criteria are met. It is important to note that whilst eight datasets were collected in the current study, it was not considered appropriate to exclude individual datasets simply because they did not conform to desired criteria. By treating the East Kilbride datasets with caution (on the basis that ambient concentrations were very low and that this compromises the orthogonal regression), the authors believe that the most rigorous approach has been adhered to.

The following five logic steps have been applied to determine whether an instrument meets the criteria for equivalence:

1. Calculate all the parameters discussed in Section 4.2. Is the between-sampler uncertainty of all the 24-hour data less than 3 µg m^{-3}?
   TRUE: Proceed to 2 below.
   FALSE: **Instrument deemed not to meet criteria of equivalence.**

2. Are the slopes of all the individual and combined datasets either all greater or all less than 1, and/or are the intercepts all greater or all less than 0?
   TRUE: Proceed to 4 below.
   FALSE: Proceed to 3 below.

3. Is the expanded uncertainty for any dataset (excluding the sub-50 % LV datasets) greater than the 25 % DQO?
   TRUE: Proceed to 4 below.
   FALSE: **Instrument deemed to meet criteria of equivalence.**

4. Apply the appropriate slope and/or intercept correction as defined in the three scenarios below.
   - If the slope of the 'All Data' dataset is statistically significant, correct all individual and combined datasets by the slope of the entire dataset. OR
   - If the intercept of the 'All Data' dataset is statistically significant, correct all individual and combined datasets by the intercept of the entire dataset. OR
   - If both the slope and intercept of the 'All Data' dataset are statistically significant, correct all individual and combined datasets by the slope and intercept of the entire dataset.

5. Recalculate all the parameters for the corrected datasets as discussed in Section 4.2. Is the expanded uncertainty for any dataset (excluding the sub-50 % LV datasets) greater than the 25 % DQO?
   TRUE: **Instrument deemed not to meet criteria of equivalence.**
   FALSE: **Instrument deemed to meet criteria of equivalence with slope and/or intercept correction**

5. RESULTS BY INSTRUMENT

5.1 PM_{10} KFG Reference Sampler

5.1.1 PM_{10} KFG Description and Set Up

The four PM_{10} KFGs used in this study were taken from the UK National Network of six 8-port samplers, and were manufactured by Sven Leckel GmbH (Berlin, Germany). The instruments had a flow rate of 2.3 m^3 hr^{-1} (approximately 38.3 l min^{-1}), and controlled and reported volumes to ambient conditions. Emfab filters (Pall Corp., NY, USA; Type: EMFAB TX40HI20-WW; Part No.: 7221) were loaded up to 8 days in advance, though were removed within 1 hour of sample changeover. Sample changeover occurred at 10 am or 11 am each day, depending on LSO preferences. On a few occasions, filters were removed late, and these have been excluded from the analysis. The parts of the heads containing the filters were constructed of polyoxymethylene (POM), and the filter was held in place by Teflon rings and a rubber o-ring, with a wire mesh support screen. These heads were of an old design (the filter holder of the newer heads are made of metal with a POM filter cassette, as discussed in $PM_{2.5}$ Leckel below), however, both versions conform to EN12431. The instruments were equipped with 3 m^3 h^{-1} pumps. Samples were only deemed valid if the total volume collected was at least 49.7 m^3 (90 % data capture).

5.1.2 Problems Encountered with PM_{10} KFG

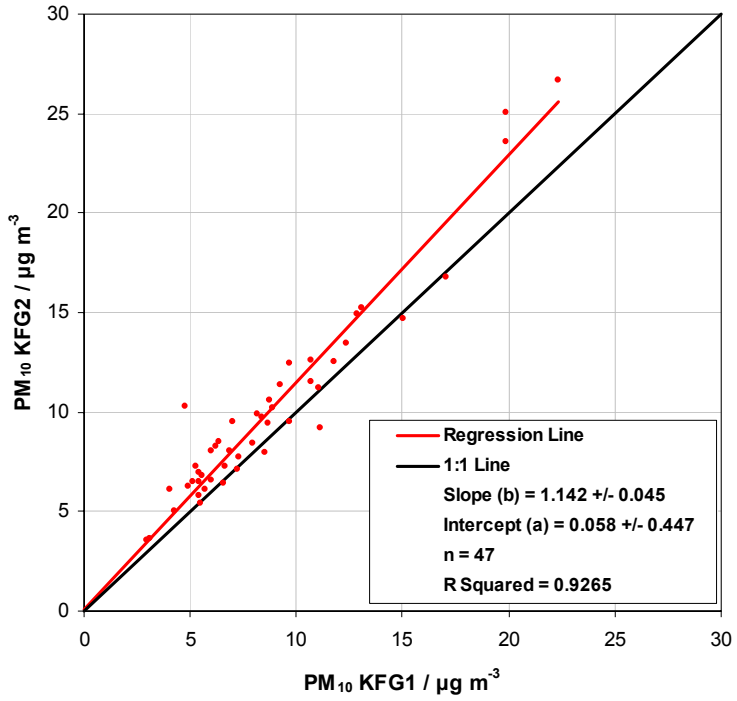
The main problem with the PM_{10} KFG was that the sampler would stop on occasions when there were high PM_{10} concentrations, coupled with high humidity. Further, a number of filters were severely damaged by the design of PM_{10} heads, which caused a significant reduction in the data capture rate. The following parts were sent to the instrument manufacturer (Sven Leckel GmbH, Berlin, Germany) for analysis: three of the thirty two heads; one of the four pumps; a selection of damaged filters; filters that had caused the instruments to stall, and some unsampled filters. It was shown that the filters would block the passage of air when they had a small amount of water on them, and the pressure drop would cause the instrument to turn the pumps off, even if new more powerful 6 m^3 h^{-1} pumps were used. When wet, the filters would be pressed hard against the Teflon rings lying under the filters due to the high pressure drop, causing the inner edges of the Teflon rings to cut the filters. Further, the filters that caused the instrument to stall showed the impressions of the lower Teflon rings at their backs. It was recommended that the filters should be inserted in the filter holders without the lower Teflon rings (but with the upper Teflon rings). In our opinion, the design of the reference inlet may have the effect of directing water droplets in the air, not just those smaller than 10 µm in size, onto the filter. This issue will be raised with the CEN Working Group.

The independent netcen audit at East Kilbride indicated that there was a leak of approximately 20 % in flow rate in one of the PM_{10} KFGs heads (referred to as KFG1). Subsequent tests by the LSO over the next eight days confirmed that the same fault was

detectable in all eight heads. This leak was present for the entire period of the East Kilbride Summer campaign, but was not during the East Kilbride Winter, or Birmingham Summer campaigns (where the instrument had previously been). As the leak occurred between the pump and the filter, the instrument believed it had the correct flow rate, yet the flow going through the head was actually 20 % lower. Theoretically, this would lead to 20 % reduction in sample mass, coupled with a slight increase in sample mass due to an increased cutpoint in the sample head. For the period where KFG1 was leaking; **Figure 5.1** shows the orthogonal regression of both KFG1 and the collocated sampler referred to as KFG2. The intercept is not statistically different from 0, using the criterion: $|a| > 2.u_a$. However, the slope is significantly different from 1, using the criterion: $|b-1| > 2.u_b$. On this basis, KFG1 was corrected using the slope of the following equation:

$$KFG1_{Corrected} = 1.142 \cdot KFG1 \qquad \textbf{E 5.1}$$

Figure 5.1: Chart showing the scatter of the collocated PM_{10} KFGs for East Kilbride in Summer.



This approach was considered to be the best method for including the East Kilbride Summer dataset. An alternative approach would have been to have used the KFG1 data only. However, there would then have been no obvious way to elucidate whether an individual PM_{10} KFG point was an outlier. Moreover, the equations used in the data analysis require duplicate measurements, or else the between-sampler uncertainty of the PM_{10} KFG becomes zero. As the concentrations observed at East Kilbride were very low, if an instrument failed on the expanded uncertainty criteria at this site alone, it was not considered sufficient for the candidate instrument to fail (see Section 4.3). However, it should also be noted that the corrected East Kilbride Summer PM_{10} KFG data are included in the 'All Data' dataset.

5.1.3 Discussion of Equivalence Criteria for PM_{10} KFG

The between-sampler uncertainty and number of points deleted by the Grubbs' test for each of the 13 datasets are summarised in **Table 5.1**. The PM_{10} KFG had a between-sampler uncertainty of 1.05 µg m^{-3}, which as it is less than 2 µg m^{-3}, means that the KFG is suitable for use as a reference method in these analyses. The percentage of samples greater than 50 % of the LV was not always above the 20 % criterion recommended in The Guidance (**Tables in Appendix D**). However, it is considered that the PM concentrations measured were generally representative of those found in the United Kingdom. PM concentrations in Scotland (such as at East Kilbride) are low, and there were periods of high ammonium nitrate concentrations at Teddington (based on data from London Marylebone Road, about 16 km away). The roadside PM concentrations measured at Bristol are typical of many roadside locations across the UK.

Table 5.1: Table showing the between-sampler performance data for the PM_{10} KFG reference method. n_{bs} (number of between-sampler data-pairs) is shaded green if it is greater than 40, orange if between 30 and 39, and red if less than 30. u_{bs} (between-sampler uncertainty) is shaded green if less than or equal to 2, and red if greater than 2. n_G is the number of data-pairs deleted by Grubbs' Test. n_{Gmax} (maximum number of data-pairs that could be deleted by Grubbs' Test) is shaded green if they are 3 or less, or red if greater than 3.

PM_{10} KFG	Dataset	n_{bs}	u_{bs} / µg m^{-3}	n_G	n_{Gmax}
Individual Campaigns	Birmingham Winter	59	1.45	2	2
	Birmingham Summer	59	1.24	0	0
	Teddington Winter	47	0.87	3	4
	Teddington Summer	62	1.15	2	2
	Bristol Summer	52	1.00	2	2
	Bristol Winter	51	0.62	1	1
	East Kilbride Summer	47	0.96	1	1
	East Kilbride Winter	47	0.65	2	2
All Campaigns	All Data	424	1.05	-	-
Annual Limit Value of 40 µg m^{-3}	< 20 µg m^{-3}	297	1.05	-	-
	> 20 µg m^{-3}	127	1.06	-	-
Daily Limit Value of 50 µg m^{-3}	< 25 µg m^{-3}	336	1.04	-	-
	> 25 µg m^{-3}	88	1.07	-	-

- Denotes Not Applicable.

5.2 $PM_{2.5}$ Leckel Reference Sampler

5.2.1 $PM_{2.5}$ Leckel Description and Set Up

The four $PM_{2.5}$ Leckel sampling heads used in this study were manufactured by Sven Leckel GmbH (Berlin, Germany) and were initially used in the Europe wide research study to formulate EN14907 [12]. The instruments employed in this study were the best available at the time of the project inception, however, they differ from those in EN14907 in that there is no sheath air shielded sampling inlet. The sheath air system was introduced to allow for the automated changing of filters. Sunlight shining on the filter holder may therefore be a problem, however, the Europe wide CEN study for formulating EN14907 [12] tested both the samplers used in the current study and the sheath air cooled version, with no observed difference in the results. EN14907 states: "The sampling system shall be made of an inert, non-corroding, electrically conducting material: preferably stainless steel or anodised aluminium or aluminium alloy". The units employed in this study were constructed of anodised aluminium (and as such conforms to EN14907) with a POM filter cassette. However, the instruments currently made by Sven Leckel GmbH are made from stainless steel as anodised aluminium has been shown to remove nitric acid, and so shift the equilibrium in the following reversible reaction and cause the loss of ammonium nitrate aerosols [13,14,15]:

$$NH_3(g) + HNO_3(g) \Leftrightarrow NH_4NO_3(s) \qquad \textbf{E 5.2}$$

Where:

NH_3 (g) = ammonia (gas phase).

HNO_3 (g) = nitric acid (gas phase).

NH_4NO_3 (s) = ammonium nitrate (aerosol phase).

The instruments had a flow rate of 2.3 m^3 hr^{-1} (approximately 38.3 l min^{-1}), and controlled and reported volumes to ambient conditions. Sample changeover occurred at 10 am or 11 am each day, depending on LSO preferences. The instruments were single head samplers (unlike the eight head PM_{10} KFG samplers), and the Emfab filters (Pall Corp., NY, USA; Type: EMFAB TX40HI20-WW; Part No.: 7221) were loaded immediately prior to sampling. Filters were removed within 1 hour of sample changeover. On a few occasions where the filters were removed late, these data have been excluded from the analysis. Samples were only deemed valid if the total volume collected was at least 49.7 m^3 (90 % data capture).

5.2.2 Problems Encountered with $PM_{2.5}$ Leckel

The $PM_{2.5}$ Leckel was found to be highly reliable, though as with the PM_{10} KFG, the sampler would stop on occasions where there were high $PM_{2.5}$ concentrations coupled with high humidity. A sample head; some filters that had caused the instrument to stop; and a pump were sent to Sven Leckel GmbH in addition to the PM_{10} KFG parts described in Section 5.1.2. As with the PM_{10} KFG, it was shown that the samplers stopped as the Emfab filter media was

blocking the passage of air when wet. In our opinion, the design of the reference inlet may have the effect of directing water droplets in the air, not just those smaller than 2.5 µm in size, onto the filter. This issue will be raised with the CEN Working Group.

5.2.3 Discussion of Equivalence Criteria for $PM_{2.5}$ Leckel

The between-sampler uncertainty and the number of points deleted by Grubbs' test for each of the 11 datasets are summarised in **Table 5.2**. More paired data were identified as outliers for the $PM_{2.5}$ Leckel than were identified for the PM_{10} KFG, Partisol 2025 and SM200 Mass (**Appendix B.2**). This is because the $PM_{2.5}$ Leckel was the most consistent of the filter mass based measurements, and so marginal outliers due to 'operator' error were more easily identifiable than for other instruments where the general scatter of the instrument is of a similar magnitude to the 'operator error'. The $PM_{2.5}$ Leckel was shown to have a between-sampler uncertainty of 0.53 µg m^{-3}, which is less than the 2 µg m^{-3} criterion and means that the Leckel is suitable for use as a reference method in these analyses. The percentage of samples greater than 50 % of the LV was greater than the 20 % criterion recommended in The Guidance in all but the East Kilbride Summer dataset (**Figure D.8**).

Table 5.2: Table showing the between-sampler performance data for the $PM_{2.5}$ Leckel reference method. n_{bs} (number of between-sampler data-pairs) is shaded green if it is greater than 40, orange if between 30 and 39, and red if less than 30. u_{bs} (between-sampler uncertainty) is shaded green if less than or equal to 2, and red if greater than 2. n_G is the number of data-pairs deleted by Grubbs' Test. n_{Gmax} (maximum number of data-pairs that could be deleted by Grubbs' Test) is shaded green if they are 3 or less, or red if greater than 3.

$PM_{2.5}$ Leckel	Dataset	n_{bs}	u_{bs} / µg m^{-3}	n_G	n_{Gmax}
Individual Campaigns	Birmingham Winter	66	0.50	3	5
	Birmingham Summer	49	0.34	1	1
	Teddington Winter	63	0.76	3	4
	Teddington Summer	52	0.51	1	1
	Bristol Summer	52	0.59	3	3
	Bristol Winter	53	0.64	2	2
	East Kilbride Summer	57	0.27	3	3
	East Kilbride Winter	46	0.30	3	3
All Campaigns	All Data	438	0.53	-	-
Annual Limit Value of 25 µg m^{-3}	< 12.5 µg m^{-3}	267	0.42	-	-
	> 12.5 µg m^{-3}	161	0.68	-	-

- Denotes Not Applicable.

5.3 Partisol 2025

5.3.1 Partisol 2025 Description and Set Up

The Partisol 2025 (Thermo Electron Corporation, East Greenbush, NY, USA) is an automated sampler capable of collecting up to sixteen consecutive 24 hour PM_{10} filter samples. The specific operating procedures employed in this study are listed below. The operation of the Partisol 2025 in configurations different from those employed in this study may constitute a different method, and it cannot be assumed that the conclusions are transferred. The Partisol 2025 should not be confused with the Partisol 2025-D dichotomous sampler, which was not tested in this study.

- An R&P PM_{10} inlet with rain bottle (R&P Part Number: 00506-0000) was used.
- The flowrate was 16.67 +/1 0.01 l min^{-1}, and this corresponds to 24 m^3 for a 24 hour sample. The flow rate was maintained volumetrically and reported to ambient conditions.
- Emfab filters were used (Pall Corp., NY, USA; Type: EMFAB TX40HI20-WW; Part No.: 7221).
- The filter cassettes were constructed of polycarbonate with stainless steel filter screens.
- Up to sixteen filters were loaded at once, and these were removed every one to two weeks in accordance with current operating procedures in the UK National Network.
- Daily data records were recorded in the instrument data buffer, and these were retrieved using onsite telemetry. Samples were only deemed valid if the total volume collected was at least 21.6 m^3 (90 % data capture).

5.3.2 Problems Encountered with the Partisol 2025

The Partisol 2025 was found to be highly reliable, and the only problem encountered was that the filter cassettes jammed on one occasion. Unlike the PM_{10} KFG and $PM_{2.5}$ Leckel, the filters did not become overloaded, probably on account of the significantly lower sample volumes employed. However, from our experience with using Teflon filters in the Partisol 2025 in the National Network, should the filters become overloaded then the instrument will shut down and will not restart again without manual intervention. The instrument distributor (Air Monitors UK) has reported experience of Emfab filters becoming overloaded for 24 hour samples in the Partisol 2025. Changing the sample pump diaphragm every six months (and more frequently in high ozone conditions) was shown to limit this issue.

5.3.3 Discussion of Equivalence Criteria for the Partisol 2025

The performance of the Partisol 2025 is summarised in **Figure D.1**. The equivalence procedure as set out in Section 4.3 is as follows:

1. The 24-hour between-sampler uncertainty (1.21 µg m^{-3}) was less than the 3 µg m^{-3} criterion, and as such the Partisol 2025 is suitable for consideration as a candidate method in these analyses.

2. The slopes of all the individual and combined datasets are both greater and less than 1 (range: 0.943 to 1.131), and the intercepts are both greater and less than zero (range: -1.883 to +1.667). As such, the expanded uncertainty can be calculated without the need for any correction for slope or intercept.

3. The expanded uncertainty (W_{CM}) was less than 25 % for all individual and combined datasets at both the daily and annual mean LVs. As such, the Partisol 2025 is deemed to **meet the criteria for equivalence** employed in this study. There were a similar number of daily LV exceedences for the PM_{10} KFG and Partisol 2025.

5.4 TEOM

5.4.1 TEOM Description and Set Up

The UK network is largely founded on the TEOM (Thermo Electron Corporation, East Greenbush, NY, USA). The TEOM draws sample flow through a 12 mm Emfab filter mounted upon an oscillating quartz tube. The change in frequency of this oscillation is proportional to the change in mass of the filter and particles collected thereon. In order to remove water, the atmosphere around the oscillating filter is held at 50 ºC. This causes the loss of some semi-volatile species such as ammonium nitrate and low temperature organic carbon (OC) aerosols. The TEOM therefore tends to under-read in comparison to the reference sampler. In addition to inbuilt slope and intercept correction factors of 1.03 and 3 µg m^{-3} respectively, the UK has adopted a policy of multiplying all TEOM concentrations by 1.3 [10]. A comparison between the TEOM and KFG was previously done at six sites around the UK (Thurrock, Port Talbot, London Marylebone Road, Harwell, Glasgow Centre and Belfast Centre), and after applying a factor of 1.3, the corrected TEOM dataset was shown to still underestimate KFG concentrations at locations with a highly volatile PM fraction (e.g. Harwell) [16]. The methods employed in data analysis were different to those employed herein and just one reference and one candidate instrument were operated in each location.

The specific operating procedures employed in this study are listed below. The operation of the TEOM in configurations different from those employed in this study may constitute a different method, and it cannot be assumed that the conclusions are transferred.

- An R&P PM_{10} inlet with rain bottle (R&P Part Number: 00506-0000) was used.
- The flowrate was 16.67 ± 0.01 l min^{-1}, and this corresponds to 24 m^3 for a 24 hour sample. The flow rate was maintained volumetrically and reported to ambient conditions.
- Hourly concentration records were recorded in the instrument data buffer, and these were retrieved using onsite or remote telemetry. 24-Hour averages were only valid if there was at least 90 % data capture (i.e. 22 valid 1-hour measurements).
- The flow rate was iso-kinetically split with 3 ± 0.01 l min^{-1} going to the oscillating filter and 13.7 ± 0.01 l min^{-1} being bypassed to the sample pump.
- The air temperature, filter temperature and cap temperature were all maintained at 50 ± 0.01 °C, and there was no Nafion Drier (as is used in the TEOM SES (Sample Equilibration System)).

The TEOM data are herein considered under four scenarios:

i. With no correction factors: **TEOM (0,1,1);**
ii. With inbuilt intercept correction of 3 µg m^{-3} and slope correction of 1.03: **TEOM (3,1.03,1);**
iii. With inbuilt intercept correction of 3 µg m^{-3} and slope correction of 1.03, and a further slope correction factor of 1.3: **TEOM (3,1.03,1.3)**;

iv. With inbuilt intercept correction of 3 µg m^{-3} and slope correction of 1.03 and a further slope correction factor obtained by systematically multiplying by a factor between 1 and 3 in 0.01 increments: **TEOM (3,1.03,x)**.

It is the purpose of this document to define correction factors for TEOM (0,1,1), TEOM (3,1.03,1) and TEOM (3,1.03,x). TEOM (3,1.03,1.3) is only considered in the context of whether the current correction factors employed by the UK could lead to equivalence.

5.4.2 Problems Encountered with the TEOM

The TEOM was highly reliable, and the only problems were related to the occasional incorrect seating of the 12 mm oscillating filter by the LSO. Should the power or air conditioning in the trailer fail, and the instruments reset, then it was evident from looking at the comparison of both instruments that it can take up to 12 hours for the instruments to stabilise, whereas if the instruments were not collocated, the data would otherwise look OK. As such, we recommend that 12 hours should be routinely deleted for the TEOM subsequent to a power or air conditioning failure.

5.4.3 Discussion of Equivalence Criteria for TEOM (0,1,1)

The performance of the TEOM (0,1,1) is summarised in **Figure D.2**. The equivalence procedure as set out in Section 4.3 is as follows:

1. The 24-hour between-sampler uncertainty (0.52 µg m^{-3}) was less than the 3 µg m^{-3} criterion, and as such, the TEOM (0,1,1) is suitable for consideration as a candidate method in these analyses.

2. The intercepts of all individual and combined datasets are both greater and less than zero (range: -0.748 to +5.306). However, the slopes of the 13 datasets are all less than 1 (range: 0.391 to 0.826). As such, the datasets should be corrected before the expanded uncertainty can be considered.

3. Not applicable.

4. The slope and intercept of the 'All Data' dataset are both statistically significant, and were used to generate a correction factor and term using equation **E 5.3** below:

$$TEOM\,(0,1,1)_{Corrected} = \frac{(TEOM\,(0,1,1) - 2.961)}{0.535} \qquad \textbf{E 5.3}$$

5. The performance of the TEOM $(0,1,1)_{Corrected}$ is summarised in **Figure D.3**. The expanded uncertainty (W_{CM}) was greater than 25 % for most of the datasets. As such, the TEOM (0,1,1) is deemed to **not meet the criteria for equivalence** employed in this study.

5.4.4 Discussion of Equivalence Criteria for TEOM (3,1.03,1)

The performance of the TEOM (3,1.03,1) is summarised in **Figure D.4**. The equivalence procedure as set out in Section 4.3 is as follows:

1. The 24-hour between-sampler uncertainty (0.53 µg m^{-3}) was less than the 3 µg m^{-3} criterion, and as such, the TEOM (3,1.03,1) is suitable for consideration as a candidate method in these analyses.

2. The intercepts of the individual and combined datasets were all greater than zero (range: +2.250 to +10.791), and the slopes were are all less than 1 (range: 0.404 to 0.856). As such, the datasets should be corrected before the expanded uncertainty can be considered.

3. Not applicable.

4. The slope and intercept of the 'All Data' dataset are both statistically significant, and were used to generate a correction factor and term using equation **E 5.4** below:

$$TEOM\,(3,1.03,1)_{Corrected} = \frac{\left(TEOM\,(3,1.03,1) - 6.113\right)}{0.553} \qquad \textbf{E 5.4}$$

5. The performance of the TEOM $(3,1.03,1)_{Corrected}$ is summarised in **Figure D.5**. The expanded uncertainty (W_{CM}) was greater than 25 % for most of the datasets. As such, the TEOM (0,1,1) is deemed to **not meet the criteria for equivalence** employed in this study.

5.4.5 Discussion of Equivalence Criteria for TEOM (3,1.03,1.3)

The performance of the TEOM (3,1.03,1.3) is summarised in **Figure D.6**. As TEOM (3,1.03,1.3) has already been corrected for slope and intercept, further correction factors cannot be applied. The expanded uncertainty (W_{CM}) was greater than 25 % for most of the datasets. As such, the TEOM (3,1.03,1.3) is deemed to **not meet the criteria for equivalence** employed in this study. The slopes of the Bristol datasets were closer to unity than those of the Teddington datasets, which may be indicative of the higher volatile fraction at Teddington.

5.4.6 Discussion of Equivalence Criteria for TEOM (3,1.03,x)

Systematically changing the "correction factor" to values between 1 and 3 (as per TEOM (3,1.03,x)) indicated that there was no factor that could be applied that would generate an expanded uncertainty of less than 25% across all datasets. As such, the TEOM (3,1.03,x) is deemed to **not meet the criteria for equivalence** employed in this study.

5.5 FDMS

5.5.1 FDMS Description and Set Up

The FDMS (Thermo Electron Corporation, East Greenbush, NY, USA) was developed as an improvement to the TEOM in order to correct for the loss of semi-volatile particles. The system operates at 30 ºC rather than 50 ºC to reduce particle losses. In addition, the inlet air is dried to a relative humidity of 15 to 20 % using Nafion driers. These work by passing the ambient air through a small tube that is made of a permeable membrane called Nafion. Dry air is passed around the outside of the thin tube which draws water from the sample air through the membrane. Larger particles may sometimes be obstructed by this thin tube. The instrument alternates between sampling ambient aerosols, and sampling aerosol-free air *via* a peltier-cooled 47 mm Emfab bypass filter. The mass of the 12 mm oscillating filter is monitored while sampling both particle laden and particle free air, and three parameters are output: Mass Concentration (*i.e.* total aerosol mass); Base concentration (*i.e.* non-volatile mass fraction) and Reference Concentration (*i.e.* volatile mass fraction). All parameters were recorded, however, only the Mass Concentration output is considered in this Section. The specific operating procedures employed in this study are listed below. The operation of the FDMS in configurations different from those employed in this study may constitute a different method, and it cannot be assumed that the conclusions are transferred. Unlike the TEOM (which can be logged with data loggers), the FDMS has to be contacted by remote or onsite telemetry to query the data buffer, as the analogue output is a 1-hour rolling average.

- The bypass filter was Emfab and maintained at 4 ± 0.1ºC
- The air temperature, filter temperature and cap temperature were maintained at 30 ºC.
- The instrument alternated between 6 minutes sample and 6 minutes baseline.
- The piping inside the trailer between the inlet and the Nafion drier was lagged to keep the air inside this section of tube as close to ambient as possible.
- An R&P PM_{10} inlet with rain bottle (R&P Part Number: 00506-0000) was used. The $PM_{2.5}$ unit additionally had a $PM_{2.5}$ sharp cut cyclone (R&P Part Number: 57-005896). This was the only difference between the PM_{10} and $PM_{2.5}$ FDMS.
- The flowrate was 16.67 ± 0.01 l min^{-1}, and this corresponds to 24 m^3 for a 24 hour sample. The flow rate was maintained volumetrically and reported to ambient conditions.
- Hourly concentration records were recorded in the instrument data buffer, and these were retrieved using onsite or remote telemetry. 24-Hour averages were only valid if there was at least 90 % data capture (i.e. 22 valid 1-hour measurements).
- The flow rate was iso-kinetically split with 3 ± 0.01 l min^{-1} going to the oscillating filter and 13.7 ± 0.01 l min^{-1} being bypassed to the sample pump *via* the outside of the Nafion drier.

5.5.2 Problems Encountered with the FDMS

The FDMS was found to be very sensitive to the temperature of the enclosure as the efficiency of the Nafion drier drops considerably above 22 ºC. Conversely, if it is too cold water droplets will begin to form in the sample stream and so will not be removed by the Nafion drier. In-line with manufacturer's recommendations, the trailers were maintained at 20 to 25 ºC as the Nafion drier was indirectly maintained at roughly 2 ºC lower, through the chilling of the 4 ºC filter. The recommended trailer temperature was later lowered to 18 to 22 ºC by the instrument manufacturer. If the dew point of the air after the Nafion drier is greater than 2 ºC, then a '128' error code is reported. This occurred on many occasions with the instruments in Birmingham and East Kilbride, but not at all with the instruments that were in Teddington and Bristol. This was attributed to possible differences between the air conditioning systems of the two trailers. When a '128' error code was observed, these data were deleted, as it was indicative that water could be collecting on both the oscillating 12 mm and 4 ºC 47 mm Emfab filters. Later tests at the instrument distributor's facility (Air Monitors UK) showed that two hours of data should be deleted after the '128' error code, as the rate of loss of water from the 47 mm filter was too fast to be corrected for by the 6 minute switching cycle.

At East Kilbride (where ambient PM concentrations were typically very low), the FDMS was consistently shown to read negative concentrations, and this was confirmed by the negative intercepts in the regression of the FDMS against the PM_{10} KFG and $PM_{2.5}$ Leckel (**Figures D.7 and D.8**). Baseline tests were performed by placing a filter with 98 % efficiency at 0.02 µm (Balston, Haverhill, MA, USA) on the four FDMSs at the East Kilbride site, and were repeated at the instrument distributor's facility (Air Monitors UK). It was shown that one of the PM_{10} instruments had a baseline of +3 µg m^{-3}, which was traced to contamination in the system. This has not been corrected in the data, as it was not possible to distinguish the magnitude of this offset over the fifteen months that the instrument was in operation. The other three FDMS instruments were shown to have baselines as low as -3 µg m^{-3}, but these baselines were shown to return to zero µg m^{-3} when both the 12 and 47 mm Emfab filters were replaced. There are two possibilities for this negative offset:

1. There was contamination in the bypass filter sample train that is carried through to the oscillating filter in the bypass mode;
2. Ammonium nitrate, low temperature organic carbon aerosols, and water (particularly if there has been a '128' error code) slowly evaporate off the 4 ºC filter and are deposited on the 12 mm oscillating filter. This effect is amplified when there are significant particle deposits on the oscillating filter that enable the uptake of the volatile species released by the 4 ºC filter.

The Teddington/Bristol instruments were not tested. No corrections were applied to the data as it was not possible to distinguish the relative magnitude of the problem over the entire fifteen months that the instruments were operated.

Should the power or air conditioning in the trailer fail, and the instruments reset, then it was evident from looking at the comparison of both instruments that it took up to 12 hours for the instruments Base Concentration and Reference Concentration to stabilise. However, the Mass Concentration (*i.e.* Total Mass) stabilised after about 3 hours, and as such, we recommend that 3 hours should be routinely deleted for the FDMS subsequent to a power or air conditioning failure.

5.5.3 Discussion of Equivalence Criteria for PM_{10} FDMS

The performance of the PM_{10} FDMS is summarised in **Figure D.7**. The equivalence procedure as set out in Section 4.3 is as follows:

1. The 24-hour between-sampler uncertainty (1.12 µg m^{-3}) was less than the 3 µg m^{-3} criterion, and as such, the PM_{10} FDMS is suitable for consideration as a candidate method in these analyses.

2. The slopes of the individual and combined datasets are both greater and less than 1 (range: 0.905 to 1.111), and the intercepts are both greater and less than zero (range: -3.558 to +1.872). As such, the expanded uncertainty can be calculated without the need for any correction for slope or intercept.

3. The expanded uncertainty (W_{CM}) was less than 25 % for all individual and combined datasets at both the daily and annual LVs. As such, the PM_{10} FDMS is deemed to **meet the criteria for equivalence employed in this study**. There were a similar number of daily LV exceedences for the PM_{10} KFG and PM_{10} FDMS.

5.5.4 Discussion of Equivalence Criteria for $PM_{2.5}$ FDMS

The performance of the $PM_{2.5}$ FDMS is summarised in **Figure D.8**. It is important to note that the axes extend from -10 to +70 µg m^{-3}, as the 24-hour average concentrations were occasionally negative at East Kilbride. The equivalence procedure as set out in Section 4.3 is as follows:

1. The 24-hour between-sampler uncertainty (0.96 µg m^{-3}) was less than the 3 µg m^{-3} criterion, and as such, the $PM_{2.5}$ FDMS is suitable for consideration as a candidate method in these analyses.

2. The slopes of the individual and combined datasets are both greater and less than 1 (range: 0.903 to 1.268), and the intercepts are both greater and less than zero (range: -4.181 to +0.819). As such, the expanded uncertainty can be calculated without the need for any correction for slope or intercept.

3. The expanded uncertainty (W_{CM}) was less than 25 % for all but the following three datasets:
    i. The less than 50% LV (12.5 µg m^{-3}) dataset;
    ii. East Kilbride Winter (calculated W_{CM} of 33.1%);
    iii. Birmingham Winter (calculated W_{CM} of 28.6%).

    As discussed in Section 4.3, the failure of the instrument to meet the W_{CM} criteria for the <50% LV dataset, or the individual datasets for East Kilbride, is not considered suitable justification for rejection. In Section 4.2 it was discussed that "It is important to note that for lower LVs, a non-zero intercept becomes statistically more significant to the calculation of W_{CM}" In the case of the Birmingham Winter dataset, it was found that calculating W_{CM} for higher values of the LV resulted in the criterion being met for all eight field campaign datasets. For example, using the Daily $PM_{2.5}$ LV of 35 µg m^{-3} assumed by CEN [6] reduces the expanded uncertainty of the Birmingham Winter dataset to 18.7 %. Correcting the data for either slope or intercept results in an increase in the number of exceedences at the 25 µg m^{-3} LV, though correcting for both slope and intercept together shows an improvement. Given the marginal exceedence of the criterion for the Birmingham Winter dataset, and that the $PM_{2.5}$ LV is not yet finalised, the $PM_{2.5}$ FDMS was deemed to **meet the criteria for equivalence employed in this study**.

The $PM_{2.5}$ FDMS has been tested against the United States Federal Reference Method (FRM) that uses stretched Teflon membrane filters [17,18]. These studies have generally shown agreement in the wintertime, but an overestimation of $PM_{2.5}$ by the FDMS in the summertime. This discrepancy has been attributed to the Teflon membrane filters losing ammonium nitrate in the warm summer months. A similar effect was observed with Teflon filters in a PM_{10} Partisol 2025 at sites in London [19], and is also known to effect quartz filters [20]. This seasonal effect was not observed with Emfab filters in the current study.

5.6 SM200

5.6.1 SM200 Description and Set Up

The SM200 (Opsis AB, Furulund, Sweden) measures the attenuation of beta radiation through an unsampled filter, and then takes a 24-hour sample before again measuring the beta attenuation. This measurement provides a concentration herein referred to as 'SM200 Beta'. Further, the filters are weighed before and after sampling (**Appendix A**), and this is used along with the sample volume to calculate a second concentration measurement herein referred to as 'SM200 Mass'. The instruments used in this study were manufactured in Sweden and are a modification of an earlier instrument manufactured in Italy (also known as the SM200). The specific operating procedures employed in this study are listed below. The operation of the SM200 in configurations different from those employed in this study may constitute a different method, and it cannot be assumed that the conclusions are transferred.

- The instrument was operated with 2 micron stretched Teflon membrane filters with PMP (polymethylpentene) support ring (Pall Corp., NY, USA; Type: 2 µm Teflo; Part No.: R2PJ047). These were used at the manufacturer's request (although other media can be used) as these provide the least resistance to the beta radiation, and hence the lowest detection limit. This filter media is the one most commonly used in the United States Federal Reference Method (FRM).
- Prior to the first Beta measurement, the filters were conditioned at 38 ºC for 90 minutes with no air flowing through the filters.
- The PM_{10} heads are manufactured by Opsis and based on a design developed by Sven Leckel GmbH to give a PM_{10} cut at 16.7 l min^{-1}.
- Both the pre and post beta measurements use a 9.9 MBq (Mega Bequerel) C_{14} source, and the measurement is averaged over 120 minutes.
- The flowrate was 16.67 l min^{-1} ± 0.1 % and this corresponds to 23.97 m^3 for a 23 hour 58 minute sample (with approximately 2 minutes required to change the filters). The sampling chamber was maintained at ambient temperature, pressure and humidity, *via* a sheath air shielded sample inlet. The volume is reported to ambient conditions.
- Filter cassettes were constructed of POM.
- Prior to the second Beta measurement, the filters were again conditioned at 38 ºC for 90 minutes with no air flowing through the filters. At this temperature, water and highly volatile organic species will be lost. However, ammonium nitrate is known to be stable on filters at temperatures greater than 50 ºC if there is no airflow through them [11,21].
- Daily data records were recorded in the instrument data buffer, and these were retrieved using onsite telemetry. Samples were only valid if there was at least 90 % Sample Volume.

5.6.2 Problems Encountered with the SM200

Initially the instruments were provided with a different type of stretched Teflon filter media to that described in Section 5.6.1 that was of inconsistent thickness (Millipore, Billerica, MA, USA). This was shown to give inconsistent particle collection and so effect the beta measurements. As such, there are no data available for the Opsis SM200 for the Birmingham Winter and Teddington Winter Field Campaigns.

The Teflon membrane of the Pall Teflon filter media was typically only 46 µm thick and so was easily prone to damage. Filters with holes in them (either received from the manufacturers damaged or damaged during pre weighing) were not used in the samplers. Unlike Emfab filters, the mass of sampled 'Teflo' filters was generally unaffected by damage.

It was difficult to ascertain which filter was sampled on a specific day for the following reasons. This does not the beta measurement, as the identity of the filter is not required for this calculation:

- There was no facility to input filter numbers in to the instrument.
- As it was used for post sampling beta measurements, the instrument would eject the filter from the previous day's sample around four hours after the sample had ended.
- The filter cassettes contain no unique identifying code.
- It was only possible to write the filter number on the underside of the filter support ring, and this was obscured by the filter cassette.

Even by physically checking which filter was ejected from the instrument on a daily basis, it was not immediately obvious which filter was sampled on which day. Samples were identified by lining up the filter mass with the SM200 Beta and PM_{10} KFG concentrations, which introduces an opportunity for human error. Filters are now available with embedded microdots that can be used for automated filter recognition (MTL, Minneapolis, USA); however, if these filters were to be used in the SM200, the microdots should not be in the section of the filter used for Beta analysis.

5.6.3 Discussion of Equivalence Criteria for SM200 Beta

The performance of the SM200 Beta is summarised in **Figure D.9**. Although two field campaign datasets are missing, there are still six datasets, which are greater than the minimum of four needed to determine equivalence. The equivalence procedure as set out in Section 4.3 is as follows:

1. The 24-hour between-sampler uncertainty (2.14 µg m^{-3}) was less than the 3 µg m^{-3} criterion, and as such, the SM200 Beta is suitable for consideration as a candidate method in these analyses.

2. The slopes of the individual and combined datasets are both greater and less than 1

(range: 0.944 to 1.189), and the intercepts are both greater and less than zero (range: -0.542 to +3.962). As such, the expanded uncertainty can be calculated without the need for any correction for slope or intercept

3. The expanded uncertainty was less than 25 % for all but the following four dataset-LV permutations:
   i. The less than 50% daily mean LV (25 µg m^{-3}) at the daily LV;
   ii. The less than 50% annual mean LV (20 µg m^{-3}) dataset at the annual LV;
   iii. East Kilbride Summer at both the daily and annual LV.

   As discussed in Section 4.3, the failure of the instrument to meet the W_{CM} criteria for the <50% LV dataset, or the individual datasets for East Kilbride, is not considered suitable justification for rejection. As such, the SM200 Beta was deemed to **meet the criteria for equivalence employed in this study**. There were a slightly greater number of daily LV exceedences for the SM200 Beta than for the PM_{10} KFG.

5.6.4 Discussion of Equivalence Criteria for SM200 Mass

The performance of the SM200 Mass is summarised in **Figure D.10**. Although two field campaign datasets are missing, there are still six datasets, which are greater than the minimum of four needed to determine equivalence. The equivalence procedure as set out in Section 4.3 is as follows:

1. The 24-hour between-sampler uncertainty (1.41 µg m^{-3}) was less than the 3 µg m^{-3} criterion, and as such, the SM200 Mass is suitable for consideration as a candidate method in these analyses.

2. The intercepts of the individual and combined datasets are both greater and less than zero (range: -2.151 to +3.295). However, the slopes of the individual and combined datasets are all less than 1 (range: 0.791 to 0.910), and so the datasets should be corrected before the expanded uncertainty can be considered.

3. Not applicable.

4. The slope and intercept of the 'All Data' dataset are both statistically significant, and were used to generate a correction factor and term using equation **E 5.5** below:

$$SM200Mass_{Corrected} = \frac{(SM200Mass - 1.286)}{0.819} \qquad \textbf{E 5.5}$$

5. The performance of the SM200 $Mass_{Corrected}$ is summarised in **Figure D.11**. The expanded uncertainty (W_{CM}) was less than 25 % for all but the less than 50% Daily LV (25 µg m^{-3}) dataset at the LV. As discussed in Section 4.3, the failure of the instrument to meet the W_{CM} criteria for the <50% LV dataset, is not considered suitable justification for rejection. As such, the SM200 Mass is deemed to **meet the criteria for equivalence employed in this study after application of slope and intercept correction factors**. There were a slightly greater number of daily LV exceedences for the SM200 Mass Corrected than for the PM_{10} KFG.

5.6.5 Comparison of SM200 Beta and SM200 Mass

The comparison of the SM200 Mass and SM200 Beta candidate methods is shown in **Figure D.12**. SM200 Beta consistently reads significantly greater than SM200 Mass. The reason for this is not clear, however, previous studies have only looked at the Beta measurement, with similar correlations to the PM_{10} KFG as those found herein [22,23].

5.7 BAM

5.7.1 BAM Description and Set Up

The BAM (Met-One, Grants Pass, Oregon, USA) measures the beta attenuation of a section of moveable filter tape before and after sampling. Some local authorities in the UK use the BAM. The tape area is automatically changed hourly, and the instrument operates at room temperature to minimise losses of semi-volatiles; however, water can cause the instrument to overestimate PM concentrations [24,25]. The BAM is not fitted with an ambient temperature and pressure monitor, and so only samples and reports to US standard conditions of 1013 hPa and 25 °C. The specific operating procedures employed in this study are listed below. The operation of the BAM in configurations different from those employed in this study may constitute a different method, and it cannot be assumed that the conclusions are transferred.

- A PM_{10} inlet was used with ridges to prevent rain getting through to the impaction surface [26] (Met-One Part No. BX8-802)
- The instrument had a flow rate of 16.67 l min^{-1} both controlled (by an adjustable critical orifice) and reported to 25 °C and 1013 hPa.
- The filter material was provided directly by Met-One who source from several different manufacturers to the following specifications: Borosilicate micro fibre glass, acrylic resin binder nominal 0.2 µm glass fibre construction. Collection efficiency 99.9 % for 0.3 µm particles.
- Sample Time: 50 minutes with 2 minutes shuttling time. Beta measurements occurred for 4 minutes at the beginning and end of every sample. C_{14} Beta source. Max beta energy 156 kV; 50 to 60 kV mean. Travel distance in air: 20 to 30 cm.
- The baselines were tested every 1 to 2 months by running for 24 hours with a 0.2 µm ULTIPOR N66 filter (Pall Corp., NY, USA; Part No. 4001 NAEY) on the sample tube in place of the PM_{10} inlet. The offset was calculated and inputted in to the instrument to be automatically subtracted. Occasionally the offset was calculated incorrectly and the data were corrected manually.
- Hourly concentration records were recorded in the instrument data buffer, and these were retrieved using onsite or remote telemetry. 24-Hour averages were only valid if there was at least 90 % data capture (i.e. 22 valid 1-hour measurements).

In addition to equivalence criteria being applied to the BAM, the BAM was corrected to ambient conditions and is herein referred to as $BAM_{Ambient}$. Ambient temperatures and pressures were calculated as the average of those measurements reported by the other instruments on-site, and the following equation was used to correct the hourly data:

$$BAM_{Ambient} = BAM \cdot \left(\frac{P_{Ambient}}{1} \right) \cdot \left(\frac{298}{T_{Ambient} + 273.15} \right) \qquad \textbf{E 5.6}$$

Where:

$P_{Ambient}$ = Ambient Pressure in Atmospheres.

$T_{Ambient}$ = Ambient Temperature in ºC.

5.7.2 Problems Encountered with the BAM

The BAM was generally found to be highly reliable; however, occasionally an instrument would fail a leak of flow check. This was usually attributed to glass fibre being stuck on the tape holding nozzle. However on one occasion, there was a broken o-ring in the head. As a result of this, the frequency of leak and flow checks was increased. Data were not deleted if there was shown to have been a leak, as it was not known when the leak occurred and deleting all possibly effected data would have resulted in very low data capture.

5.7.3 Discussion of Equivalence Criteria for the BAM

The performance of the BAM is summarised in **Figure D.13**. The equivalence procedure as set out in Section 4.3 is as follows:

1. The 24-hour between-sampler uncertainty (2.06 µg m^{-3}) was less than the 3 µg m^{-3} criterion, and as such, the BAM is suitable for consideration as a candidate method in these analyses. However, there was significant noise in the hourly data (with a between-sampler uncertainty of 3.84 µg m^{-3}), and as such, these data should be treated with caution.

2. The intercepts of the individual and combined datasets are both greater and less than zero (range: -3.173 to +3.724). However, the slopes of the individual and combined datasets are all greater than 1 (range: 1.080 to 1.497) and so the datasets should be corrected before the expanded uncertainty can be considered.

3. Not applicable.

4. The slope of the 'All Data' dataset was statistically significant, whereas the intercept was not. As such, the 'All Data' slope was used to correct the BAM using equation **E 5.7** below:

$$BAM_{Corrected} = \frac{BAM}{1.211} \qquad \textbf{E 5.7}$$

5. The performance of the $BAM_{Corrected}$ is summarised in **Figure D.14**. The expanded uncertainty was less than 25 % for all but the following three dataset-LV permutations:
    i. The less than 50% daily LV (25 µg m^{-3}) dataset at the daily LV;
    ii. The less than 50% annual LV (20 µg m^{-3}) dataset at the annual LV;
    iii. East Kilbride Winter at both the daily and annual LV.

    As discussed in Section 4.3, the failure of the instrument to meet the W_{CM} criteria for the <50% LV dataset, or the individual datasets for East Kilbride, is not considered suitable justification for rejection. As such, the BAM is deemed to **meet the criteria for equivalence employed in this study after application of a slope correction factor**. There were a similar number of daily LV exceedences for the BAM as for the PM_{10} KFG.

These findings are consistent with a four-month study carried out in London Marylebone Road in 1998 by KCL-ERG (Kings College London - Environmental Research Group). A BAM was operated alongside a Partisol gravimetric sampler using Teflon filters, and a 19 % higher concentration was observed with the BAM [27,28].

5.7.4 Discussion of Equivalence Criteria for $BAM_{Ambient}$

The performance of $BAM_{Ambient}$ is summarised in **Figure D.15**. The equivalence procedure as set out in Section 4.3 is as follows:

1. The 24-hour between-sampler uncertainty (2.15 µg m^{-3}) was less than the 3 µg m^{-3} criterion, and as such, the $BAM_{Ambient}$ is suitable for consideration as a candidate method in these analyses. However, there was significant noise in the hourly data (with a between-sampler uncertainty of 4.01 µg m^{-3}), and as such, these data should be treated with caution.

2. The intercepts of the individual and combined datasets are both greater and less than zero (range: -3.378 to +3.984). However, the slopes of the individual and combined datasets are all greater than 1 (range: 1.116 to 1.560) and so the datasets should be corrected before the expanded uncertainty can be considered.

3. Not applicable.

4. The slope of the 'All Data' dataset was statistically significant, whereas the intercept was not. As such, the 'All Data' slope was used to correct the BAM using equation **E 5.8** below:

$$BAM_{Ambient\ Corrected} = \frac{BAM_{Ambient}}{1.273} \qquad \textbf{E 5.8}$$

5. The performance of the $BAM_{Corrected}$ is summarised in **Figure D.14**. The expanded uncertainty was less than 25 % for all but the following two dataset-LV permutations:
   i. The less than 50% annual LV (20 µg m^{-3}) dataset at the annual LV;
   ii. East Kilbride Winter at the annual LV only.

   As discussed in Section 4.3, the failure of the instrument to meet the W_{CM} criteria for the <50% LV dataset, or the individual datasets for East Kilbride, is not considered suitable justification for rejection. As such, the $BAM_{Ambient}$ is deemed to **meet the criteria for equivalence employed in this study after application of a slope correction factor**. $BAM_{Ambient\ Corrected}$ was judged to better comply with the equivalence criteria than $BAM_{Corrected}$, and as such every effort should be made to correct the BAM to ambient conditions if the meteorological data are available to do so. There were a similar number of daily LV exceedences for the BAM as for the PM_{10} KFG.

5.8 Smart BAM

5.8.1 Smart BAM Description and Set Up

The Smart BAM (Met-One, Grants Pass, Oregon, USA) was developed as a retrofit to the BAM to heat the sample stream in order to remove water from that would otherwise contribute to the mass measurement. The specific operating procedures employed in this study are listed below. The operation of the Smart BAM in configurations different from those employed in this study may constitute a different method, and it cannot be assumed that the conclusions are transferred.

- A PM_{10} inlet was used with ridges to prevent rain getting through to the impaction surface [29] (Met-One Part No. BX8-802)
- The instrument had a flow rate of 16.67 l min^{-1} ± 1 %, which unlike the BAM was volumetrically controlled and reported to ambient conditions.
- The sample stream was constantly heated at 20 % of the heater capacity, and if the relative humidity dropped below 45 %, the sample stream was heated at 100 % of the heater capacity.
- The filter material was provided directly by Met-One who source from several different manufacturers to the following specifications: Borosilicate micro fibre glass, acrylic resin binder nominal 0.2 µm glass fibre construction. Collection efficiency 99.9 % for 0.3 µm particles.
- Sample Time: 50 minutes with 2 minutes shuttling time. Beta measurements occurred for 4 minutes at the beginning and end of every sample. C_{14} Beta source. Max beta energy 156 kV; 50 to 60 kV mean. Travel distance in air: 20 to 30 cm.
- The baselines were tested every 1 to 2 months by running for 24 hours with a 0.2 µm ULTIPOR N66 filter (Pall Corp., NY, USA; Part No. 4001 NAEY) on the sample tube in place of the PM_{10} inlet. The offset was calculated and inputted in to the instrument to be automatically subtracted. Occasionally the offset was calculated incorrectly and the data were corrected manually.
- Hourly concentration records were recorded in the instrument data buffer, and these were retrieved using onsite or remote telemetry. 24-Hour averages were only valid if there was at least 90 % data capture (i.e. 22 valid 1-hour measurements).

5.8.2 Problems Encountered with the Smart BAM

At Teddington and Birmingham each of the instruments were initially set up with either broken temperature or humidity sensors, which led to very low initial data capture. Occasionally an instrument would fail a leak or flow check. This was usually attributed to glass fibre being stuck on the tape holding nozzle. As a result of this, the frequency of leak and flow checks was increased. Data were not deleted if there was shown to have been a leak, as it was not known when the leak occurred and deleting all possibly effected data would have resulted in very low data capture.

Comparison of the Smart BAM against the PM_{10} KFG (**Figure D.17**) showed a different distribution in the data above 30 µg m^{-3} relative to that below 30 µg m^{-3}, and this is indicative that semi-volatile species are being lost at high concentrations where typically a higher percentage of the PM is ammonium nitrate. The instruments were returned to the ESU (Enviro Technology, Stroud, UK), and tests were performed. It was shown that the external temperature of the sample inlet below the heater tape varied between 65 and 75 °C; much higher than the 45 °C recommended by the manufacturer. This discrepancy was traced to the 400 W US configuration (AC = 115 V; 60 Hz) heater tape supplied with the instruments as opposed to the 200 W European configuration (AC = 230 V; 50 Hz) heater tape that should have been supplied. As the instrument regulated the heater to either 20 or 100 % of maximum as a function of relative humidity, the sample inlet was being heated to too high a temperature, and so semi-volatile species were lost. As such the tests cannot be completed, and no conclusions for the Smart BAM instrument can be reached within the remit of the current programme.

5.9 Comparison of PM_{10} $FDMS_{Base}$ against TEOM

5.9.1 Comparison of PM_{10} $FDMS_{Base}$ against TEOM (0,1,1)

As discussed in Section 5.5.1, the PM_{10} FDMS provides a measurement of the non-volatile mass fraction (herein referred to as PM_{10} $FDMS_{Base}$), and this is a comparable (though not identical) parameter to the TEOM. There follows a comparison of PM_{10} $FDMS_{Base}$ against TEOM (0,1,1). The criteria employed in this comparison are analogous to those reported in Section 4.2. However, W_{CM} is replaced by $W_{F\text{-}T}$, this being the expanded uncertainty of the orthogonal relationship between PM_{10} $FDMS_{Base}$ and TEOM (0,1,1). This is calculated in an analogous method to that discussed in Section C.1, and is shaded red if greater than 25 % (though there are no DQOs associated with this parameter).

The methodology of determining equivalence (Section 4.3) was followed for reasons of continuity, and the comparison of PM_{10} $FDMS_{Base}$ against TEOM (0,1,1) is summarised in **Figure D.18**.

1. Not applicable.

2. The intercepts of the individual and combined datasets are both greater and less than zero (range: -8.189 to +0.819). However, the slopes of the individual and combined datasets are all greater than 1 (range: 1.137 to 1.727), and so the datasets should be corrected before the expanded uncertainty can be considered.

3. Not applicable.

4. The slope and intercept of the 'All Data' dataset were both statistically significant. As such, the 'All Data' slope and intercept were used to generate **E 5.9** below:

$$TEOM\,(0,1,1) = \left(\frac{\left(PM_{10} FDMS_{Base} + 2.061 \right)}{1.360} \right) \qquad \textbf{E 5.9}$$

5. The comparison of PM_{10} $FDMS_{Base\ Corrected}$ against TEOM (0,1,1) is summarised in **Figure D.19**. The expanded uncertainty was occasionally greater than 25 %, however, this equation provides a reasonable method of comparing TEOM (0,1,1) and PM_{10} $FDMS_{Base}$.

The PM_{10} FDMS intercept was shown to vary as a function of the frequency at which the filters were changed (Section 5.5.2). PM_{10} $FDMS_{Base}$ should not be affected by this intercept offset as the air does not go through the 4 ºC bypass filter in this mode. However, the magnitude of the intercept correction term used in **E 5.9** should be treated with caution. A comparison of the TEOM and $FDMS_{Base}$ in London by KCL-ERG showed that PM_{10} $FDMS_{Base}$ plotted against TEOM (0,1,1) resulted in a regression analysis of slope = 1.08; intercept = –2.1 µg m^{-3}; and R = 0.92 (with the FDMS on the Y axis) [19]. These results are clearly

different from those shown in the current study.

5.9.2 Comparison of PM_{10} $FDMS_{Base}$ against TEOM (3,1.03,1.3)

The comparison of PM_{10} $FDMS_{Base}$ against TEOM (3,1.03,1.3) is summarised in **Figure D.20**.

1. Not applicable.

2. The slopes of the individual and combined datasets are both greater and less than 1 (range: 0.820 to 1.277). However, the intercepts of the individual and combined datasets are all less than zero (range: -11.554 to -2.603), and so the datasets should be corrected before the expanded uncertainty can be considered.

3. Not applicable.

4. The slope of the 'All Data' dataset was statistically significant, whereas the intercept was very close to 1 (1.001). As such, the 'All Data' intercept was used to generate **E 5.10** below:

$$TEOM(3,1.03,1.3) = \left(PM_{10}FDMS_{Base} + 5.826\right) \qquad \textbf{E 5.10}$$

5. The comparison of PM_{10} $FDMS_{Base\ Corrected}$ against TEOM (3,1.03,1.3) is summarised in **Figure D.21**. The expanded uncertainty was occasionally greater than 25 %, however, if a TEOM were to be replaced by a PM_{10} FDMS, this equation provides a reasonable method of determining whether a change in daily LV exceedences was due to the change in monitoring method or an actual change in ambient concentrations.

As explained in Section 5.9.1, the PM_{10} FDMS intercept was shown to vary as a function of the frequency at which the filters were changed. PM_{10} $FDMS_{Base}$ should not be affected by this intercept offset as the air does not go through the 4 ºC bypass filter in this mode.

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GLOSSARY

a	Intercept
AEA	Atomic Energy Authority
AQEG	Air Quality Expert Group
ASL	Above Sea Level
AURN	Automatic Urban and Rural Network
b	Slope
BAM	Beta Attenuation Monitor
$BAM_{Ambient}$	BAM corrected to Ambient Conditions
$BAM_{Ambient\ Corrected}$	$BAM_{Ambient}$ Slope Corrected
$BAM_{Corrected}$	BAM slope corrected
c	Intercept of corrected dataset
CAFE	Clean Air For Europe
CEN	Comité Européen de Normalisation
CM	Checkweight Mass
CMCU	Central Management and Co-ordination Unit of the AURN
CV	Critical Value
d	Slope of corrected dataset
DD1	Daughter Directive 1
Defra	Department for the Environment, Food and Rural Affairs
DQO	Data Quality Objective
EC	European Commission
EN12341	CEN PM_{10} Standard
EN14907	CEN $PM_{2.5}$ Standard
ESD	Extreme Studentized Deviate
ET	Enviro Technology
EU	European Union
FDMS	Filter Dynamics Measurement System
HNO_3 (g)	Nitric acid (gas phase)
KCL-ERG	Kings College London - Environmental Research Group
KFG	Klein Filtergerat
LSO	Local Site Operator
LV	Limit Value
LVS	Low Volume Sampler
$M_{check,aft}$	Mass of checkweight weighed immediately after sample filter
$M_{check,bef}$	Mass of checkweight weighed immediately prior to sample filter
m_{filter}	Mass of Filter
$m_{tare,aft}$	Mass of tare filter weighed immediately after sample filter

$m_{tare,bef}$	Mass of tare filter weighed immediately prior to sample filter
n_{bs}	Number of between sampler datapairs
n_{c_s}	Number of candidate against reference datapairs
n_{EC}	Number of Daily LV exceedences for the candidate method
n_{ES}	Number of Daily LV exceedences for the reference method
n_G	Number of datapairs deleted by Grubbs' Test
n_{Gmax}	Maximum number of datapairs that could be deleted by Grubbs' Test
NH_3 (g)	Ammonia (gas phase)
NH_4NO_3 (s)	Ammonium nitrate (aerosol phase)
NPL	National Physical Laboratory
n_{ref}	Number of between reference sampler 24 hour measurement results
NY	New York
OC	Organic Carbon
$P_{Ambient}$	Ambient Pressure
Partisol 2025	Candidate method
PM	Particulate Matter
PM_{10}	Concentration of particles less than 10 microns in diameter
PM_{10} FDMS	FDMS with PM_{10} inlet candidate method
PM_{10} $FDMS_{Base}$	Non-volatile PM_{10} mass fraction measured on FDMS.
PM_{10} $FDMS_{Base\ corrected}$	Corrected non-volatile PM_{10} mass fraction measured on FDMS.
PM_{10} KFG	PM_{10} reference method
$PM_{2.5}$	Concentration of particles less than 2.5 microns in diameter
$PM_{2.5}$ FDMS	FDMS with $PM_{2.5}$ inlet candidate method
$PM_{2.5}$ Leckel	$PM_{2.5}$ reference method
PMP	Polymethylpentene
POM	Polyoxymethylene
Post1	Weighing session 1 after sampling
Post2	Weighing session 2 after sampling
Pre1	Weighing session 1 prior to sampling
Pre2	Weighing session 2 prior to sampling
PTFE	Poly tetrafluoro ethylene
R&P	Rupprecht & Patashnick
RM	Relative Mass
RSS	Relative residuals calculated from the orthogonal regression
S_{Blank}	Blank Spread
SM200 Beta	Candidate method based on beta attenuation of filters from SM200
SM200 $Beta_{Corrected}$	SM200 Beta slope corrected
SM200 Mass	Candidate method based on weighing filters from Opsis SM200

$SM200\ Mass_{Corrected}$	SM200 Mass slope corrected
Smart BAM	BAM with heated inlet
S_{Post}	Post Spread
S_{Pre}	Pre Spread
$T_{Ambient}$	Ambient Temperature
TEOM	Tapered Element Oscillating Microbalance
TEOM(0,1,1)	TEOM with no inbuilt slope of intercept correction factors
$TEOM(0,1,1)_{Corrected}$	TEOM(0,1,1) corrected for slope and intercept
TEOM(3,1.03,1)	TEOM with inbuilt intercept of 3 and slope of 1.03 correction factors
$TEOM(3,1.03,1)_{Corrected}$	TEOM(3,1.03,1) corrected for slope and intercept
TEOM(3,1.03,1.3)	TEOM with inbuilt intercept of 3 and slope of 1.03 correction factors, then multiplied by an external 1.3 correction factor
TEOM(3,1.03,x)	TEOM with inbuilt intercept of 3 and slope of 1.03 correction factors, then multiplied by an external correction factor x
TM	Tare Mass
TS	Test Stat
u_a	Uncertainty of Intercept
u_b	Uncertainty of Slope
u_{bs}	Between sampler Uncertainty
$u_{c\text{-}s}(y_i)$	Uncertainty in the results of the Candidate Method from comparison with the Standard Method
UK	United Kingdom
UKAS	United Kingdom Accreditation Service
u_{ref}	Between sampler uncertainty of the reference method
US	United States
USA	United States of America
USEPA	United States Environmental Protection Agency
$w_{c,CM}(y_i)$	Combined relative uncertainty of the Candidate Method
W_{CM}	Expanded Uncertainty at Limit Value
$W_{F\text{-}T}$	Expanded uncertainty of the orthogonal relationship between PM_{10} $FDMS_{Base}$ and TEOM (3,1.03,1.3)
WG	Working Group
x_i	Average concentration of reference method
y_i	Average concentration of candidate method
$y_{i,corr}$	y_i corrected for slope of intercept
Δ_i	Absolute difference between data-pairs
$\Delta_{i=max}$	Maximum absolute difference between data-pairs
σ_n	Standard Deviation

APPENDIX A

FILTER WEIGHING METHODOLOGY

A.1 Methodology Employed in CEN Standards

The PM_{10} standard: EN12341 states that quartz fibre filters should be used. The proposed $PM_{2.5}$ standard: EN14907 allows for glass fibre, quartz fibre, PTFE (Poly tetrafluoro ethylene) or PTFE coated glass fibre (Commonly known as Emfab). As it is expected that EN12341 may be revised to become consistent with EN14907, it was considered reasonable that any of the four filter media listed in EN14907 could be employed in both the PM_{10} and $PM_{2.5}$ reference samplers.

EN12341 defines only limited criteria for the weighing of filters. EN14907 provides more stringent guidelines for weighing filters and as such, these procedures have been followed for the tests reported in this document. EN14907 states the following criteria for the weighing of filters for the Low Volume Sampler (LVS):

- The temperature and the relative humidity shall be continuously monitored and controlled to (20 ± 1) K and (50 ± 5) % RH respectively.
- Unloaded filters shall be conditioned in the weighing room for a minimum of 48 hours before weighing. Filters shall be weighed twice, with an interval of at least 12 hours, to confirm that the filter weight has stabilised. If the masses differ by a mass more than 40 µg the particular filter shall be discarded. The unloaded filter mass shall be taken as the average of the two separate measurements.
- Unloaded filters may be stored in the weighing room for up to 28 days before sampling.
- All filters shall be left unfolded and protected during storage and transport, for example in the filter holder, in clean glass petri dishes, or similar containers.
- If the minimum hourly mean ambient temperature ($T_{Ambient}$) over the sampling period is above 23 °C, the filter shall be kept at or below the temperature $T_{Ambient}$ for a maximum time of 15 days before introduction to the weighing room. If $T_{Ambient}$ is equal to or below 23 °C, the filter may be kept at or below a temperature of 23 °C for the maximum time of 15 days before introduction to the weighing room.
- Loaded filters shall be placed in the weighing room for a minimum of 48 h before weighing, and then again after a further 24 h to 72 h. If the masses differ by more than 60 µg the result shall not be taken into account. The loaded filter mass shall be taken as the average of the two separate measurements.

These criteria were considered when formulating and implementing the weighing protocols used herein, and are addressed specifically in the following sections of this appendix.

A.2 Preliminary Laboratory Experiments

In line with The Guidance, NPL were commissioned by Bureau Veritas to perform laboratory tests with a view to determining the best filter media and weighing conditions to employ in the field study [11,29]. These tests were based on the criteria listed in EN14907, and the relevant key findings implemented in the field study are summarised below.

All four filter media listed in EN14907 were studied both experimentally and through the available literature, and the findings therein are summarised in **Table A.1**. Emfab was chosen as the filter media for the PM_{10} KFG, $PM_{2.5}$ Leckel and Partisol 2025 in the field study (Pall Corp., NY, USA; Type: EMFAB TX40HI20-WW; Part No.: 7221). At the manufacturer's request, stretched Teflon membrane filters were used in the Opsis SM200 (Pall Corp., NY, USA; Type: 2 µm Teflo; Part No.: R2PJ047).

Table A.1: Table summarising the performance of different filter media against six criteria.

Critereon	Filter Material			
	PTFE Membrane	Quartz	Glass Fibre with Binder	Emfab
Temperature and Humidity Effects	Very good	Moderate	Moderate	Very Good
Structural Integrity	Very good	Poor	Good	Good
Flow Resistance	Poor	Good	Good	Good
Chemical Effects	Good	Moderate	Moderate	Good
Particle Sampling Efficiency	Good	Good	Good	Good
Static Charge Effects	Poor	Moderate	Moderate	Moderate

All filters used in the field study were weighed on a 0.1 µg resolution balance (UMT5, Mettler, Leicester, UK). The drift was shown to 1 µg min^{-1}, and it took approximately 50 seconds to weigh each filter. The simplest and most effective method of removing static was found to be both storing and weighing filters on aluminium foil, and this was used in the field study.

Both Teflon membrane and Emfab were shown to have little dependence on weighing room temperature and humidity. In order to further minimise humidity effects on filter media, the masses of loaded filters were calculated relative to a tare weight of the same material. The tare corrected procedure was shown to be quicker than re-zeroing the balance, and was therefore selected as the most efficient way of controlling balance drift.

Transportation of filters between the different organisations involved in the study was not shown to adversely effect the mass measurements. In line with EN14907, filters were transported between sites in Analyslides (Pall Corp., NY, USA). These hold the filter in place

very well, and provide a highly effective method of transporting filters, though care must be taken that sampled filters are placed sample side up. In practice, it was found that as the holders are a snug fit, it was difficult to get the filters out of the Analyslides, without causing a slight amount of damage.

Emfab filters were stamped with a unique filter number using a stamp that automatically incremented by one every time. This ensured that it was impossible for duplicate filters to be generated, and by identifying the filter rather than just the container, filter mix-up was minimised. Tests were performed to show that stamping the filters did not effect the reproducibility of filter weighings, however, it was observed that those areas of the filter that were stamped restricted airflow through the filter. This was not thought to effect the measurement. Teflon membrane filters could not be stamped as it caused the membrane to split, and as the SM200 measures Beta of the filter stamping them would compromise measurements. Instead, the filter number was written around the outside of the filter ring. This method was of limited success, as it was difficult to read the filter number, and there were occasions where 2 lots of filters with the same number were generated. Filters are now available with identifying microdots embedded in the filter media which can further minimise the possibility of mix-up (MTL, Minneapolis, USA).

A.3 Implementation of Weighing Protocols

As EN14907 calls for filters to be conditioned several days between weighings and the frequent weighing of tare filters, the automated weighing facilities available at the time were not able to cope with updated weighing protocol. NPL was therefore subcontracted to weigh filters manually for the field study. In all cases, filters were kept in the weighing room for less than 28 days in accordance with EN14907. The glove box used for weighing was maintained at (20 ± 1) °C and (50 ± 5) % RH in line with EN14907. Occasions when the measured humidity fell outside the prescribed limits were noted. For a short period early in the Programme a series of filters was weighed with high relative humidity due to laboratory control problems. Where the effected weighings were post sampling weights, the filters were reweighed. Where the effected filters were pre sampling weights, the results were included, as it was not possible to reweigh them; they were weighed relative to a tare filter kept in identical conditions; and the laboratory experiments had shown that the mass of un-sampled Emfab filters is essentially unaffected by relative humidity when the protocol is followed. Analysis of the finalised data indicated that there was no effect on the outcome of the equivalence tests when these filters were used. Since the project started, a new automated balance has become available which stores filters in stacks and uses 47mm circular checkweights so can vastly increase throughput (MTL, Minneapolis, USA).

A protocol was proposed in the NPL preliminary report. This involved weighing an Emfab check-filter and metal checkweights of 50 or 100 mg at the beginning and end of every set of approximately 28 sample filters. To minimise errors, the checkweight was always placed in

the middle of the cross shaped weighing pan. A tare filter was to be weighed every second sample filter to compensate for balance drift. Experiments had shown that over a period of 2 weeks of weighings, the Emfab tare filter could lose about 10 µg. The check-filter was included in order to correct for any loss of material on the tare filter, as it would be weighed less frequently. It was proposed that if any significant difference in the mass of the check-filter was observed relative to the checkweights, then the check-filter should be replaced before any further weighings are carried out.

For the first two sites (Teddington and Birmingham), filters were weighed as per the protocol proposed in the NPL report with the exception of the check-filters. In practice the use of a check-filter was not implemented as a 10 µg drift in tare weight was considered within the error of the measurement, and any attempts to correct for this would probably induce further error. Further, it is statistically invalid to correct either tare or sample filters relative to a different check-filter if the original were to become damaged.

At the time that the instruments were moved to the second two sites (East Kilbride and Bristol) the weighing protocol was again reassessed. In the light of balance drift being less than anticipated, and in order to increase throughput the tare filter was weighed every fourth sample filter. In addition, protocols were tightened to check the instrument zero, and weigh both the 50 mg and 100 mg checkweight frequently (whereas before only one checkweight was weighed, and it was not necessarily the same weight for each of the pre and post weighings). Further, it was evident that the Emfab tare filter would become damaged due to frequent weighings, and so for the second two sample sites sample filters were weighed relative to the checkweight rather than the tare filter. As Emfab tare filters show little variation with humidity and temperature, this methodology is considered valid. Teflon filters were generally not weighed relative to the checkweight unless the tare filter was severely damaged. This methodology was chosen as the checkweight weighed approximately 80 mg less than the filters; and this spread may induce significant error on the measurements.

If the filters were weighed relative to a filter tare, the **Tare Mass (TM)** of the filter was calculated for each weighing session using **E A.1** below:

$$TM = \frac{\left(m_{tare,bef} + m_{tare,aft}\right)}{2} \qquad \textbf{E A.1}$$

Where:

$m_{tare,bef}$ = Mass of tare filter weighed immediately prior to sample filter.

$m_{tare,aft}$ = Mass of tare filter weighed immediately after sample filter.

Conversely, if the filters were weighed relative to the checkweight, then the **Checkweight Mass (CM)** of the filter was calculated for each weighing session using **E A.2** below:

$$CM = \frac{\left(m_{check,bef} + m_{check,aft}\right)}{2} \quad \textbf{E A.2}$$

Where:

$M_{check,bef}$ = Mass of checkweight weighed immediately prior to sample filter.

$M_{check,aft}$ = Mass of checkweight weighed immediately after sample filter.

Depending on whether the sample filter was weighed relative to the checkweight or a tare filter, the **Relative Mass (RM)** of the filter was calculated for each weighing session using one of the following equations:

$$RM = m_{filter} - TM \quad \textbf{E A.3}$$

$$RM = m_{filter} - CM \quad \textbf{E A.4}$$

Where:

m_{filter} = Mass of sample filter

Particulate Mass (PM) is calculated using the following equation in accordance with EN14907. In the event of the balance being unstable during a single weighing session, then that weighing session was ignored in the calculation of PM:

$$PM = \left(\frac{RM_{Post1} + RM_{Post2}}{2}\right) - \left(\frac{RM_{Pre1} + RM_{Pre2}}{2}\right) \quad \textbf{E A.5}$$

Where:

Pre1	denotes weighing session 1 prior to sampling
Pre2	denotes weighing session 2 prior to sampling
Post1	denotes weighing session 1 after sampling
Post2	denotes weighing session 2 after sampling

Pre Spread (S_{Pre}), Post Spread (S_{Post}) and Blank Spread (S_{Blank}) were calculated using the following equations. Regardless of whether the relative mass of the sample filter was calculated relative to a tare filter or checkweight, the Blank Spread was only calculated from tare filters:

$$S_{Pre} = RM_{Pre1} - RM_{Pre2} \quad \textbf{E A.6}$$

$$S_{Post} = RM_{Post1} - RM_{Post2} \quad \textbf{E A.7}$$

$$S_{Blank} = \left(\frac{TM_{Post2} + TM_{Post1}}{2}\right) - \left(\frac{TM_{Pre2} + TM_{Pre1}}{2}\right) \quad \textbf{E A.8}$$

There were a total of approximately 25,000 filter weighings over an 18 month period. It was

not possible to weigh all filters within the 15 day timeframe suggested in EN14907. However, as filters were removed immediately from the reference samplers and placed in the refrigerator, it was not necessary to determine if $T_{Ambient}$ exceeded 23 ºC. It is felt that as 15 days was impractical for a relatively small scale field study, it is less likely to be attainable if this methodology were adopted by a National or Regional network, and as such, the methodology employed herein is representative of how the reference samplers would be operated in practice.

A.4 Analysis of Protocols Employed

The distributions of pre and post weight for all Emfab filters weighed relative to the tare filter and checkweight are shown in **Figure A.1**. If filters lose relative mass between weighings, then the distribution will be shifted to the right, whereas if there is a gain in the relative mass the distribution will shift to the left. It is evident from those filters pre-weighed relative to the tare filter that there is a gain of relative mass (Figure A.1A), that is not apparent when filters are pre weighed relative to the checkweight (Figure A.1C). This is possibly due to the tare filter imperceptibly losing mass through constant weighing. The shift was in the order of 20 µg, which corresponds to 0.36 µg m^{-3} for PM_{10} KFG and $PM_{2.5}$ Leckel filters, and 0.83 µg m^{-3} for Partisol 2025 filters, which can be considered insignificant.

The post weighings relative to the checkweight (Figure A.1D) shows that there is a loss in filter mass for PM_{10} KFG filters that is less pronounced for $PM_{2.5}$ Leckel filters, and not apparent for Partisol 2025 filters. This difference is in line with the relative amount of particulate collected on the filter, and may be attributed to the loss of particle bound water. This finding supports earlier studies that suggest weighing room humidity should be lowered in future CEN standards.

The distribution of post weighings relative to the tare filter (Figure A.1B) is fairly evenly distributed. This could be indicative that the tare filter is no longer losing mass, or that the relative gain due to the tare filter, and loss due to particle bound water are cancelling each other out.

The distributions of pre and post weight for Teflon membrane filters weighed relative to both the tare filter and checkweight are shown in **Figure A.2**. The distribution of the pre spread is relatively Gaussian, which is indicative that there was no systematic loss of material from the tare filters. Further, the distribution of the post spread is also relatively Gaussian, which is consistent with the SM200 taking the same volume samples as the Partisol 2025.

EN14907 states that unloaded filters should be rejected if the difference between the masses of the two pre weighings is greater than 40 µg. Similarly, EN14907 states that sampled filters should be rejected if the difference between the masses of the two post weighings is greater than 60 µg. In practice, filters were not rejected based on these criteria, as this would

severely impact data capture rate. The observed distributions of repeat mass measurements are considered unlikely to have had a significant effect on the results.

Figure A.1: Distribution for Emfab filters of (**A**) Pre spread weighed relative to a tare filter; (**B**) Post spread weighed relative to a tare filter; (**C**) Pre spread weighed relative to the checkweight and (**D**) Post spread weighed relative to the checkweight.

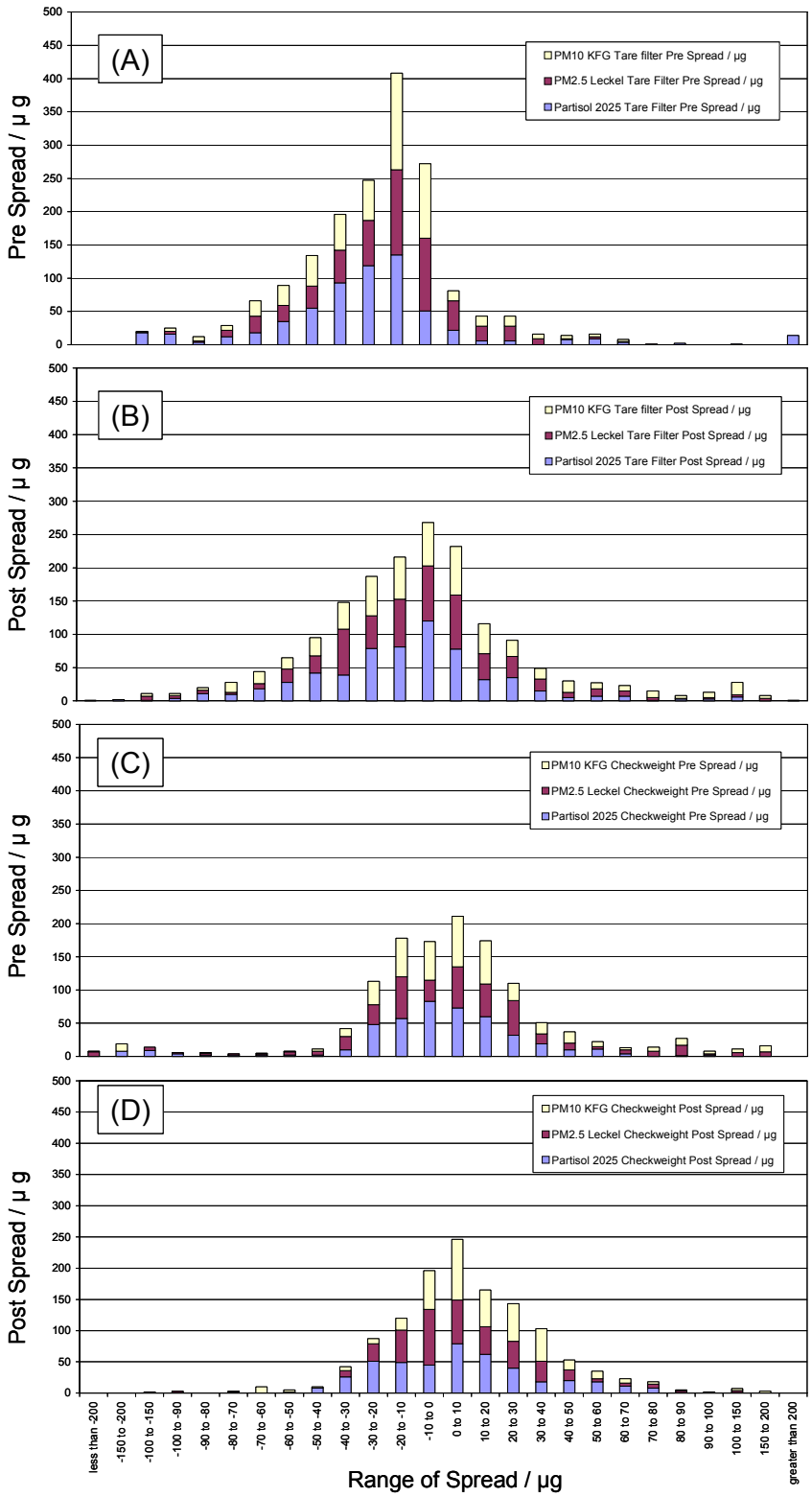
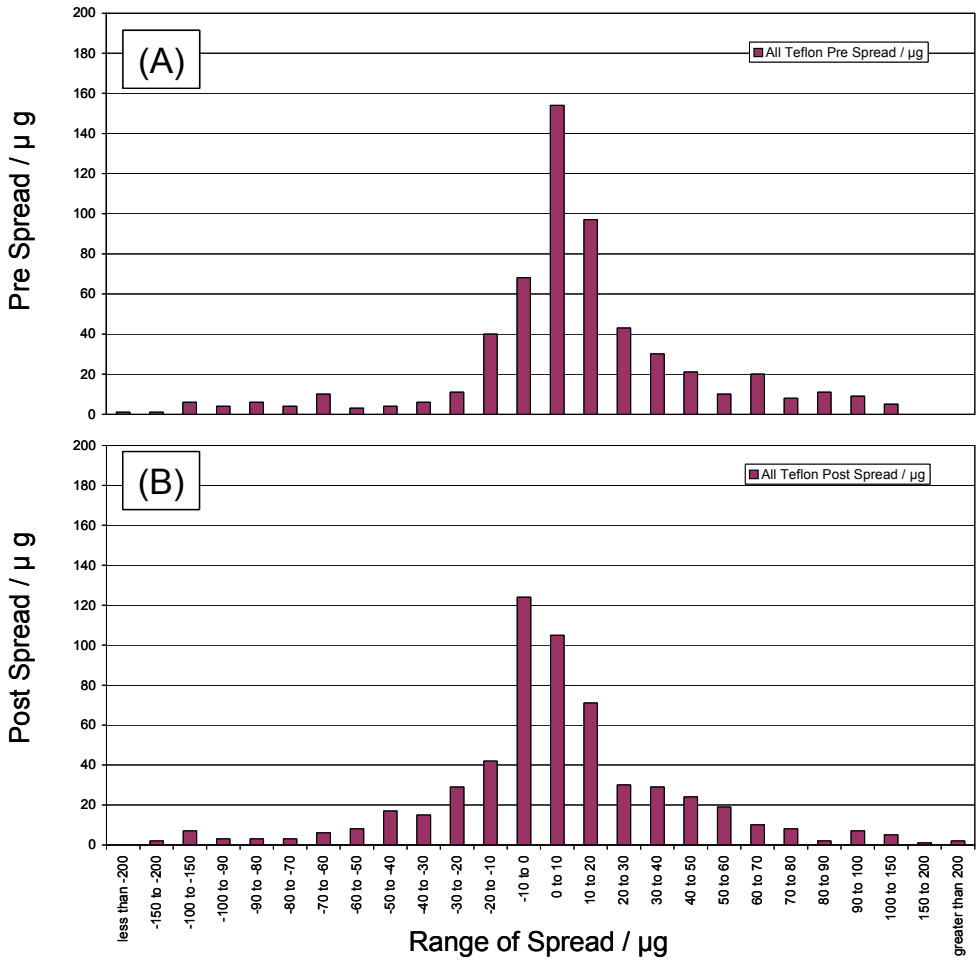


Figure A.2: Distribution for Teflon filters of (A) Pre spread weighed relative to both the tare filter and checkweight and (B) Postspread weighed relative to both the tare filter and checkweight.



APPENDIX B

GRUBBS' TEST

B.1 Method of Applying Grubbs' Test

Grubbs' Outlier Test [30,31] at the 99 % Confidence Level was used to remove a maximum of three outliers (This being approximately 5 % of data-pairs). This method is also called the ESD method (Extreme Studentized Deviate).

The **Absolute difference between data-pairs (Δ_i)** are calculated, and the data pair with the **Maximum absolute difference between data-pairs ($\Delta_{i=max}$)** is identified. It is this data-pair on which the Grubbs' Test is performed.

$$\Delta_i = \left| x_{i,1} - x_{i,2} \right| \qquad \textbf{E B.1}$$

$$\Delta_{i=\max} = \left| x_{i,1} - x_{i,2} \right|_{i=\max} \qquad \textbf{E B.2}$$

Where:

$x_{i,1}$ and $x_{i,2}$ are parallel measurements for a single 24 or 1-hour period i.

i=max is the data-pair with the largest absolute difference.

The **Mean ($\overline{bs}$)** and **Standard Deviation (σ_n)** are calculated using the following equations. The standard deviation is based on the entire population (n), rather than the more commonly used nonbiased (n-1) method:

$$\sigma_n = \sqrt{\frac{\left(n_{bs} \cdot \left(\sum_{i=1}^{n_{bs}} \Delta_i^{\,2} \right) \right) - \left(\left(\sum_{i=1}^{n_{bs}} \Delta_i \right)^2 \right)}{n_{bs}^{\,2}}} \qquad \textbf{E B.3}$$

$$\overline{bs} = \frac{\sum_{i=1}^{n_{bs}} \Delta_i}{n_{bs}} \qquad \textbf{E B.4}$$

Where:

n_{bs} = number of between-sampler 24 hour or 1-hour measurement results.

The **Test Stat (TS)** is calculated for the data-pair with the highest absolute difference:

$$TS = \frac{x_{i=\max} - \overline{bs}}{\sigma_n} \qquad \textbf{E B.5}$$

The **Critical Value (CV)** at the 99 % confidence level is obtained from **Table B.1**. TS and CV are compared:

If TS < CV, then the data-pair corresponding to $x_{i=max}$ is not considered to be statistically

significant from the other data-pairs, and is not deleted.

If TS > CV, then the data-pair corresponding to $x_{i=max}$ is considered to be statistically significant from the other data-pairs, and is deleted. The process is repeated, for the new $x_{i=max}$, and calculating new values of n_{bs} $\overline{bs}$, and σ_n.

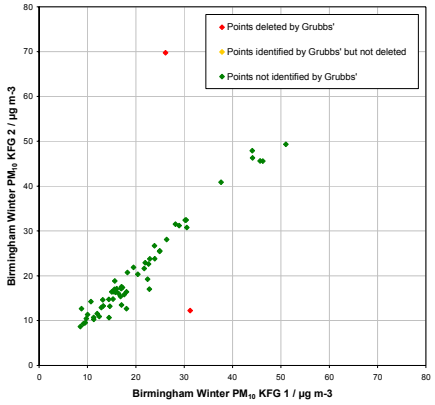
Table B.1: Table summarising the Critical Value (CV) for each value of n_{bs}. Values in black were obtained directly [32], and those in red were linearly interpolated from the known values.

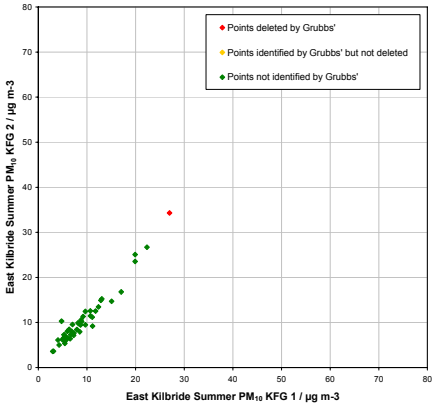
n_{bs}	CV	n_{bs}	CV	n_{bs}	CV	n_{bs}	CV
1	-	36	3.191	71	3.476	106	3.6192
2	-	37	3.204	72	3.481	107	3.6224
3	1.155	38	3.216	73	3.486	108	3.6256
4	1.492	39	3.228	74	3.491	109	3.6288
5	1.749	40	3.24	75	3.496	110	3.632
6	1.944	41	3.2505	76	3.501	111	3.635
7	2.097	42	3.261	77	3.506	112	3.638
8	2.221	43	3.2715	78	3.511	113	3.641
9	2.323	44	3.282	79	3.516	114	3.644
10	2.41	45	3.292	80	3.521	115	3.647
11	2.485	46	3.302	81	3.5254	116	3.65
12	2.55	47	3.3105	82	3.5298	117	3.653
13	2.607	48	3.319	83	3.5342	118	3.656
14	2.659	49	3.3275	84	3.5386	119	3.659
15	2.705	50	3.336	85	3.543	120	3.662
16	2.747	51	3.3445	86	3.547	121	3.6646
17	2.785	52	3.353	87	3.551	122	3.6672
18	2.821	53	3.3605	88	3.555	123	3.6698
19	2.854	54	3.368	89	3.559	124	3.6724
20	2.884	55	3.3755	90	3.563	125	3.675
21	2.912	56	3.383	91	3.5668	126	3.6776
22	2.939	57	3.39	92	3.5706	127	3.6802
23	2.963	58	3.397	93	3.5744	128	3.6828
24	2.987	59	3.404	94	3.5782	129	3.6854
25	3.009	60	3.411	95	3.582	130	3.688
26	3.029	61	3.4172	96	3.5856	131	3.6904
27	3.049	62	3.4234	97	3.5892	132	3.6928
28	3.068	63	3.4296	98	3.5928	133	3.6952
29	3.085	64	3.4358	99	3.5964	134	3.6976
30	3.103	65	3.442	100	3.6	135	3.7
31	3.119	66	3.4478	101	3.6032	136	3.7024
32	3.135	67	3.4536	102	3.6064	137	3.7048
33	3.15	68	3.4594	103	3.6096	138	3.7072
34	3.164	69	3.4652	104	3.6128	139	3.7096
35	3.178	70	3.471	105	3.616	140	3.712

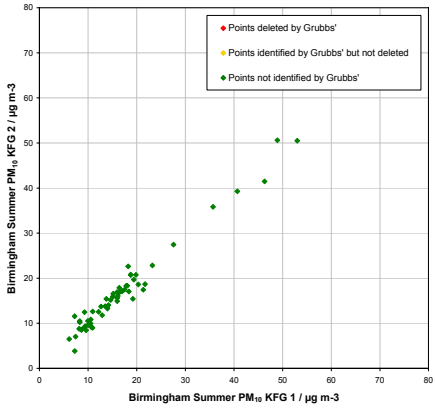
- Denotes Not Applicable

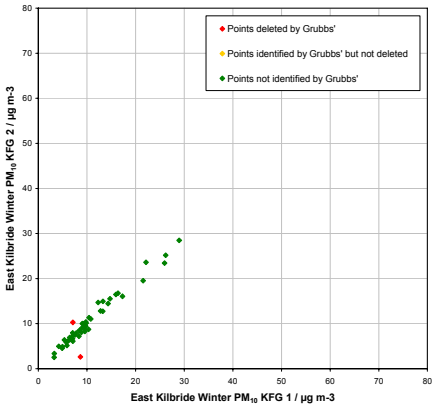
B.2 Results of Applying Grubbs' Test

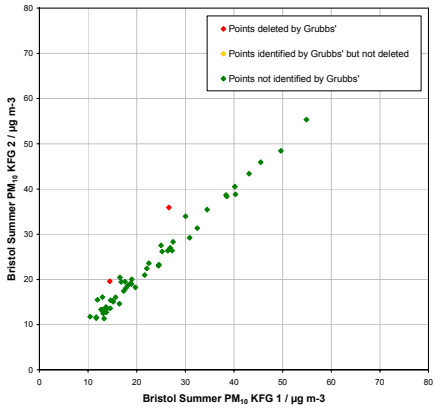
Figure B.1: The results of using Grubbs' Outlier Test for the PM_{10} KFG for all eight datasets.

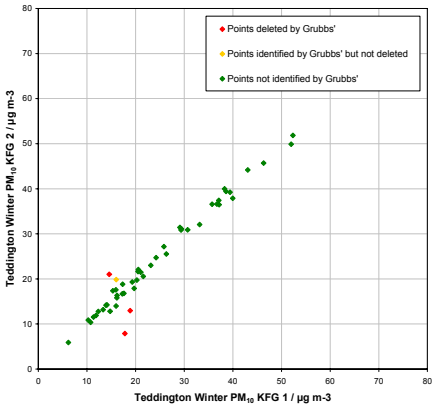


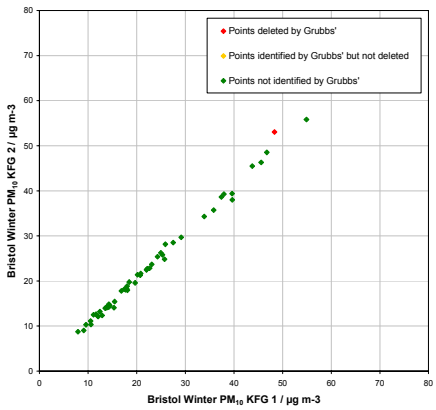












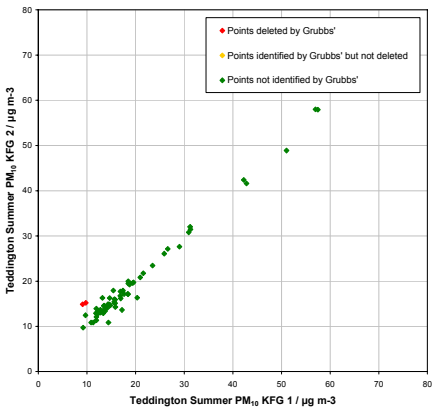
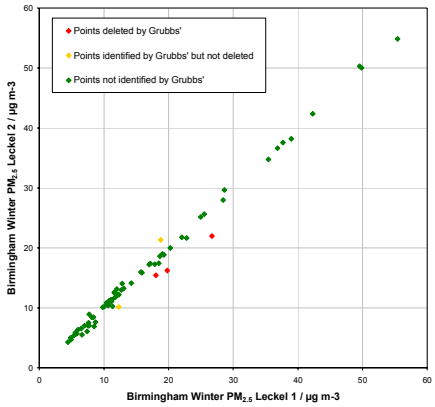
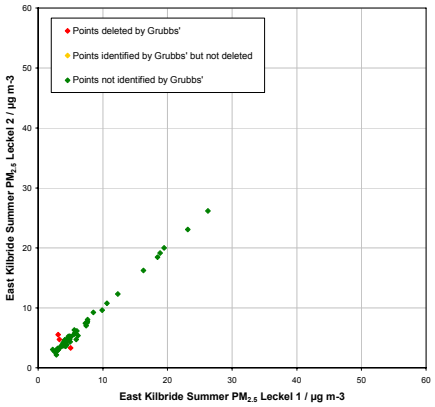
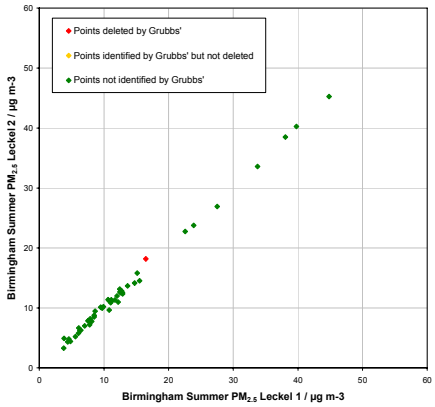
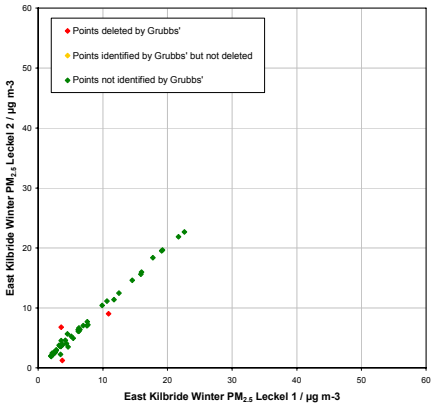


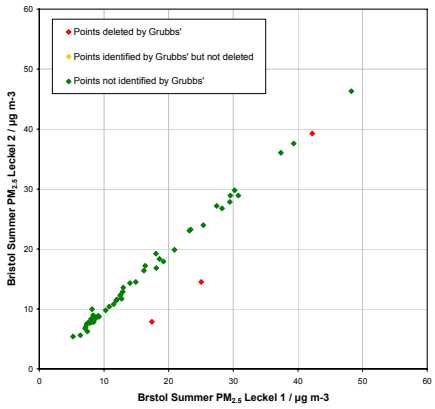
Figure B.2: The results of using Grubbs' Outlier Test for the $PM_{2.5}$ Leckel for all eight datasets.

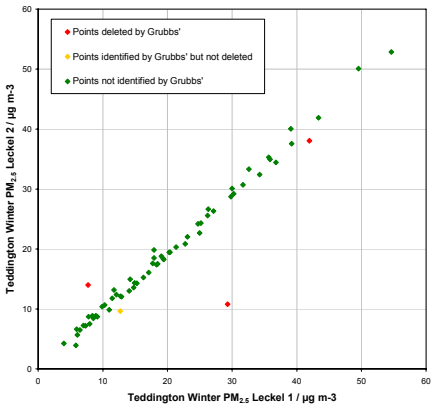


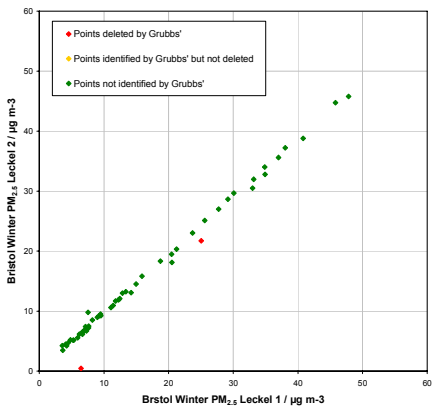












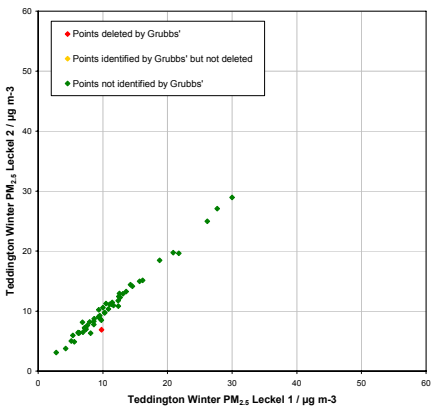
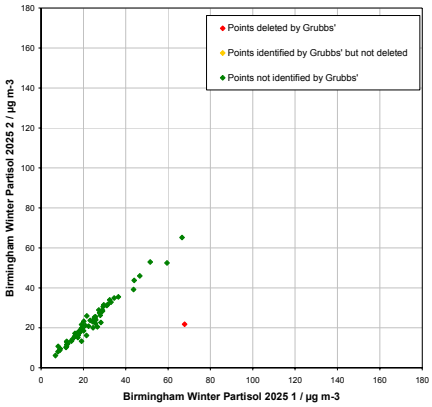
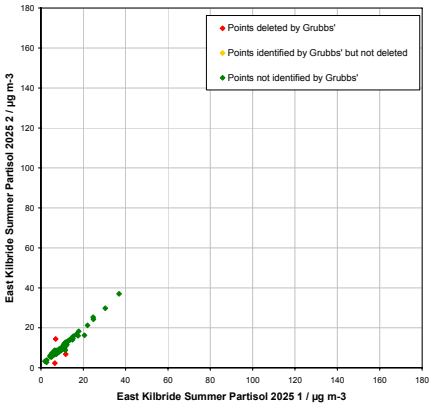
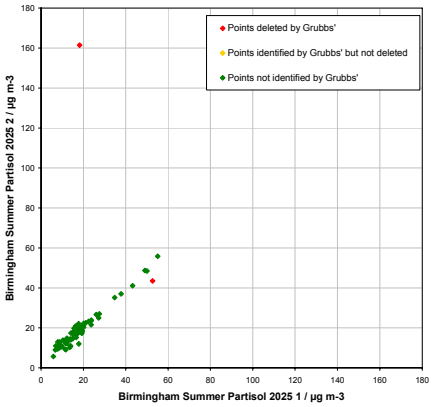
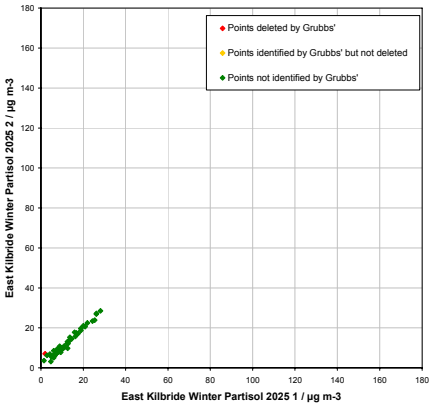


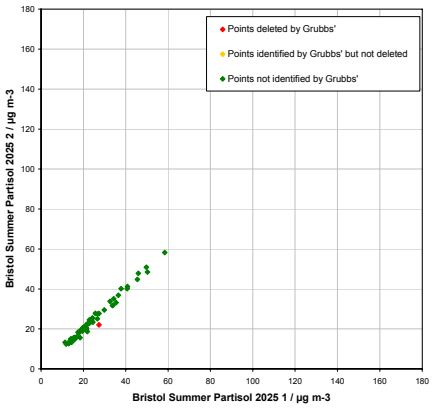
Figure B.3: The results of using Grubbs' Outlier Test for the Partisol 2025 for all eight datasets.

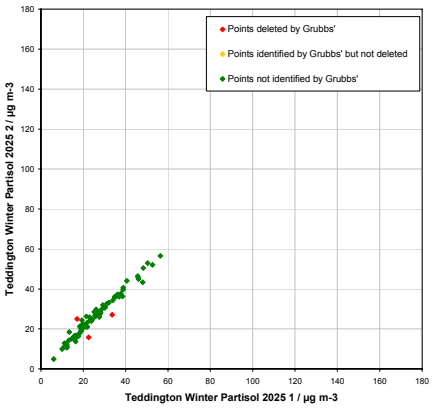


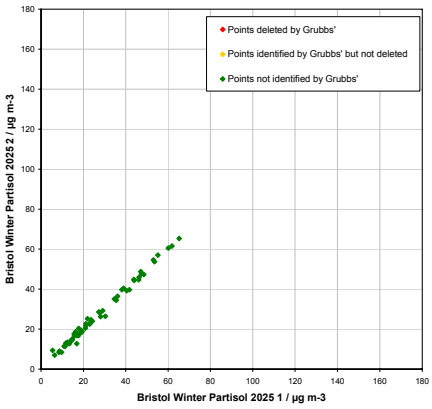












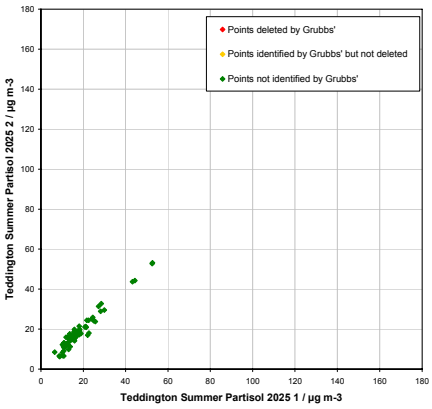
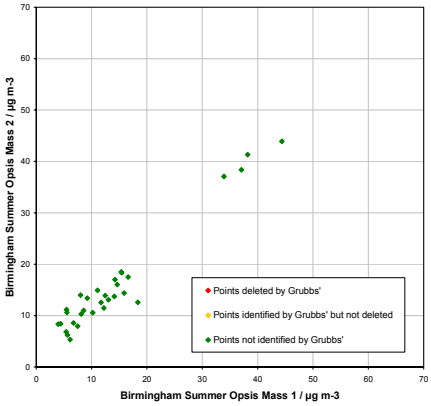
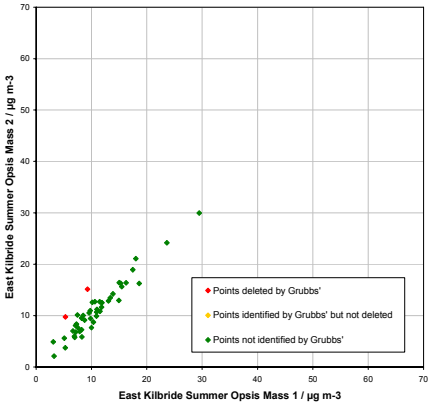
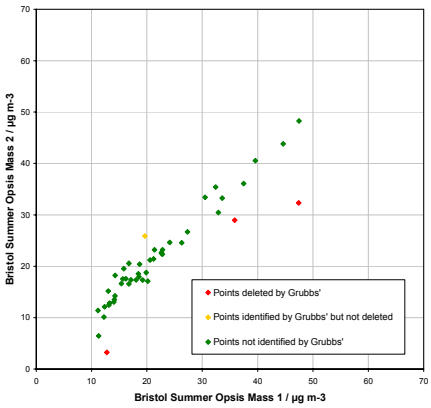
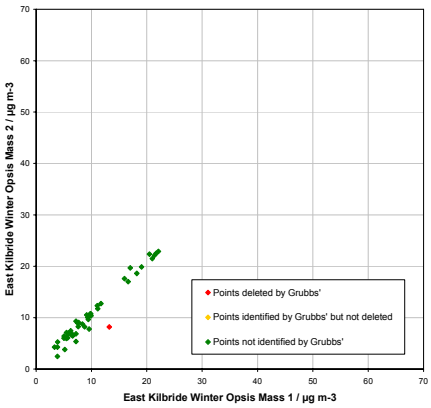


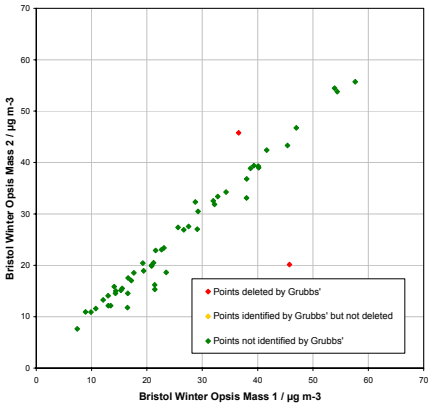
Figure B.4: The results of using Grubbs' Outlier Test for the SM200 Mass for the six datasets for which data are available.

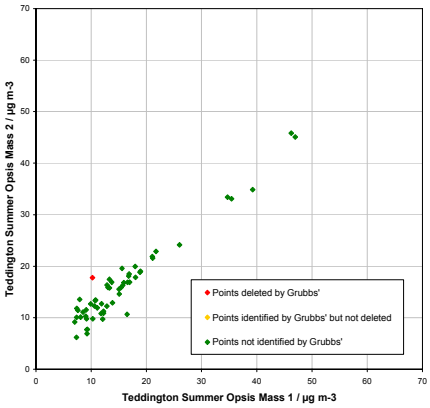












APPENDIX C

CALCULATIONS USED FOR EQUIVALENCE ANALYSIS

C.1 Equations used for Uncorrected Datasets

All calculations are done on paired data only. These equations are based on those found in The Guidance and the associated Microsoft Excel file provided for their calculation [33]. The distribution of reference and candidate instruments is assumed to be linear, and correspond to **E C.1** below:

$$y_i = a + bx_i \qquad \textbf{E C.1}$$

Where:

y_i = average concentration of candidate method.

x_i = average concentration of reference method

a = intercept

b = slope

The **Between-sampler Uncertainty** ($\mathbf{u_{bs}}$) is calculated using **E C.2** below:

$$u_{bs} = \sqrt{\frac{\sum_{i=1}^{n_{bs}} \left(y_{i,1} - y_{i,2}\right)^2}{2n_{bs}}} \qquad \textbf{E C.2}$$

Where:

$y_{i,1}$ and $y_{i,2}$ are parallel measurements for a single 24 or 1-hour period i.

n_{bs} = number of between-sampler 24 hour or 1-hour measurement results.

The **slope (b)** and I**ntercept (a)** are calculated using the following equations:

$$b = \frac{Syy - Sxx + \sqrt{\left(Syy - Sxx\right)^2 + 4\left(Sxy\right)^2}}{2Sxy} \qquad \textbf{E C.3}$$

$$a = \bar{y} - \left(b \cdot \bar{x}\right) \qquad \textbf{E C.4}$$

Where:

$$Sxx = \sum_{i=1}^{n_{c-s}} \left(x_i - \bar{x}\right)^2 \qquad \textbf{E C.5}$$

$$Syy = \sum_{i=1}^{n_{c-s}} \left(y_i - \bar{y}\right)^2 \qquad \textbf{E C.6}$$

$$Sxy = \sum_{i=1}^{n_{c-s}} \left(x_i - \bar{x}\right) \cdot \left(y_i - \bar{y}\right) \qquad \textbf{E C.7}$$

Where:

$n_{c\text{-}s}$ = number of 24 hour periods when both reference samplers and both candidate samplers were running.

$$\bar{x} = \frac{\sum_{i=1}^{n_{c-s}} x_i}{n_{c-s}} \qquad \textbf{E C.8}$$

$$\bar{y} = \frac{\sum_{i=1}^{n_{c-s}} y_i}{n_{c-s}} \qquad \textbf{E C.9}$$

The **uncertainty in the slope (u_b)** is calculated using **E C.10** below:

$$u_b = \sqrt{\frac{Syy - (Sxy^2 / Sxx)}{(n_{c-s} - 2) \cdot Sxx}} \qquad \textbf{E C.10}$$

The **uncertainty in the intercept (u_a)** is calculated using **E C.11** below:

$$u_a = \sqrt{u_b{}^2 \frac{\sum_{i=1}^{n_{c-s}} x^2}{n_{c-s}}} \qquad \textbf{E C.11}$$

r^2 is calculated using **E C.12** below:

$$r^2 = \left(\frac{\left[n_{c-s} \sum_{i=1}^{n_{c-s}} (xy) \right] - \left[\sum_{i=1}^{n_{c-s}} x \cdot \sum_{i=1}^{n_{c-s}} y \right]}{\sqrt{\left[\left(n_{c-s} \cdot \sum_{i=1}^{n_{c-s}} (x^2) \right) - \left(\sum_{i=1}^{n_{c-s}} x \right)^2 \right] \cdot \left[\left(n_{c-s} \cdot \sum_{i=1}^{n_{c-s}} (y^2) \right) - \left(\sum_{i=1}^{n_{c-s}} y \right)^2 \right]}} \right)^2 \qquad \textbf{E C.12}$$

The uncertainty in the results of the Candidate Method from comparison with the Standard Method ($u_{c\text{-}s}(y_i)$) is calculated using **E C.13** below in line with the standard description defined in ISO5725 [34]:

$$[u_{c-s}(y_i)]^2 = \frac{RSS}{(n_{c-s} - 2)} + [a + ((b-1) \cdot LV)]^2 - u_{ref}{}^2 \qquad \textbf{E C.13}$$

Where:

LV is the Limit Value.

RSS is the sum of relative residuals calculated from the orthogonal regression, and is calculated as:

$$RSS = \sum_{i=1}^{n_{c-s}} \left(y_i - a - bx_i\right)^2 \qquad \textbf{E C.14}$$

u_{ref} is the between-sampler uncertainty of the reference method, and is calculated analogous to **E C.2** using the following equation:

$$u_{ref} = \sqrt{\frac{\sum_{i=1}^{n_{bs}} \left(x_{i,1} - x_{i,2}\right)^2}{2n_{ref}}} \qquad \textbf{E C.15}$$

Where:

$x_{i,1}$ and $x_{i,2}$ are parallel measurements for a single 24 period i.

n_{ref} = number of between reference sampler 24 hour measurement results.

The combined relative uncertainty of the Candidate Method ($w_{c,CM}(y_i)$) is calculated using **E C.16** below:

$$w_{c,CM}\left(y_i\right) = 100 \cdot \left(\frac{u_{C-S}\left(y_i\right)}{LV}\right) \qquad \textbf{E C.16}$$

The **expanded uncertainty at limit value (W_{CM})** is calculated by multiplying $w_{c,CM}(y_i)$ by a coverage factor k reflecting the appropriate number of degrees of freedom resulting from the determination of $w_{c,CM}(y_i)$ using thte following equation. In view of the large number of experimental results available, a coverage factor k=2 is used.

$$W_{CM}\left(y_i\right) = k \cdot w_{c,CM}\left(y_i\right) \qquad \textbf{E C.17}$$

C.2 Equations used for Intercept Corrected Datasets

If the results of the equivalence procedure indicate that the dataset requires correction for intercept then y_i is corrected as $y_{i,corr}$ using **E C.18** below:

$$y_{i,corr} = y_i - a \qquad \textbf{E C.18}$$

The linear regression of the new corrected dataset can be expressed in the following form:

$$y_{i,corr} = c + dx_i \qquad \textbf{E C.19}$$

Where:

c = intercept of corrected dataset.

d = slope of corrected dataset.

All equations are then recalculated for the corrected dataset, however, there is an extra function in the uncertainty in the results of the corrected Candidate Method from comparison with the Standard Method ($u_{c\text{-}s}(y_{i,corr})$) to account for the uncertainty in the intercept as found in the orthogonal regression of the pre-corrected dataset. As such, $u_{c\text{-}s}(y_{i,corr})$ of the corrected dataset can be calculated as:

$$\left[u_{c-s}\left(y_{i,corr}\right)\right]^2 = \frac{RSS}{\left(n_{c-s}-2\right)} + \left[c + \left(\left(d-1\right)\cdot LV\right)\right]^2 + u_a{}^2 - u_{ref}{}^2 \qquad \textbf{E C.20}$$

C.3 Equations used for Slope Corrected Datasets

If the results of the equivalence procedure indicate that the dataset requires correction for slope then y_i is corrected as $y_{i,corr}$ using **E C.21** below:

$$y_{i,corr} = \frac{y_i}{b} \qquad \textbf{E C.21}$$

As in Section A3.2 above, the linear regression of the new corrected dataset can be expressed in the following form:

$$y_{i,corr} = c + dx_i \qquad \textbf{E C.19}$$

Where:

c = intercept of corrected dataset.

d = slope of corrected dataset.

All equations are then recalculated for the corrected dataset, however, there is an extra function in the uncertainty in the results of the corrected Candidate Method from comparison with the Standard Method ($u_{c\text{-}s}(y_{i,corr})$) to account for the uncertainty in the slope as found in the orthogonal regression of the pre-corrected dataset. As such, $u_{c\text{-}s}(y_{i,corr})$ of the corrected dataset can be calculated as:

$$\left[u_{c-s}\left(y_{i,corr}\right)\right]^2 = \frac{RSS}{\left(n_{c-s}-2\right)} + \left[c + \left(\left(d-1\right)\cdot LV\right)\right]^2 + LV^2 u_b{}^2 - u_{ref}{}^2 \qquad \textbf{E C.22}$$

C.4 Equations used for Slope and Intercept Corrected Datasets

If the results of the equivalence procedure indicate that the dataset requires correction for slope then y_i is corrected as $y_{i,corr}$ using **E C.23** below:

$$y_{i,corr} = \frac{\left(y_i - a\right)}{b} \qquad \textbf{E C.23}$$

As in Section A3.2 above, the linear regression of the new corrected dataset can be

expressed in the following form:

$$y_{i,corr} = c + dx_i \qquad \textbf{E C.19}$$

Where:

c = intercept of corrected dataset.

d = slope of corrected dataset.

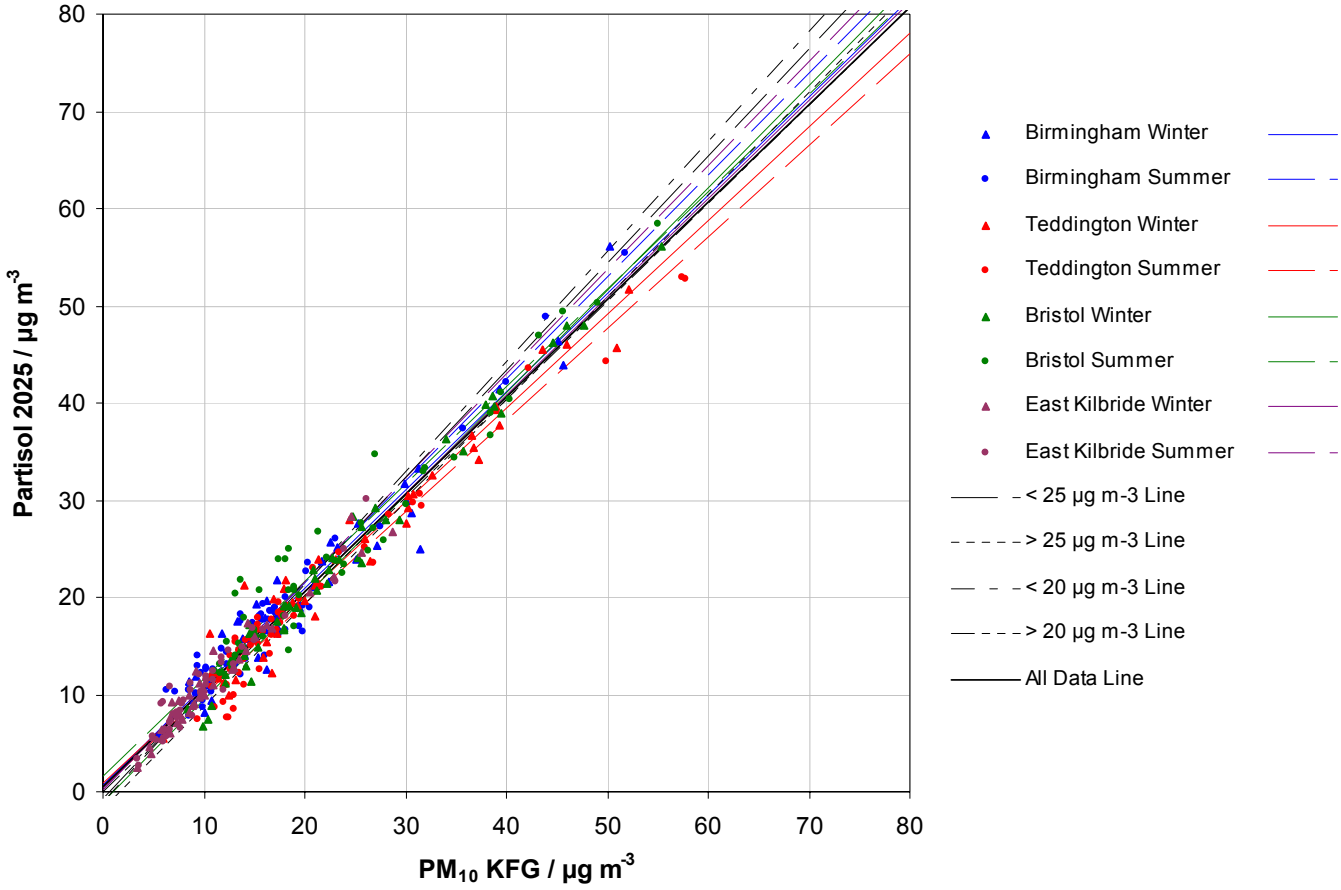
All equations are then recalculated for the corrected dataset, however, there are extra functions in the uncertainty in the results of the corrected Candidate Method from comparison with the Standard Method ($u_{c\text{-}s}(y_{i,corr})$) to account for both the uncertainty in the slope and intercept as found in the orthogonal regression of the pre-corrected dataset. As such, $u_{c\text{-}s}(y_{i,corr})$ of the corrected dataset can be calculated using the following equation:

$$\left[u_{c-s}\left(y_{i,corr}\right)\right]^2 = \frac{RSS}{\left(n_{c-s}-2\right)} + \left[c + \left(\left(d-1\right)\cdot LV\right)\right]^2 + u_a{}^2 + LV^2 u_b{}^2 - u_{ref}{}^2 \qquad \textbf{E C.24}$$

APPENDIX D

GRAPHS AND TABLES OF EQUIVALENCE DATA

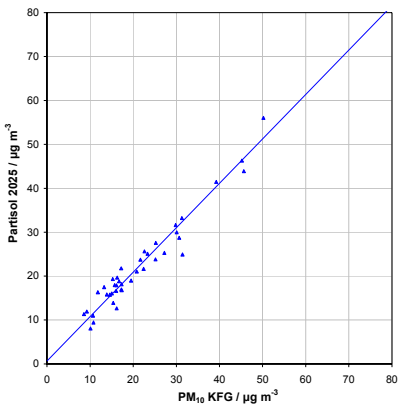
Figure D.1: Charts and Table summarising the comparison of Partisol 2025 Candidate Method against PM_{10} KFG Reference Method. The terms and colours used in the Table are discussed in Section 4.2. u_{bs}, a and u_a have units of µg m^{-3}.



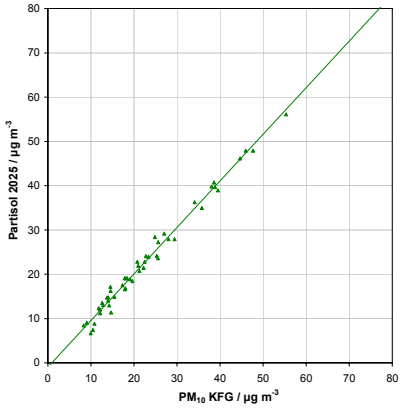
Partisol 2025	Dataset	Grubbs' Test		24 hour		Orthogonal Regression				Annual Limit Value of 40 µg m^3		Daily Limit Value of 50 µg m^3		
		n_G	n_{Gmax}	n_{bs}	u_{bs}	n_{c-s}	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{CM} / %	% > 50 % LV	W_{CM} / %	% > 50 % LV	(n_{ES},n_{EC})
Individual Campaigns	Birmingham Winter	1	1	68	1.55	40	0.944	1.012 +/- 0.039	0.646 +/- 0.916	11.58	42.5	9.51	30.0	(1,1)
	Birmingham Summer	2	2	75	1.48	56	0.956	1.049 +/- 0.030	0.443 +/- 0.553	14.40	16.1	13.22	8.9	(1,1)
	Teddington Winter	3	3	80	1.22	42	0.956	0.965 +/- 0.032	0.870 +/- 0.872	11.52	54.8	9.66	40.5	(2,1)
	Teddington Summer	0	0	68	1.47	58	0.961	0.943 +/- 0.025	0.576 +/- 0.545	11.79	22.4	11.20	17.2	(2,2)
	Bristol Summer	1	1	57	0.85	49	0.943	1.001 +/- 0.035	1.667 +/- 0.901	15.23	44.9	12.22	34.7	(1,2)
	Bristol Winter	0	0	61	0.98	50	0.986	1.052 +/- 0.018	-0.998 +/- 0.460	8.51	48.0	8.30	32.0	(1,1)
	East Kilbride Summer	3	3	59	0.68	44	0.937	1.071 +/- 0.041	0.092 +/- 0.469	15.51	6.8	15.13	2.3	(0,0)
	East Kilbride Winter	1	1	54	0.81	39	0.958	1.011 +/- 0.034	0.359 +/- 0.437	6.90	12.8	5.78	5.1	(0,0)
All Campaigns	All Data	-	-	522	1.21	378	0.961	1.003 +/- 0.010	0.530 +/- 0.220	9.93	30.7	7.99	21.2	(8,8)
Annual Limit Value of 40 µg m^3	< 20 µg m^3	-	-	262	1.18	262	0.793	1.131 +/- 0.031	-1.006 +/- 0.425	23.15	-	-	-	-
	> 20 µg m^3	-	-	118	1.21	116	0.946	1.009 +/- 0.022	0.086 +/- 0.732	10.72	-	-	-	-
Daily Limit Value of 50 µg m^3	< 25 µg m^3	-	-	298	1.17	298	0.856	1.101 +/- 0.024	-0.687 +/- 0.357	-	-	18.80	-	-
	> 25 µg m^3	-	-	82	1.25	80	0.932	1.053 +/- 0.031	-1.833 +/- 1.159	-	-	9.68	-	-

- Denotes Not Applicable.

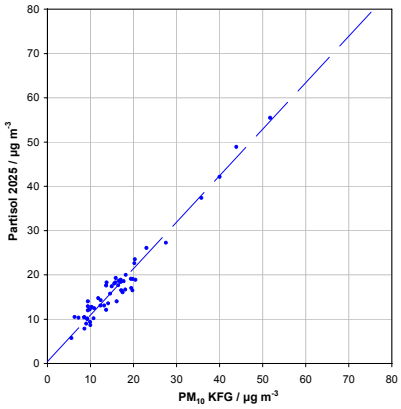
Figure D.1 Continued: Charts summarising the comparison of Partisol 2025 and PM_{10} KFG.



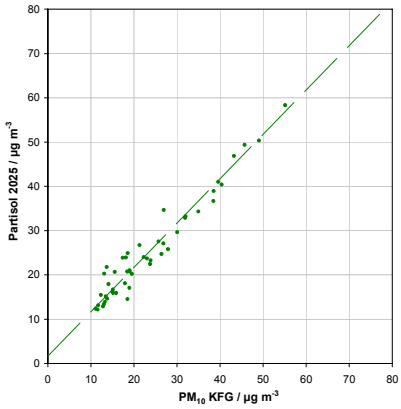
Birmingham Winter



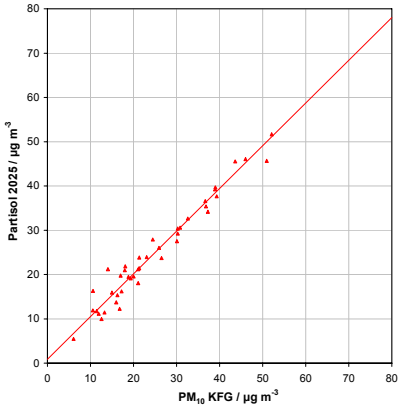
Bristol Winter



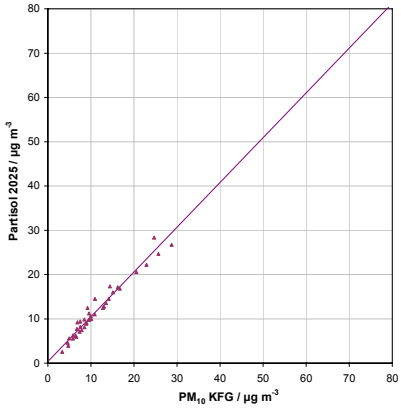
Birmingham Summer



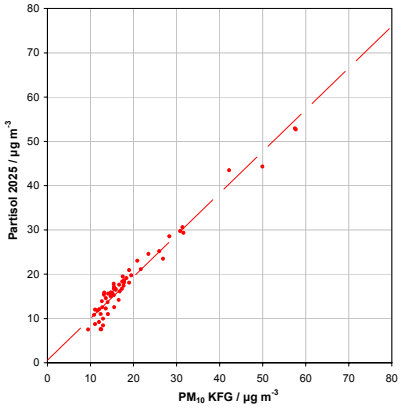
Bristol Summer



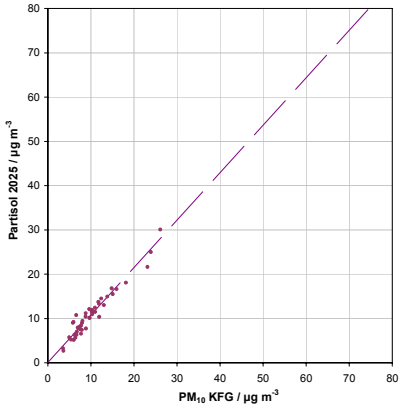
Teddington Winter



East Kilbride Winter

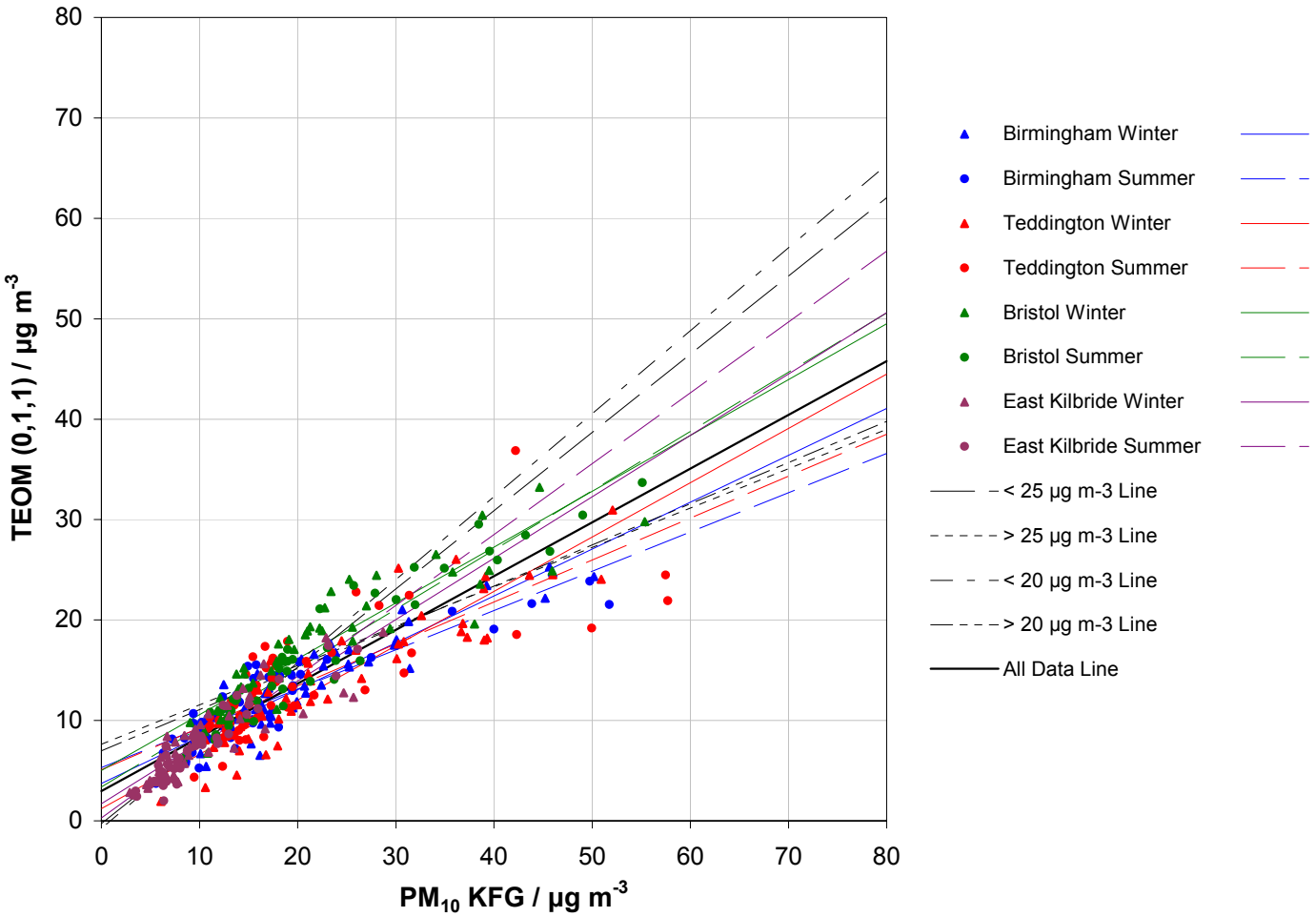


Teddington Summer



East Kilbride Summer

Figure D.2: Chart and Table summarising the comparison of TEOM (0,1,1) Candidate Method against PM_{10} KFG Reference Method. The terms and colours used in the Table are discussed in Section 4.2. u_{bs}, a and u_a have units of µg m^{-3}.



TEOM (0,1,1)	Dataset	1 hour		24 hour		Orthogonal Regression				Annual Limit Value of 40 µg m^3		Daily Limit Value of 50 µg m^3		
		n_{bs}	u_{bs}	n_{bs}	u_{bs}	n_{c-s}	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{CM} / %	% > 50 % LV	W_{CM} / %	% > 50 % LV	(n_{ES},n_{EC})
Individual Campaigns	Birmingham Winter	2600	0.55	107	0.22	59	0.873	0.467 +/- 0.023	3.708 +/- 0.530	88.26	39.0	91.91	25.4	(1,0)
	Birmingham Summer	2080	0.85	85	0.37	45	0.787	0.391 +/- 0.030	5.306 +/- 0.614	95.67	20.0	100.81	13.3	(1,0)
	Teddington Winter	2938	1.08	122	0.32	47	0.833	0.541 +/- 0.035	1.221 +/- 0.944	86.69	53.2	87.55	40.4	(2,0)
	Teddington Summer	2218	1.67	86	0.89	57	0.576	0.418 +/- 0.044	5.095 +/- 0.992	92.59	24.6	97.06	19.3	(2,0)
	Bristol Summer	1351	1.82	53	0.36	44	0.912	0.590 +/- 0.028	3.380 +/- 0.711	65.72	43.2	68.86	31.8	(1,0)
	Bristol Winter	2182	1.34	89	0.67	49	0.817	0.556 +/- 0.037	5.012 +/- 0.889	65.16	44.9	69.60	30.6	(1,0)
	East Kilbride Summer	1554	0.60	61	0.30	44	0.901	0.705 +/- 0.035	0.289 +/- 0.391	57.58	6.8	57.84	2.3	(0,0)
	East Kilbride Winter	1721	0.81	71	0.65	47	0.753	0.611 +/- 0.048	1.709 +/- 0.589	69.79	10.6	71.27	4.3	(0,0)
All Campaigns	All Data	16644	1.15	674	0.52	392	0.797	0.535 +/- 0.013	2.961 +/- 0.282	79.27	30.6	81.80	21.2	(8,0)
Annual Limit Value of 40 µg m^3	< 20 µg m^3	13535	0.89	272	0.37	272	0.669	0.826 +/- 0.030	-0.748 +/- 0.402	39.61	-	-	-	-
	> 20 µg m^3	3109	1.91	122	0.43	120	0.501	0.410 +/- 0.033	6.977 +/- 1.123	84.97	-	-	-	-
Daily Limit Value of 50 µg m^3	< 25 µg m^3	14946	0.95	309	0.38	309	0.717	0.779 +/- 0.025	-0.271 +/- 0.362	-	-	45.98	-	-
	> 25 µg m^3	1698	2.25	85	0.44	83	0.354	0.392 +/- 0.049	7.633 +/- 1.836	-	-	92.36	-	-

- Denotes Not Applicable.

Figure D.2 Continued: Charts summarising the comparison of TEOM (0,1,1) and PM_{10} KFG.

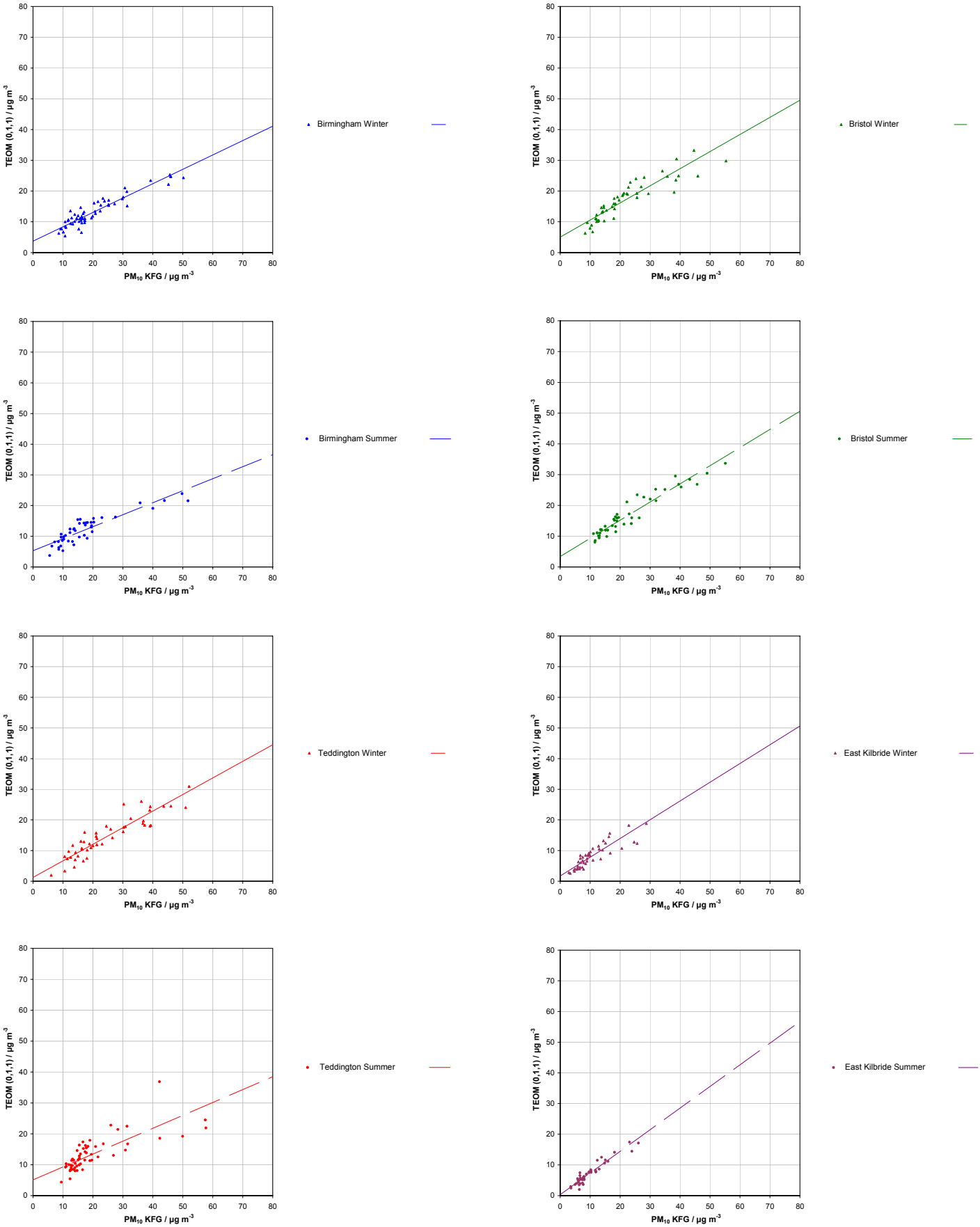
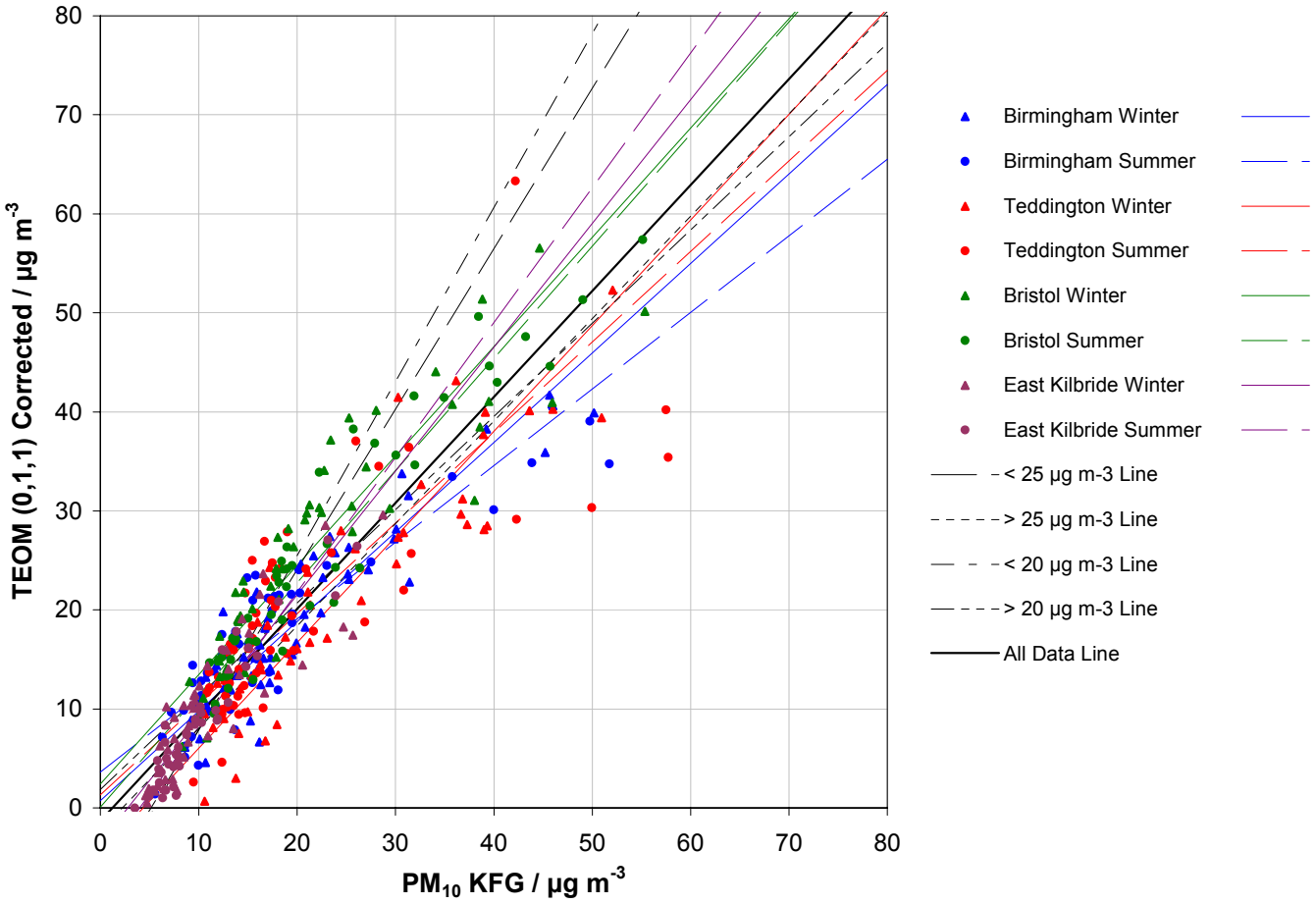


Figure D.3: Chart and Table summarising the comparison of Corrected TEOM (0,1,1) Candidate Method against PM_{10} KFG Reference Method. The terms and colours used in the Table are discussed in Section 4.2. u_{bs}, a and u_a have units of µg m^{-3}.

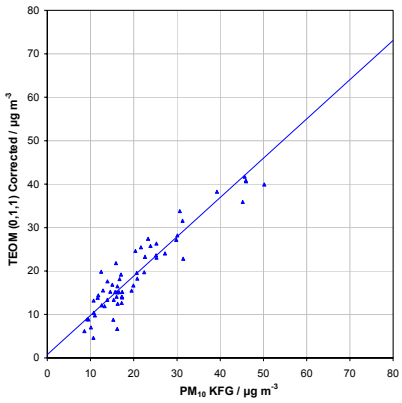
$$TEOM\,(0,1,1)_{Corrected} = \frac{(TEOM\,(0,1,1) - 2.961)}{0.535}$$



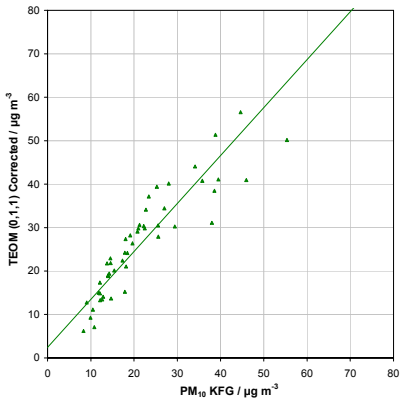
TEOM (0,1,1) Corrected	Dataset	1 hour		24 hour		Orthogonal Regression				Annual Limit Value of 40 µg m^3		Daily Limit Value of 50 µg m^3		
		n_{bs}	u_{bs}	n_{bs}	u_{bs}	n_{c-s}	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{CM} / %	% > 50 % LV	W_{CM} / %	% > 50 % LV	(n_{ES},n_{EC})
Individual Campaigns	Birmingham Winter	2600	1.03	107	0.40	59	0.873	0.904 +/- 0.043	0.734 +/- 0.989	22.06	39.0	20.58	25.4	(1,0)
	Birmingham Summer	2080	1.58	85	0.69	45	0.787	0.773 +/- 0.056	3.634 +/- 1.147	33.55	20.0	34.63	13.3	(1,0)
	Teddington Winter	2938	2.01	122	0.60	47	0.833	1.067 +/- 0.065	-4.639 +/- 1.764	27.87	53.2	21.55	40.4	(2,1)
	Teddington Summer	2218	3.12	86	1.66	57	0.576	0.914 +/- 0.082	1.330 +/- 1.854	36.53	24.6	30.43	19.3	(2,1)
	Bristol Summer	1351	3.41	53	0.67	44	0.912	1.133 +/- 0.052	0.071 +/- 1.328	32.90	43.2	30.86	31.8	(1,2)
	Bristol Winter	2182	2.51	89	1.25	49	0.817	1.104 +/- 0.068	2.412 +/- 1.661	42.21	44.9	37.12	30.6	(1,3)
	East Kilbride Summer	1554	1.12	61	0.56	44	0.901	1.361 +/- 0.065	-5.425 +/- 0.730	46.35	6.8	51.28	2.3	(0,0)
	East Kilbride Winter	1721	1.52	71	1.22	47	0.753	1.250 +/- 0.090	-3.496 +/- 1.101	37.73	10.6	39.19	4.3	(0,0)
All Campaigns	All Data	16644	2.15	674	0.96	392	0.797	1.070 +/- 0.024	-1.312 +/- 0.527	28.07	30.6	23.41	21.2	(8,7)
Annual Limit Value of 40 µg m^3	< 20 µg m^3	9953	1.51	272	0.70	272	0.669	1.757 +/- 0.056	-9.660 +/- 0.751	105.23	-	-	-	-
	> 20 µg m^3	6691	2.85	122	0.80	120	0.501	0.942 +/- 0.062	1.856 +/- 2.098	36.46	-	-	-	-
Daily Limit Value of 50 µg m^3	< 25 µg m^3	11781	1.58	309	0.70	309	0.717	1.620 +/- 0.046	-8.331 +/- 0.677	-	-	92.27	-	-
	> 25 µg m^3	4863	3.12	85	0.82	83	0.354	1.034 +/- 0.091	-2.313 +/- 3.431	-	-	33.45	-	-

- Denotes Not Applicable.

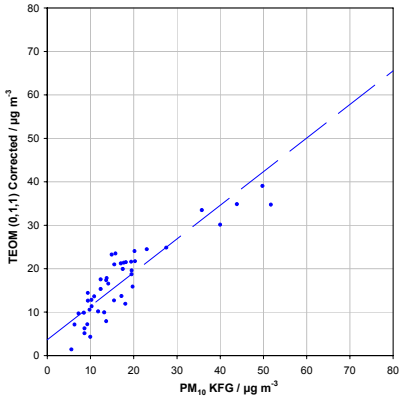
Figure D.3 Continued: Charts summarising the comparison of TEOM (0,1,1) Corrected and PM_{10} KFG.



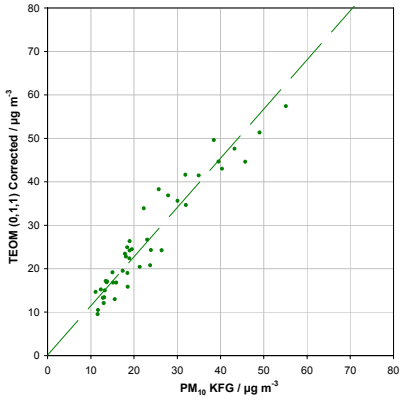
Birmingham Winter



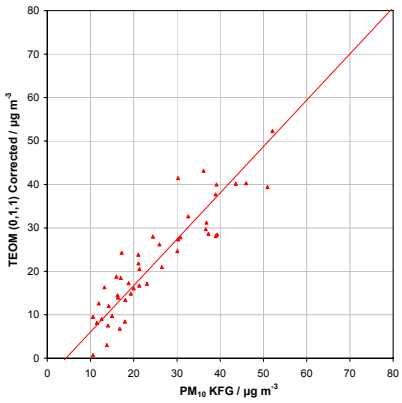
Bristol Winter



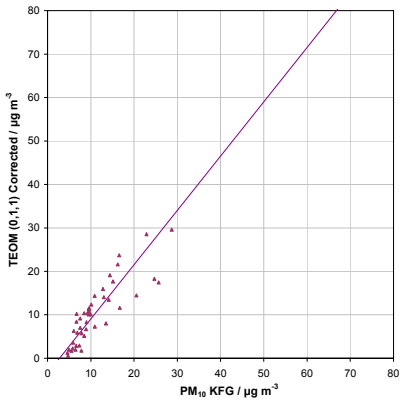
Birmingham Summer



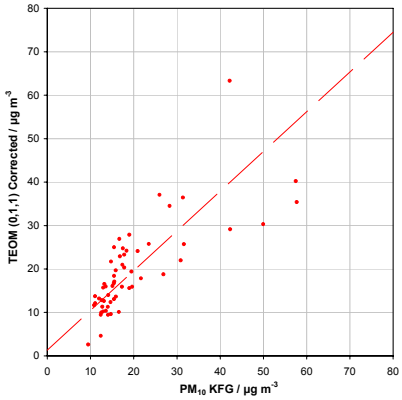
Bristol Summer



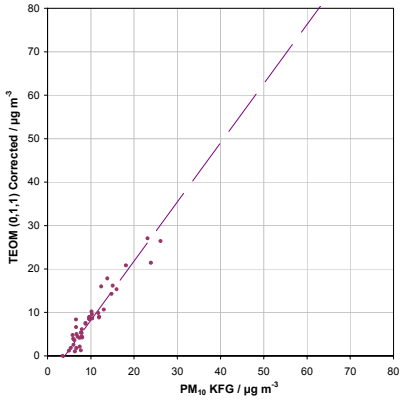
Teddington Winter



East Kilbride Winter

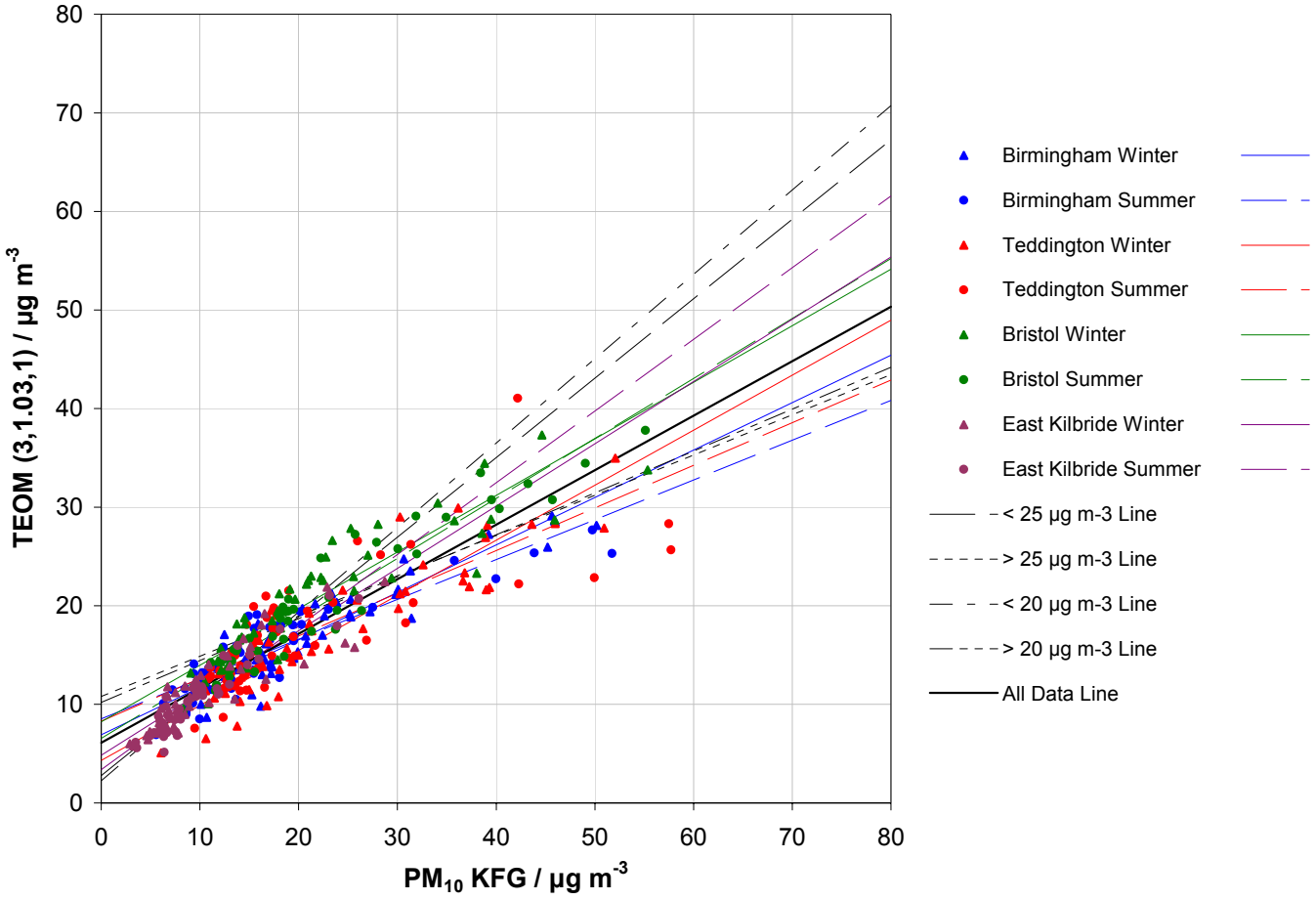


Teddington Summer



East Kilbride Summer

Figure D.4: Chart and Table summarising the comparison of TEOM (3,1.03,1) Candidate Method against PM_{10} KFG Reference Method. The terms and colours used in the Table are discussed in Section 4.2. u_{bs}, a and u_a have units of µg m^{-3}.



TEOM (3,1.03,1)	Dataset	1 hour		24 hour		Orthogonal Regression				Annual Limit Value of 40 µg m^3		Daily Limit Value of 50 µg m^3		
		n_{bs}	u_{bs}	n_{bs}	u_{bs}	n_{c-s}	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{CM} / %	% > 50 % LV	W_{CM} / %	% > 50 % LV	(n_{ES},n_{EC})
Individual Campaigns	Birmingham Winter	2600	0.57	107	0.22	59	0.873	0.481 +/- 0.024	6.897 +/- 0.545	69.48	39.0	76.27	25.4	(1,0)
	Birmingham Summer	2080	0.87	85	0.38	45	0.787	0.404 +/- 0.031	8.543 +/- 0.632	77.14	20.0	85.45	13.3	(1,0)
	Teddington Winter	2938	1.11	122	0.33	47	0.833	0.558 +/- 0.036	4.319 +/- 0.973	68.09	53.2	71.87	40.4	(2,0)
	Teddington Summer	2218	1.72	86	0.91	57	0.576	0.432 +/- 0.045	8.294 +/- 1.022	74.19	24.6	81.58	19.3	(2,0)
	Bristol Summer	1351	1.88	53	0.37	44	0.912	0.608 +/- 0.028	6.556 +/- 0.732	46.50	43.2	52.64	31.8	(1,0)
	Bristol Winter	2182	1.38	89	0.69	49	0.817	0.574 +/- 0.038	8.224 +/- 0.916	46.24	44.9	53.48	30.6	(1,0)
	East Kilbride Summer	1554	0.62	61	0.31	44	0.901	0.728 +/- 0.036	3.377 +/- 0.402	37.79	6.8	41.09	2.3	(0,0)
	East Kilbride Winter	1721	0.84	71	0.67	47	0.753	0.632 +/- 0.050	4.826 +/- 0.607	50.38	10.6	54.82	4.3	(0,0)
All Campaigns	All Data	16644	1.18	674	0.53	392	0.797	0.553 +/- 0.013	6.113 +/- 0.291	60.48	30.6	65.93	21.2	(8,0)
Annual Limit Value of 40 µg m^3	< 20 µg m^3	11845	0.87	272	0.38	272	0.669	0.856 +/- 0.031	2.250 +/- 0.414	19.94	-	-	-	-
	> 20 µg m^3	4799	1.73	122	0.44	120	0.501	0.425 +/- 0.034	10.185 +/- 1.156	66.59	-	-	-	-
Daily Limit Value of 50 µg m^3	< 25 µg m^3	13978	0.92	309	0.39	309	0.717	0.806 +/- 0.025	2.754 +/- 0.373	-	-	28.88	-	-
	> 25 µg m^3	2666	2.07	85	0.45	83	0.354	0.408 +/- 0.050	10.791 +/- 1.891	-	-	76.88	-	-

- Denotes Not Applicable.

Figure D.4 Continued: Charts summarising the comparison of TEOM (3,1.03,1) and PM_{10} KFG.

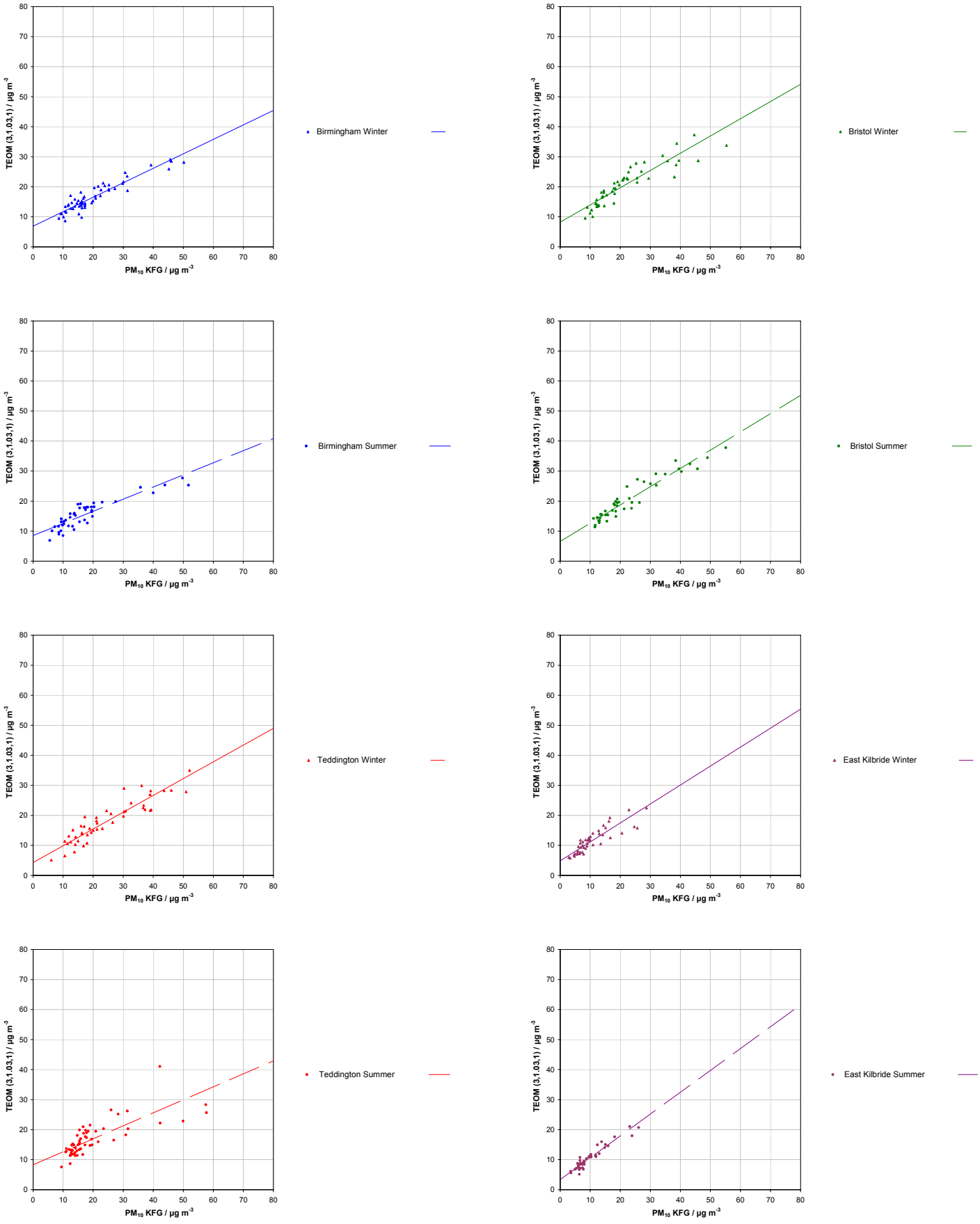
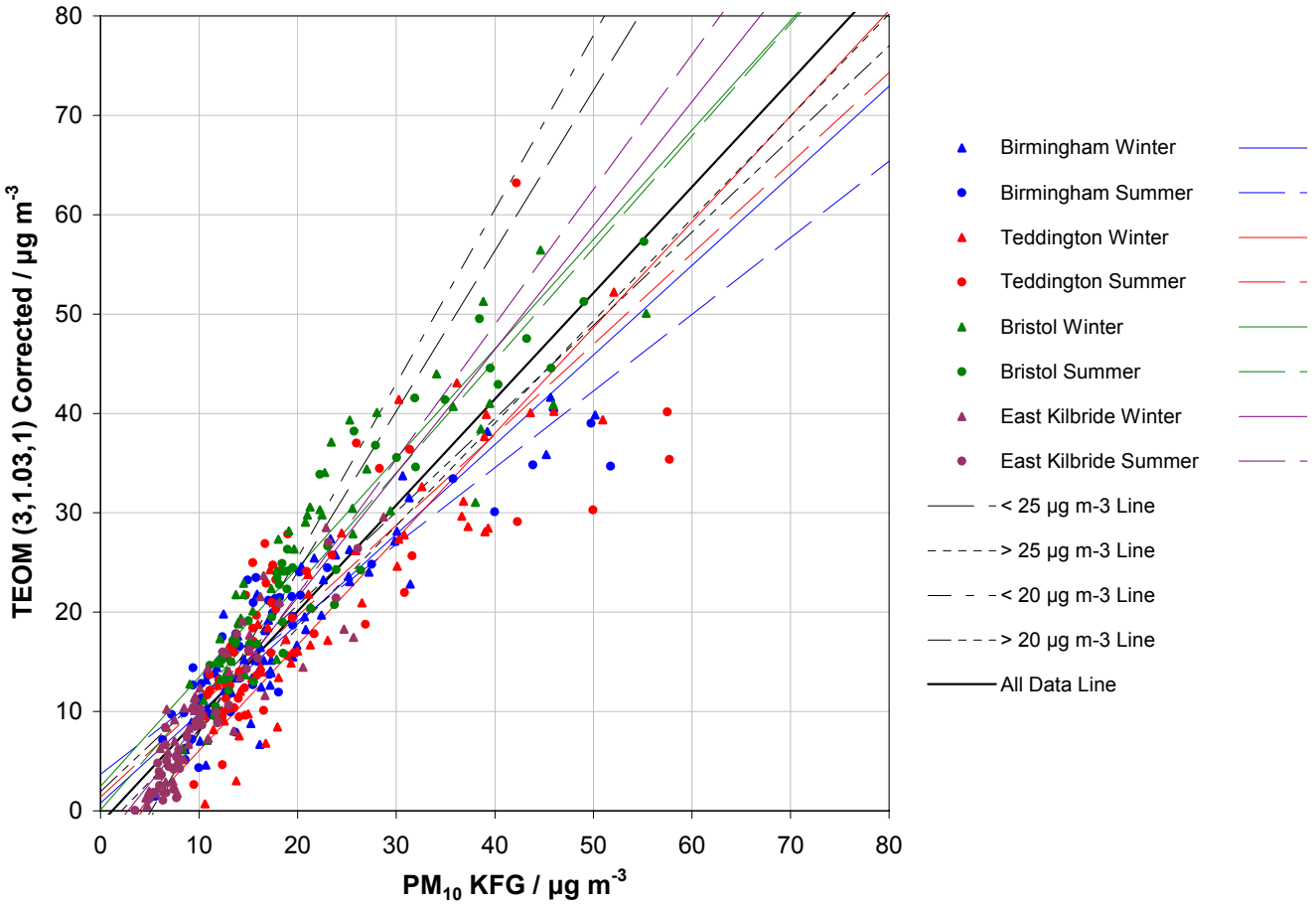


Figure D.5: Chart and Table summarising the comparison of Corrected TEOM (3,1.03,1) Candidate Method against PM_{10} KFG Reference Method. The terms and colours used in the Table are discussed in Section 4.2. u_{bs}, a and u_a have units of µg m^{-3}.

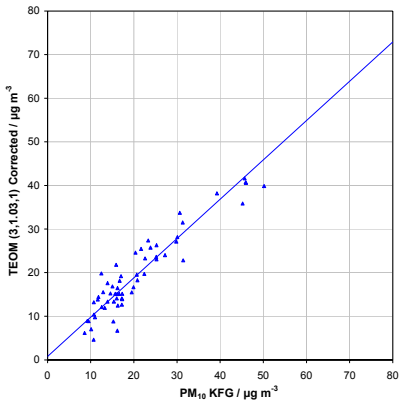
$$TEOM\,(3,1.03,1)_{Corrected} = \frac{(TEOM\,(3,1.03,1) - 6.113)}{0.553}$$



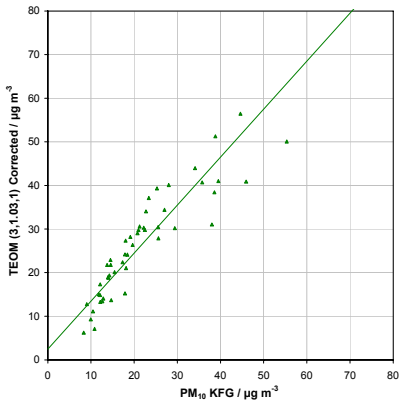
TEOM (3,1.03,1) Corrected	Dataset	1 hour		24 hour		Orthogonal Regression				Annual Limit Value of 40 µg m^3		Daily Limit Value of 50 µg m^3		
		n_{bs}	u_{bs}	n_{bs}	u_{bs}	n_{c-s}	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{CM} / %	% > 50 % LV	W_{CM} / %	% > 50 % LV	(n_{ES},n_{EC})
Individual Campaigns	Birmingham Winter	2600	1.03	107	0.40	59	0.873	0.902 +/- 0.043	0.783 +/- 0.987	22.21	39.0	20.80	25.4	(1,0)
	Birmingham Summer	2080	1.58	85	0.68	45	0.787	0.771 +/- 0.056	3.677 +/- 1.144	33.71	20.0	34.85	13.3	(1,0)
	Teddington Winter	2938	2.00	122	0.60	47	0.833	1.064 +/- 0.064	-4.574 +/- 1.760	27.90	53.2	21.59	40.4	(2,1)
	Teddington Summer	2218	3.11	86	1.66	57	0.576	0.911 +/- 0.082	1.389 +/- 1.849	36.53	24.6	30.51	19.3	(2,1)
	Bristol Summer	1351	3.40	53	0.67	44	0.912	1.130 +/- 0.051	0.122 +/- 1.324	32.59	43.2	30.50	31.8	(1,2)
	Bristol Winter	2182	2.50	89	1.25	49	0.817	1.101 +/- 0.068	2.460 +/- 1.656	41.88	44.9	36.75	30.6	(1,3)
	East Kilbride Summer	1554	1.12	61	0.56	44	0.901	1.358 +/- 0.065	-5.362 +/- 0.728	45.95	6.8	50.81	2.3	(0,0)
	East Kilbride Winter	1721	1.51	71	1.22	47	0.753	1.247 +/- 0.090	-3.434 +/- 1.098	37.35	10.6	38.73	4.3	(0,0)
All Campaigns	All Data	16644	2.14	674	0.96	392	0.797	1.067 +/- 0.024	-1.255 +/- 0.526	27.92	30.6	23.23	21.2	(8,7)
Annual Limit Value of 40 µg m^3	< 20 µg m^3	9953	1.50	272	0.70	272	0.669	1.752 +/- 0.056	-9.578 +/- 0.749	104.60	-	-	-	-
	> 20 µg m^3	6691	2.84	122	0.80	120	0.501	0.938 +/- 0.062	1.931 +/- 2.092	36.38	-	-	-	-
Daily Limit Value of 50 µg m^3	< 25 µg m^3	11810	1.58	309	0.70	309	0.717	1.615 +/- 0.046	-8.253 +/- 0.675	-	-	91.64	-	-
	> 25 µg m^3	4834	3.12	85	0.82	83	0.354	1.030 +/- 0.091	-2.194 +/- 3.422	-	-	33.37	-	-

- Denotes Not Applicable.

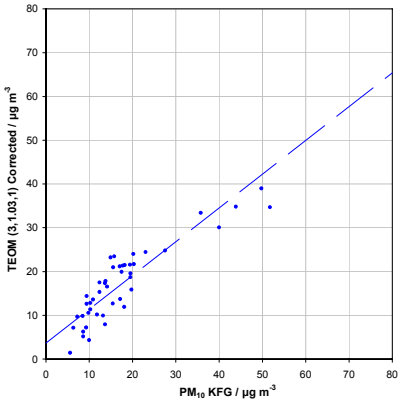
Figure D.5 Continued: Charts summarising the comparison of TEOM (3,1.03,1) Corrected and PM_{10} KFG.



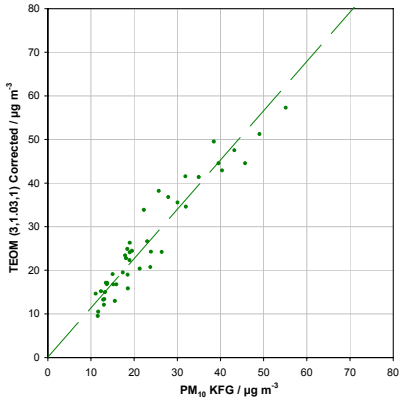
Birmingham Winter



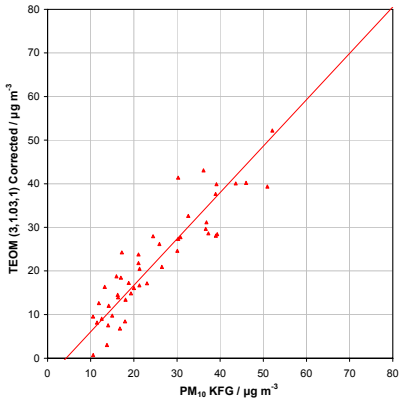
Bristol Winter



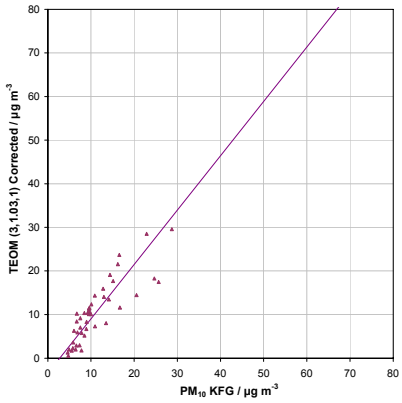
Birmingham Summer



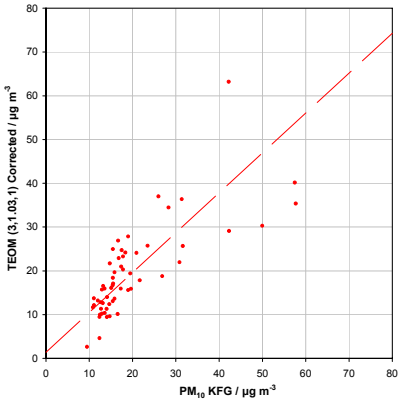
Bristol Summer



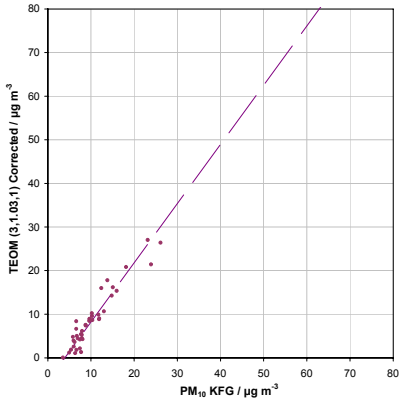
Teddington Winter



East Kilbride Winter

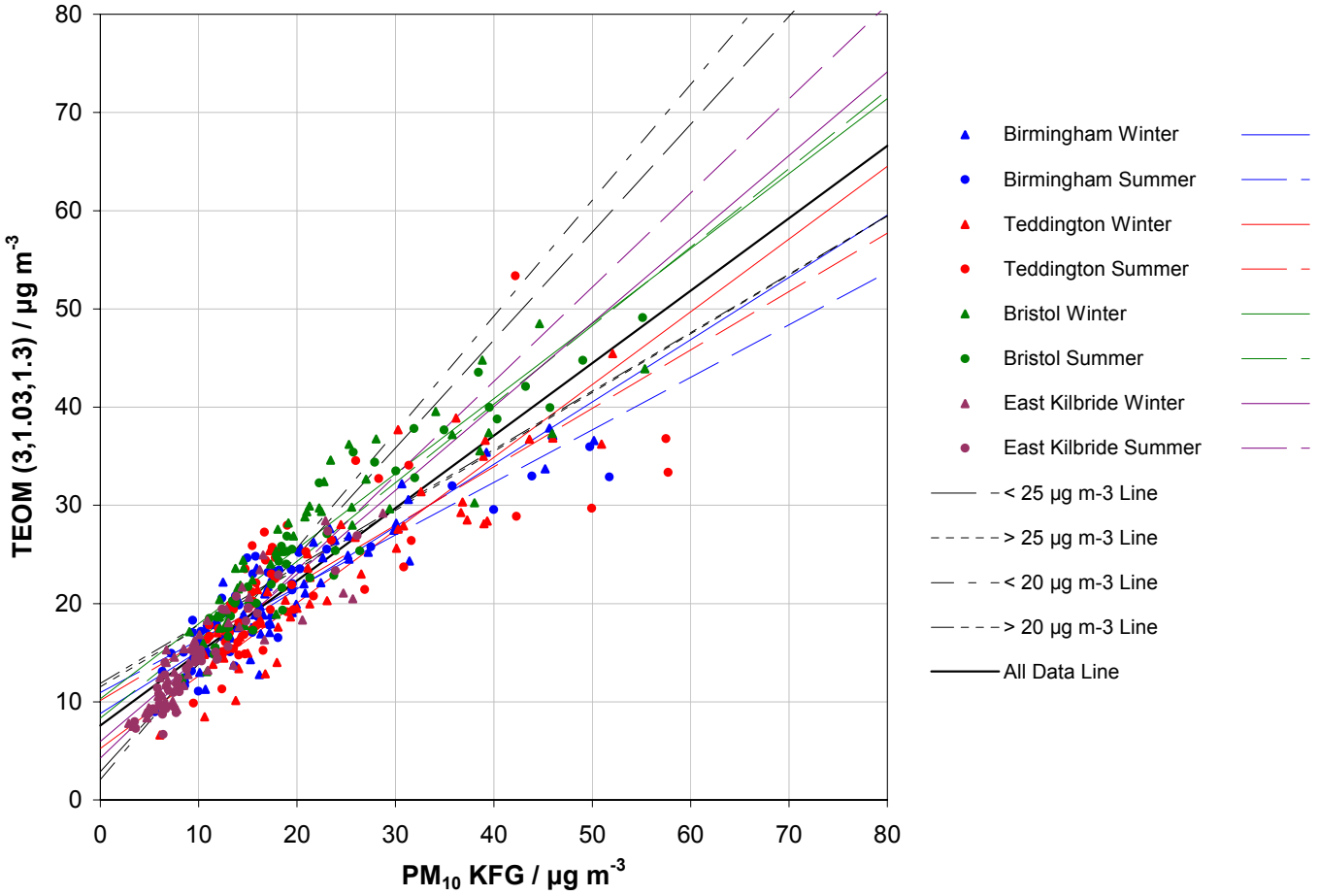


Teddington Summer



East Kilbride Summer

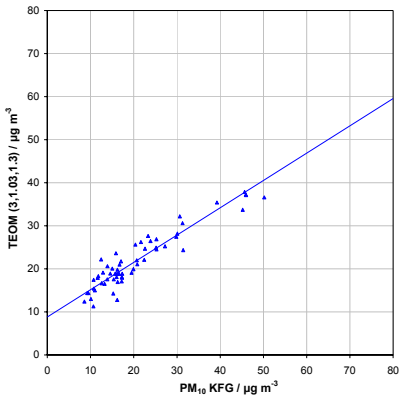
Figure D.6: Chart and Table summarising the comparison of TEOM (3,1.03,1.3) Candidate Method against PM_{10} KFG Reference Method. The terms and colours used in the Table are discussed in Section 4.2. u_{bs}, a and u_a have units of µg m^{-3}.



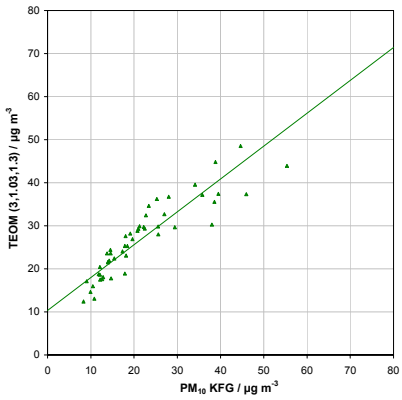
TEOM (3,1.03,1.3)	Dataset	1 hour		24 hour		Orthogonal Regression				Annual Limit Value of 40 µg m^{-3}		Daily Limit Value of 50 µg m^{-3}		
		n_{bs}	u_{bs}	n_{bs}	u_{bs}	n_{c-s}	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{CM} / %	% > 50 % LV	W_{CM} / %	% > 50 % LV	(n_{ES},n_{EC})
Individual Campaigns	Birmingham Winter	2600	0.74	107	0.29	59	0.873	0.634 +/- 0.031	8.792 +/- 0.709	30.77	39.0	38.77	25.4	(1,0)
	Birmingham Summer	2080	1.13	85	0.49	45	0.787	0.535 +/- 0.040	10.921 +/- 0.822	40.55	20.0	50.39	13.3	(1,0)
	Teddington Winter	2938	1.44	122	0.43	47	0.833	0.741 +/- 0.046	5.236 +/- 1.265	31.31	53.2	34.04	40.4	(2,0)
	Teddington Summer	2218	2.23	86	1.19	57	0.576	0.595 +/- 0.059	10.131 +/- 1.328	38.56	24.6	44.73	19.3	(2,1)
	Bristol Summer	1351	2.44	53	0.48	44	0.912	0.799 +/- 0.037	8.322 +/- 0.951	12.90	43.2	12.32	31.8	(1,0)
	Bristol Winter	2182	1.80	89	0.90	49	0.817	0.764 +/- 0.049	10.300 +/- 1.190	18.97	44.9	15.94	30.6	(1,0)
	East Kilbride Summer	1554	0.80	61	0.40	44	0.901	0.959 +/- 0.047	4.261 +/- 0.523	14.53	6.8	10.16	2.3	(0,0)
	East Kilbride Winter	1721	1.09	71	0.87	47	0.753	0.852 +/- 0.065	5.946 +/- 0.789	12.93	10.6	11.85	4.3	(0,0)
All Campaigns	All Data	16644	1.54	674	0.69	392	0.797	0.738 +/- 0.017	7.591 +/- 0.378	23.58	30.6	26.65	21.2	(8,1)
Annual Limit Value of 40 µg m^{-3}	< 20 µg m^{-3}	8402	1.05	272	0.50	272	0.669	1.180 +/- 0.040	2.075 +/- 0.538	48.29	-	-	-	-
	> 20 µg m^{-3}	8242	1.91	122	0.57	120	0.501	0.595 +/- 0.045	11.885 +/- 1.503	32.68	-	-	-	-
Daily Limit Value of 50 µg m^{-3}	< 25 µg m^{-3}	11388	1.13	309	0.50	309	0.717	1.099 +/- 0.033	2.879 +/- 0.485	-	-	33.20	-	-
	> 25 µg m^{-3}	5256	2.18	85	0.59	83	0.354	0.599 +/- 0.065	11.514 +/- 2.459	-	-	40.38	-	-

- Denotes Not Applicable.

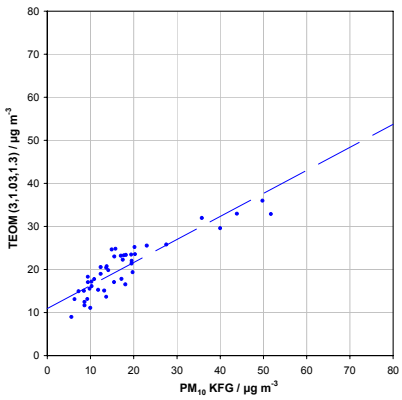
Figure D.6 Continued: Charts summarising the comparison of TEOM (3,1.03,1.3) and PM_{10} KFG.



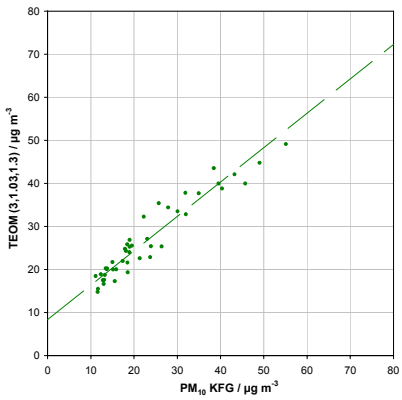
Birmingham Winter



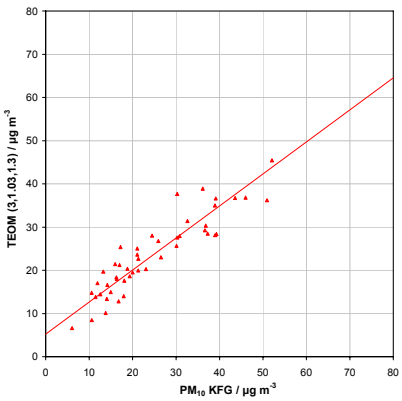
Bristol Winter



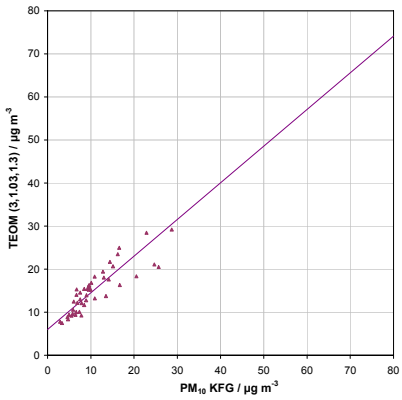
Birmingham Summer



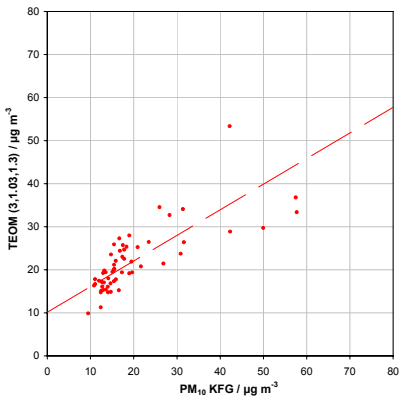
Bristol Summer



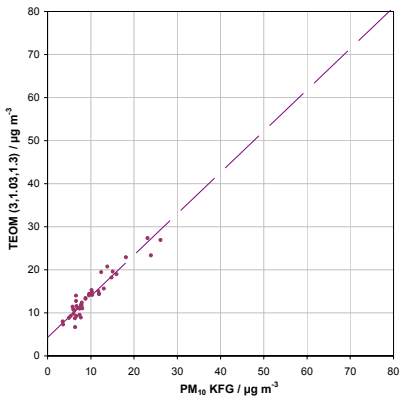
Teddington Winter



East Kilbride Winter

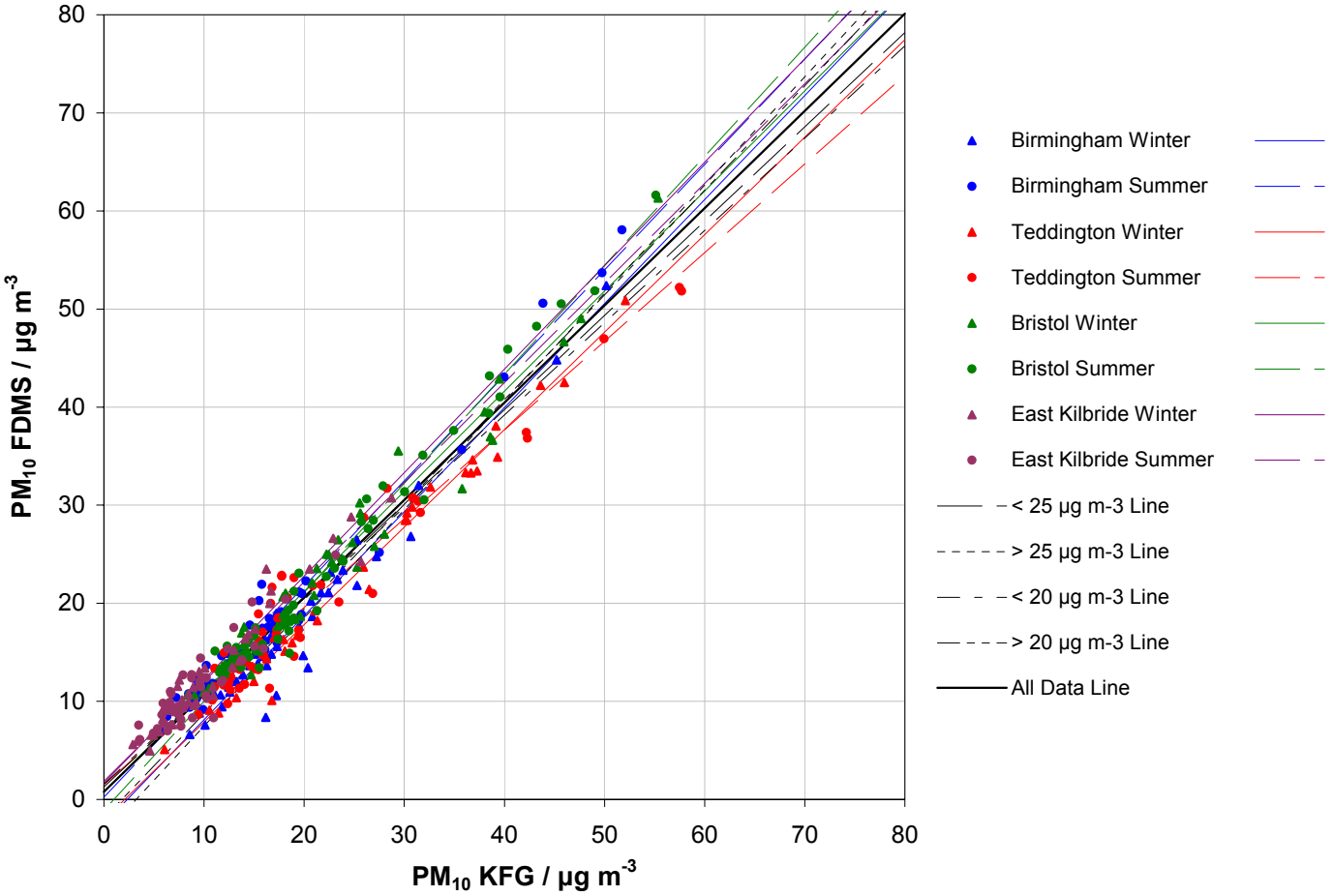


Teddington Summer



East Kilbride Summer

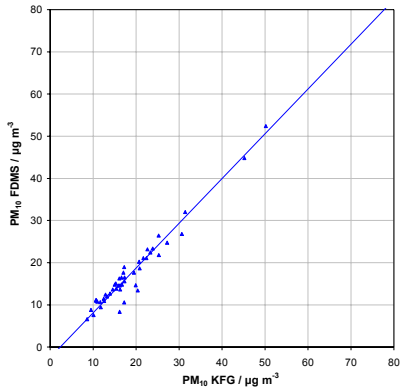
Figure D.7: Chart and Table summarising the comparison of PM_{10} FDMS Candidate Method against PM_{10} KFG Reference Method. The terms and colours used in the Table are discussed in Section 4.2. u_{bs}, a and u_a have units of µg m^{-3}.



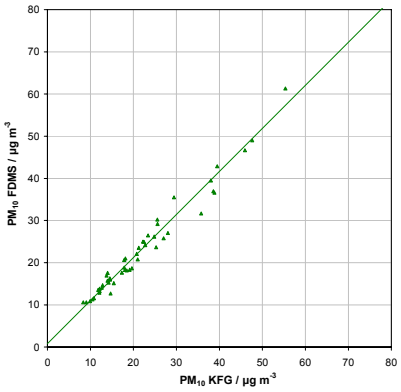
PM_{10} FDMS	Dataset	1 hour		24 hour		Orthogonal Regression				Annual Limit Value of 40 µg m^3		Daily Limit Value of 50 µg m^3		
		n_{bs}	u_{bs}	n_{bs}	u_{bs}	n_{c-s}	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{CM} / %	% > 50 % LV	W_{CM} / %	% > 50 % LV	(n_{ES},n_{EC})
Individual Campaigns	Birmingham Winter	1842	2.10	75	1.15	47	0.945	1.061 +/- 0.037	-2.481 +/- 0.749	7.52	31.9	6.39	14.9	(1,1)
	Birmingham Summer	2164	2.00	83	1.39	50	0.971	1.075 +/- 0.026	0.216 +/- 0.519	17.71	14.0	16.97	12.0	(1,3)
	Teddington Winter	2082	1.22	86	0.34	33	0.984	0.994 +/- 0.022	-2.066 +/- 0.626	12.95	54.5	10.57	48.5	(1,1)
	Teddington Summer	2461	3.10	97	1.08	56	0.942	0.905 +/- 0.030	1.487 +/- 0.675	15.89	25.0	15.73	19.6	(2,2)
	Bristol Summer	1461	1.51	60	0.80	51	0.979	1.111 +/- 0.023	-1.108 +/- 0.580	18.31	43.1	18.82	33.3	(1,3)
	Bristol Winter	2151	1.59	88	0.55	49	0.968	1.021 +/- 0.027	0.796 +/- 0.643	12.56	44.9	10.61	28.6	(1,1)
	East Kilbride Summer	1493	2.04	56	1.54	42	0.819	1.016 +/- 0.068	1.872 +/- 0.686	14.60	2.4	12.23	0.0	(0,0)
	East Kilbride Winter	1957	2.13	81	1.61	47	0.946	1.055 +/- 0.037	1.668 +/- 0.447	20.51	10.6	18.51	4.3	(0,0)
All Campaigns	All Data	15611	2.08	626	1.12	375	0.947	0.991 +/- 0.012	0.797 +/- 0.249	11.43	27.7	9.08	19.5	(7,11)
Annual Limit Value of 40 µg m^3	< 20 µg m^3	10026	1.76	271	1.16	271	0.732	0.941 +/- 0.030	1.553 +/- 0.402	10.01	-	-	-	-
	> 20 µg m^3	5585	2.55	104	0.99	104	0.916	1.067 +/- 0.031	-1.931 +/- 1.028	15.37	-	-	-	-
Daily Limit Value of 50 µg m^3	< 25 µg m^3	11704	1.77	302	1.13	302	0.802	0.962 +/- 0.025	1.278 +/- 0.361	-	-	7.97	-	-
	> 25 µg m^3	3907	2.80	73	1.04	73	0.887	1.103 +/- 0.044	-3.558 +/- 1.637	-	-	14.68	-	-

- Denotes Not Applicable.

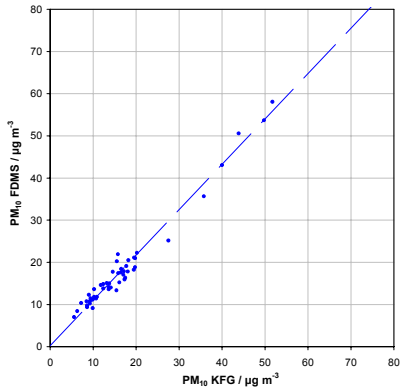
Figure D.7 Continued: Charts summarising the comparison of PM_{10} FDMS and PM_{10} KFG.



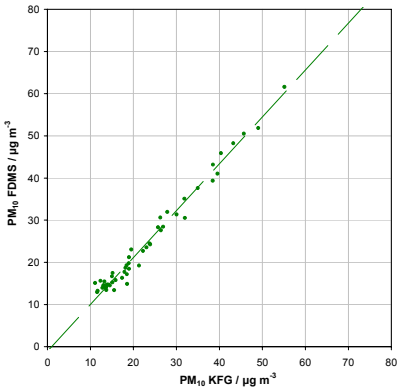
Birmingham Winter



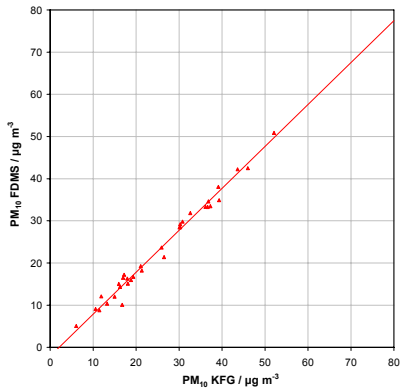
Bristol Winter



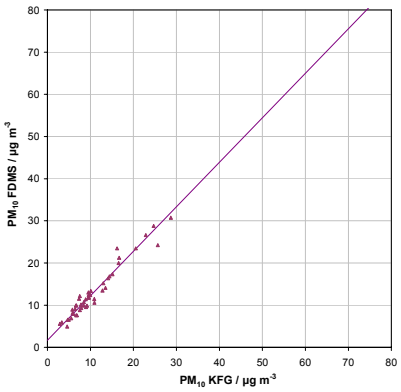
Birmingham Summer



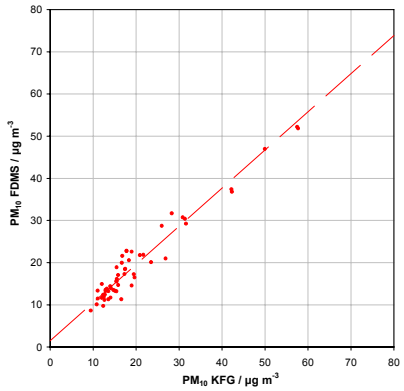
Bristol Summer



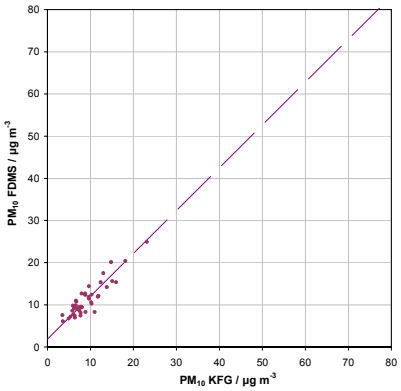
Teddington Winter



East Kilbride Winter

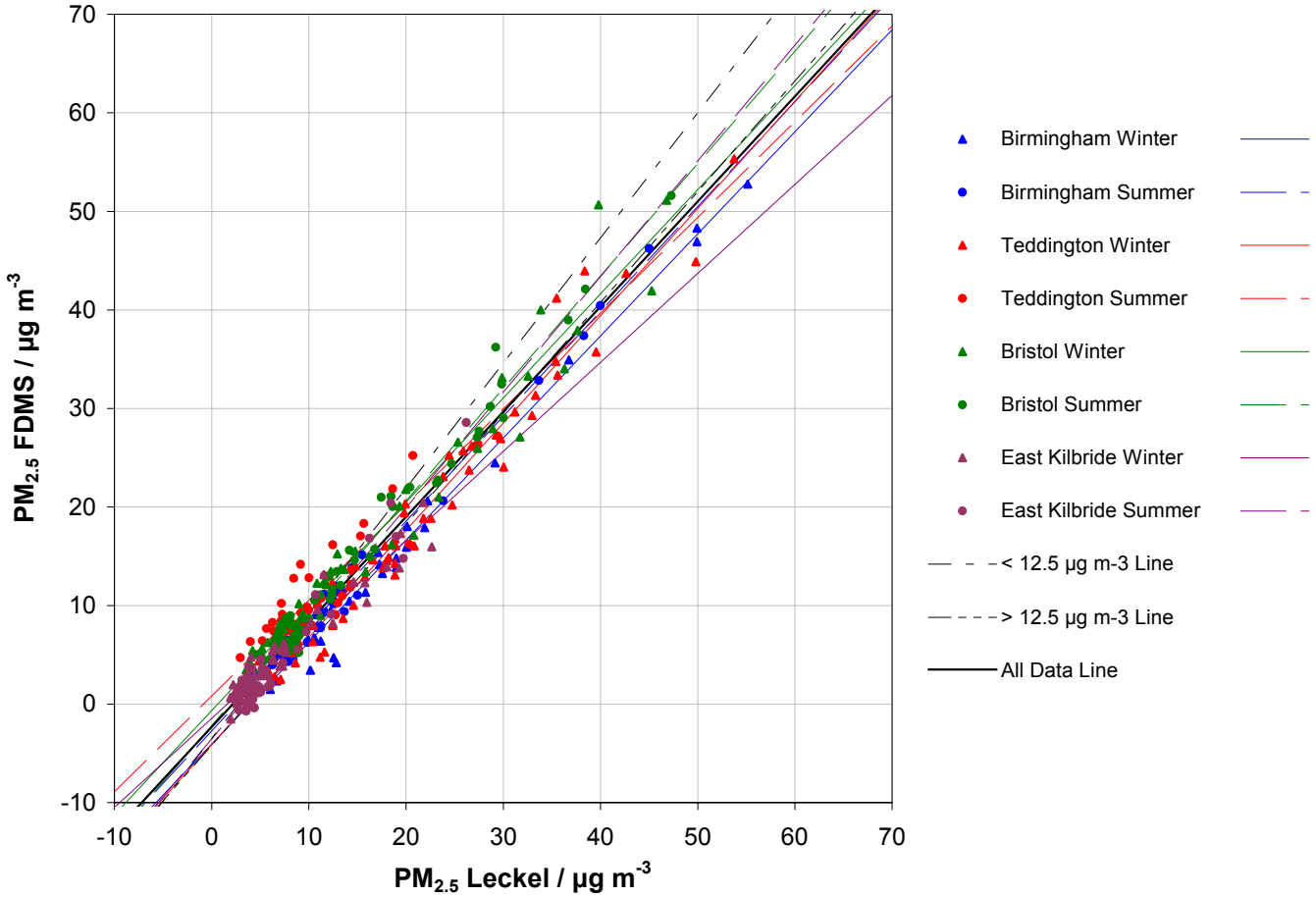


Teddington Summer



East Kilbride Summer

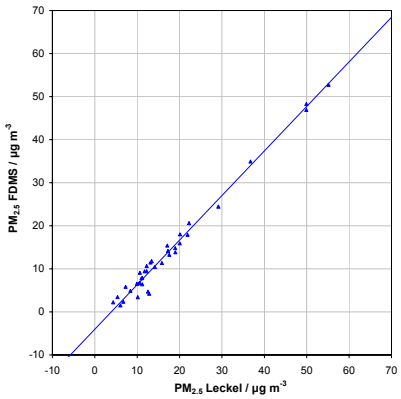
Figure D.8: Chart and Table summarising the comparison of $PM_{2.5}$ FDMS Candidate Method against $PM_{2.5}$ Leckel Reference Method. The terms and colours used in the Table are discussed in Section 4.2. u_{bs}, a and u_a have units of µg m^{-3}.



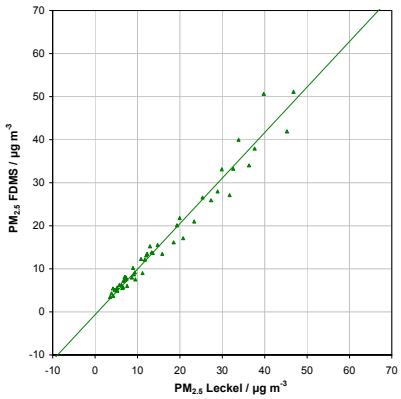
PM2.5 FDMS	Dataset	1 hour		24 hour		Orthogonal Regression				Annual Limit Value of 25 µg m-3		CEN LV of 35 µg m-3
		n_{bs}	u_{bs}	n_{bs}	u_{bs}	n_{c-s}	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{CM} / %	% > 50 % LV	W_{CM} / %
Individual Campaigns	Birmingham Winter	1106	2.94	46	1.37	37	0.982	1.036 +/- 0.023	-4.060 +/- 0.493	28.61	54.1	18.66
	Birmingham Summer	1958	1.83	72	1.03	33	0.990	1.065 +/- 0.019	-2.744 +/- 0.336	12.52	39.4	6.78
	Teddington Winter	2953	1.66	123	0.63	63	0.969	1.088 +/- 0.024	-4.130 +/- 0.551	22.62	63.5	13.25
	Teddington Summer	2207	2.06	87	0.92	40	0.852	0.971 +/- 0.061	0.819 +/- 0.757	17.28	30.0	12.37
	Bristol Summer	1460	2.89	60	1.01	51	0.981	1.140 +/- 0.022	-2.187 +/- 0.405	15.49	43.1	17.55
	Bristol Winter	2269	1.77	93	1.08	51	0.965	1.058 +/- 0.028	-0.672 +/- 0.557	19.50	43.1	15.29
	East Kilbride Summer	1338	1.78	53	1.00	48	0.934	1.173 +/- 0.044	-3.541 +/- 0.366	14.07	10.4	16.98
	East Kilbride Winter	2057	1.78	82	0.83	44	0.929	0.903 +/- 0.037	-1.478 +/- 0.355	33.15	18.2	28.93
All Campaigns	All Data	15348	2.04	616	0.96	367	0.956	1.067 +/- 0.012	-2.331 +/- 0.202	19.26	38.7	13.22
Annual Limit Value of 25 µg m-3	< 12.5 µg m-3	10079	1.86	220	0.93	217	0.702	1.270 +/- 0.046	-3.497 +/- 0.358	30.60	-	-
	> 12.5 µg m-3	5269	2.34	142	0.84	142	0.935	1.123 +/- 0.024	-4.181 +/- 0.620	24.45	-	-

- Denotes Not Applicable.

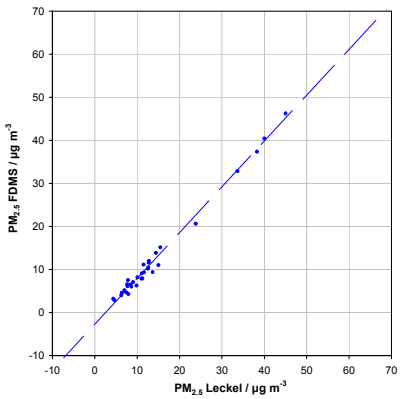
Figure D.8 Continued: Charts summarising the comparison of $PM_{2.5}$ FDMS and $PM_{2.5}$ Leckel.



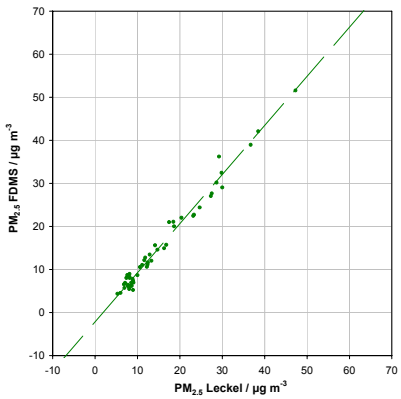
Birmingham Winter



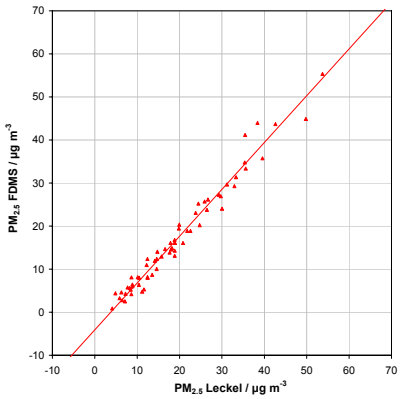
Bristol Winter



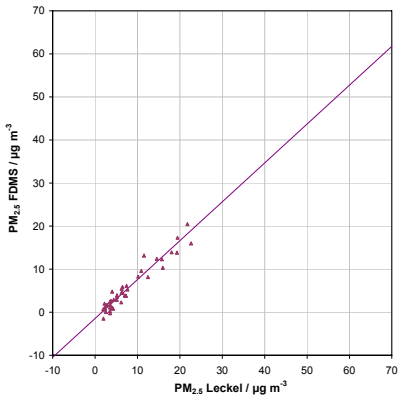
Birmingham Summer



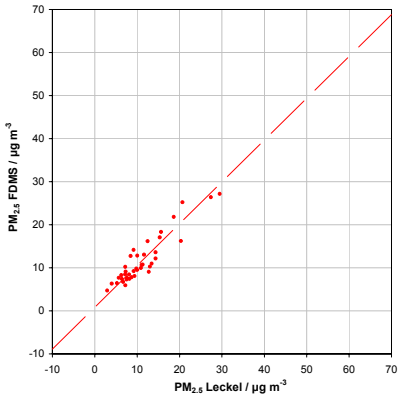
Bristol Summer



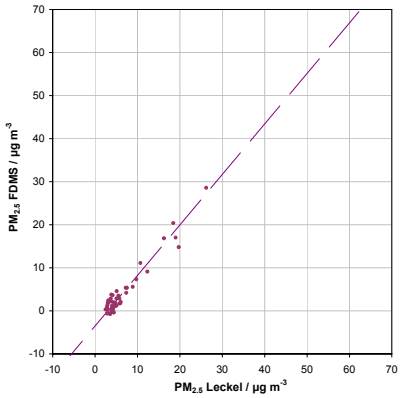
Teddington Winter



East Kilbride Winter

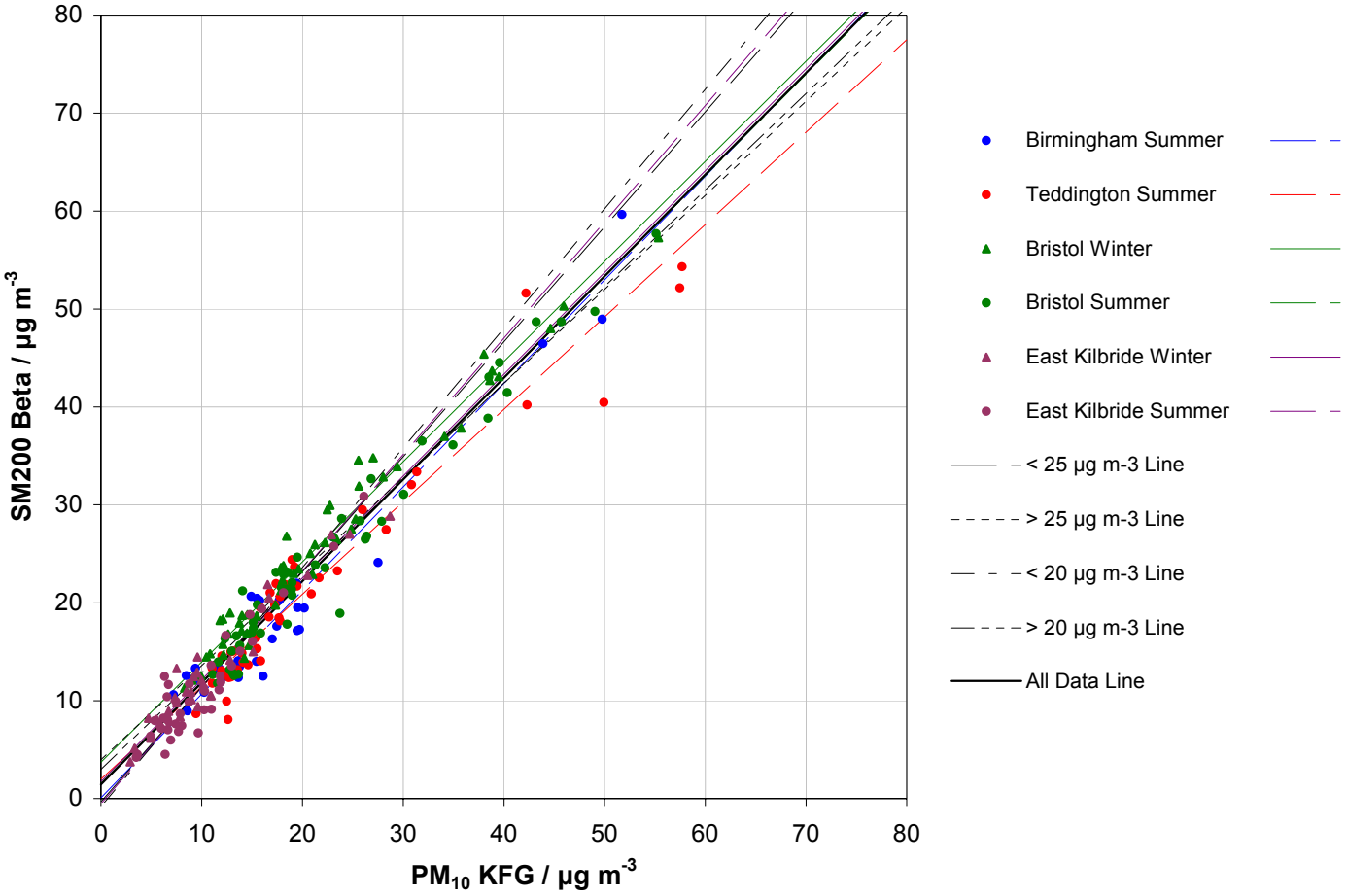


Teddington Summer



East Kilbride Summer

Figure D.9: Chart and Table summarising the comparison of SM200 Beta Candidate Method against PM_{10} KFG Reference Method. The terms and colours used in the Table are discussed in Section 4.2. u_{bs}, a and u_a have units of µg m^{-3}.



SM200 Beta	Dataset	Grubbs' Test		24 hour		Orthogonal Regression				Annual Limit Value of 40 µg m³		Daily Limit Value of 50 µg m³		
		n_G	n_{Gmax}	n_{bs}	u_{bs}	n_{c-s}	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{CM} / %	% > 50 % LV	W_{CM} / %	% > 50 % LV	(n_{ES},n_{EC})
Individual Campaigns	Birmingham Winter	-	-	-	-	-	-	- - -	- - -	-	-	-	-	-
	Birmingham Summer	-	-	46	1.44	29	0.944	1.058 +/- 0.048	0.081 +/- 1.047	17.77	20.7	15.87	13.8	(1,1)
	Teddington Winter	-	-	-	-	-	-	- - -	- - -	-	-	-	-	-
	Teddington Summer	-	-	66	3.04	45	0.932	0.944 +/- 0.038	1.978 +/- 0.889	13.79	26.7	11.46	20.0	(2,3)
	Bristol Summer	-	-	57	1.34	48	0.962	1.034 +/- 0.030	1.555 +/- 0.756	17.82	43.8	15.41	33.3	(1,1)
	Bristol Winter	-	-	64	2.88	50	0.972	1.023 +/- 0.025	3.727 +/- 0.606	24.83	46.0	20.71	30.0	(1,2)
	East Kilbride Summer	-	-	52	1.57	38	0.883	1.189 +/- 0.067	-0.542 +/- 0.750	36.21	5.3	36.33	2.6	(0,0)
	East Kilbride Winter	-	-	50	1.18	32	0.938	1.040 +/- 0.047	1.721 +/- 0.579	18.25	12.5	16.07	3.1	(0,0)
All Campaigns	All Data	-	-	335	2.14	242	0.949	1.038 +/- 0.015	1.437 +/- 0.321	19.08	28.1	16.48	19.0	(5,7)
Annual Limit Value of 40 µg m³	< 20 µg m³	-	-	174	1.89	174	0.810	1.221 +/- 0.040	-0.814 +/- 0.529	41.39	-	-	-	-
	> 20 µg m³	-	-	68	1.88	68	0.903	0.986 +/- 0.038	2.979 +/- 1.286	19.97	-	-	-	-
Daily Limit Value of 50 µg m³	< 25 µg m³	-	-	196	1.94	196	0.853	1.175 +/- 0.032	-0.355 +/- 0.466	-	-	34.52	-	-
	> 25 µg m³	-	-	46	1.66	46	0.864	0.961 +/- 0.054	3.962 +/- 2.053	-	-	15.95	-	-

- Denotes Not Applicable.

Figure D.9 Continued: Charts summarising the comparison of SM200 Beta and PM_{10} KFG.

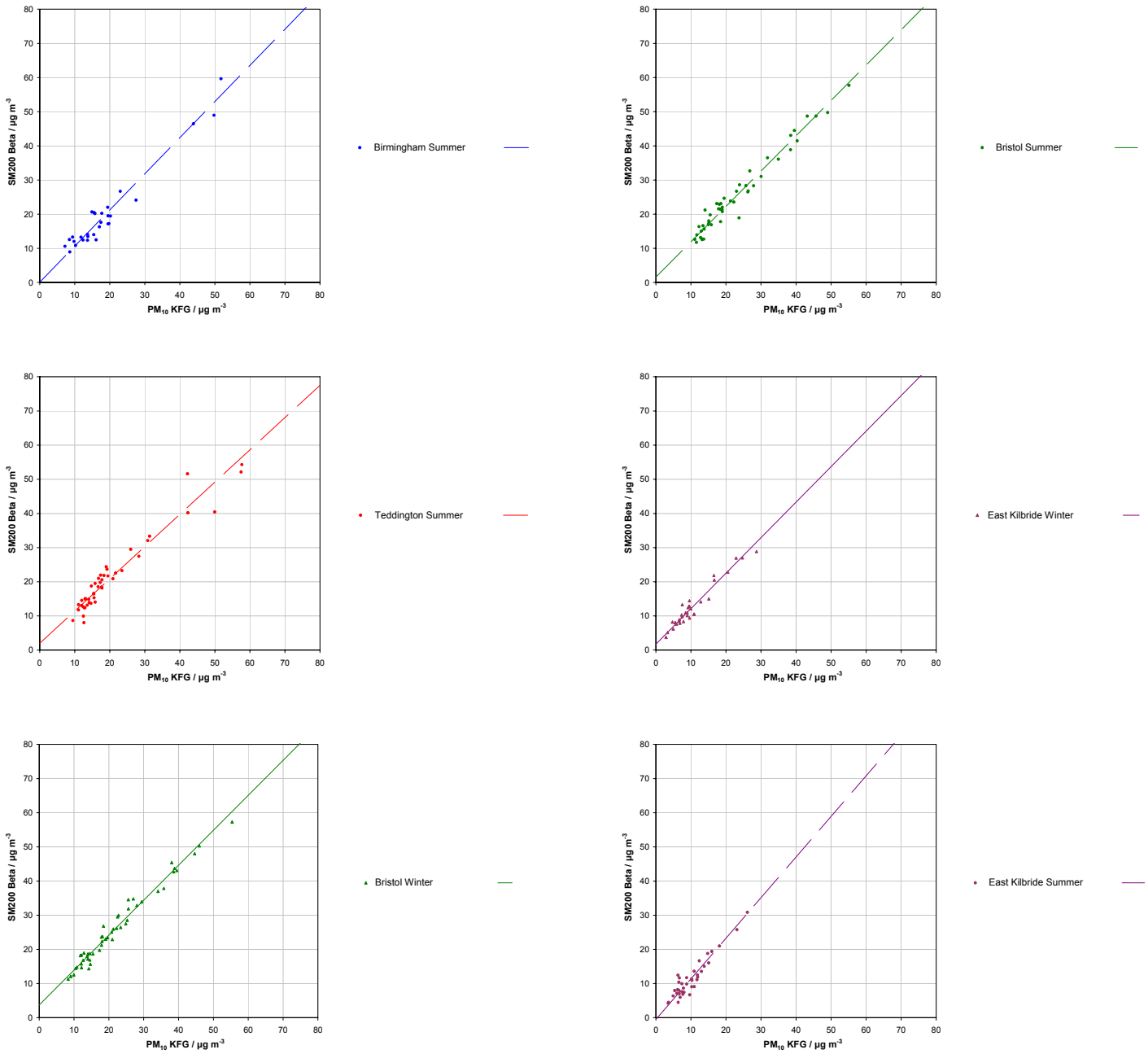
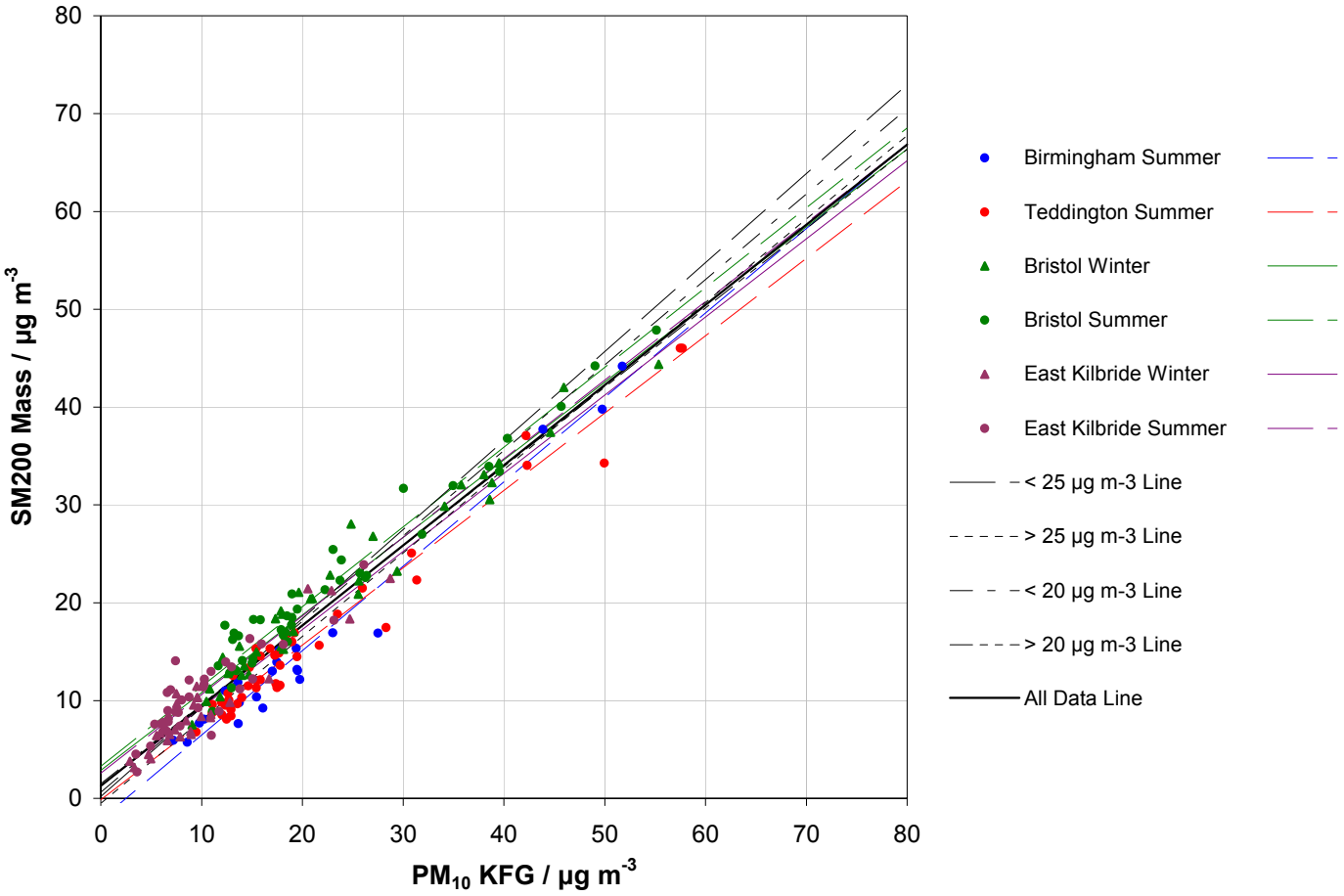


Figure D.10: Chart and Table summarising the comparison of SM200 Mass Candidate Method against PM_{10} KFG Reference Method. The terms and colours used in the Table are discussed in Section 4.2. u_{bs}, a and u_a have units of µg m^{-3}.



SM200 Mass	Dataset	Grubbs' Test		24 hour		Orthogonal Regression				Annual Limit Value of 40 µg m^3		Daily Limit Value of 50 µg m^3		
		n_G	n_{Gmax}	n_{bs}	u_{bs}	n_{c-s}	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{CM} / %	% > 50 % LV	W_{CM} / %	% > 50 % LV	(n_{ES},n_{EC})
Individual Campaigns	Birmingham Winter	-	-	-	-	-	-	- - -	- - -	-	-	-	-	-
	Birmingham Summer	0	0	31	2.08	22	0.968	0.863 +/- 0.035	-2.151 +/- 0.820	38.92	22.7	36.53	18.2	(1,0)
	Teddington Winter	-	-	-	-	-	-	- - -	- - -	-	-	-	-	-
	Teddington Summer	1	1	56	1.62	43	0.964	0.791 +/- 0.024	-0.142 +/- 0.564	43.20	25.6	42.84	20.9	(2,0)
	Bristol Summer	3	4	44	1.42	38	0.957	0.816 +/- 0.028	3.295 +/- 0.728	22.10	42.1	24.65	31.6	(1,0)
	Bristol Winter	2	2	51	1.38	37	0.958	0.794 +/- 0.028	2.861 +/- 0.724	28.48	45.9	30.70	35.1	(1,0)
	East Kilbride Summer	2	2	46	0.93	35	0.773	0.804 +/- 0.068	2.580 +/- 0.768	27.93	5.7	29.88	2.9	(0,0)
	East Kilbride Winter	1	1	46	0.94	29	0.889	0.799 +/- 0.052	1.280 +/- 0.629	34.83	13.8	35.73	3.4	(0,0)
All Campaigns	All Data	-	-	274	1.41	204	0.932	0.819 +/- 0.015	1.286 +/- 0.327	31.85	27.0	32.33	19.6	(5,0)
Annual Limit Value of 40 µg m^3	< 20 µg m^3	-	-	149	1.44	149	0.662	0.874 +/- 0.043	0.630 +/- 0.572	24.65	-	-	-	-
	> 20 µg m^3	-	-	55	1.30	55	0.894	0.810 +/- 0.037	1.515 +/- 1.297	33.35	-	-	-	-
Daily Limit Value of 50 µg m^3	< 25 µg m^3	-	-	164	1.41	164	0.740	0.910 +/- 0.037	0.191 +/- 0.533	-	-	19.58	-	-
	> 25 µg m^3	-	-	40	1.36	40	0.895	0.853 +/- 0.045	-0.518 +/- 1.768	-	-	33.12	-	-

- Denotes Not Applicable.

Figure D.10 Continued: Charts summarising the comparison of SM200 Mass and PM_{10} KFG.

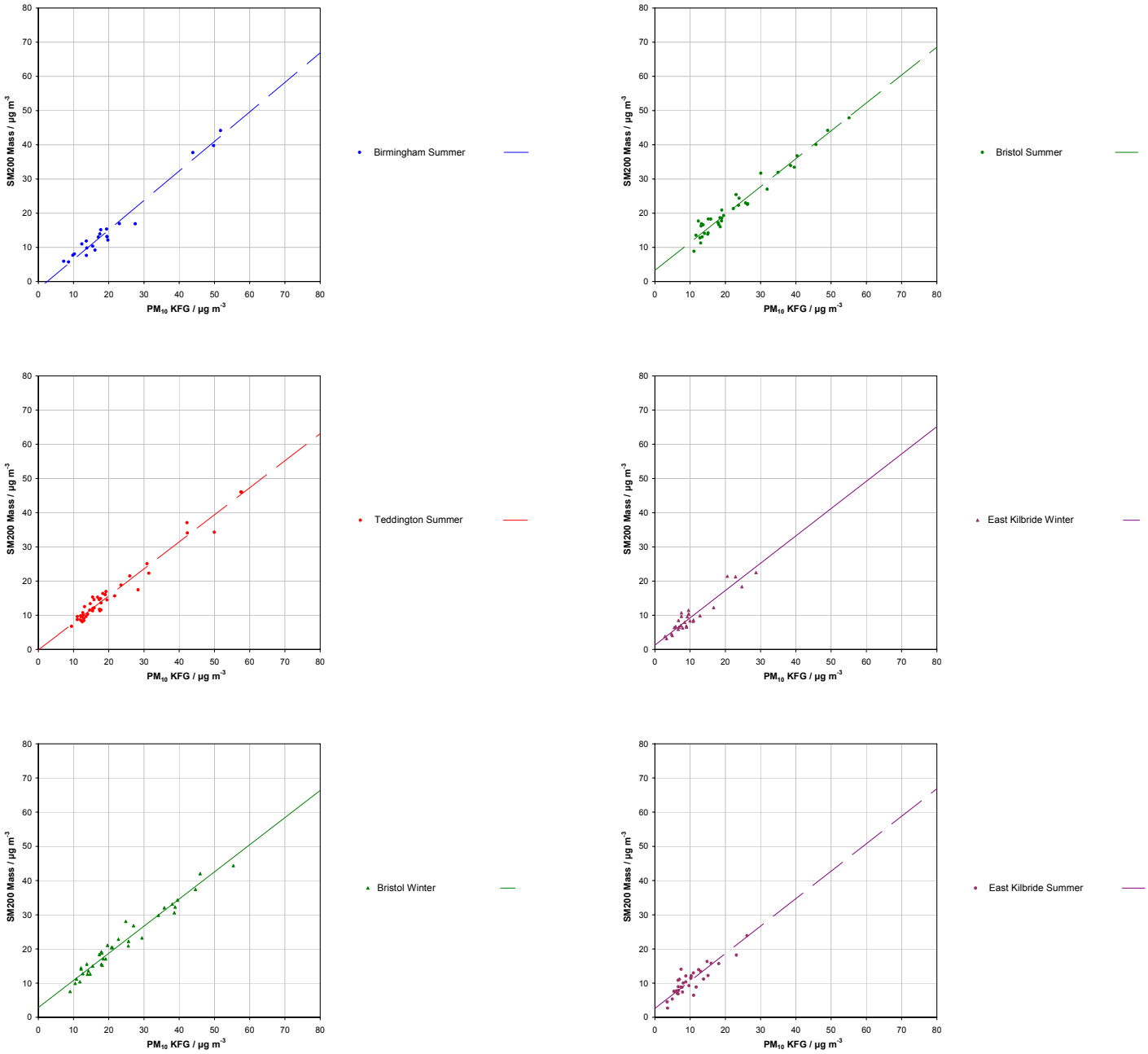
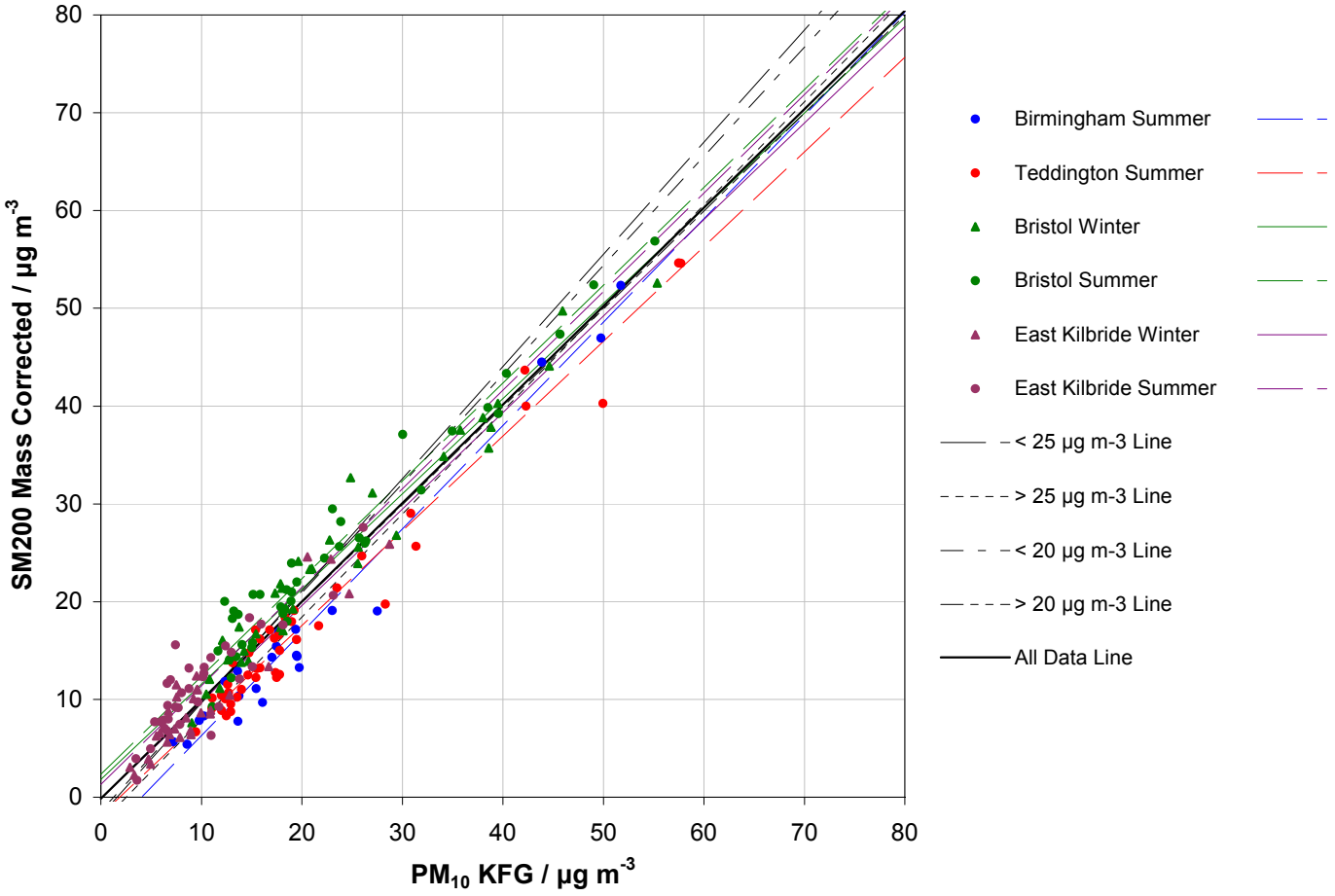


Figure D.11: Chart and Table summarising the comparison of Corrected SM200 Mass Candidate Method against PM_{10} KFG Reference Method. The terms and colours used in the Table are discussed in Section 4.2. u_{bs}, a and u_a have units of µg m^{-3}.

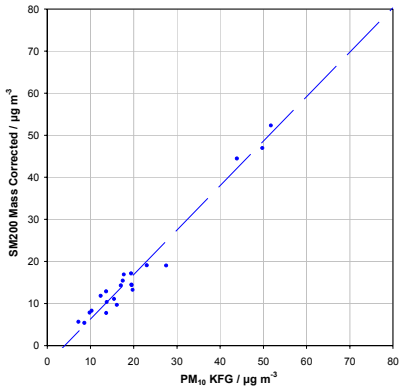
$$SM\,200Mass_{Corrected} = \frac{(SM\,200Mass - 1.286)}{0.819}$$



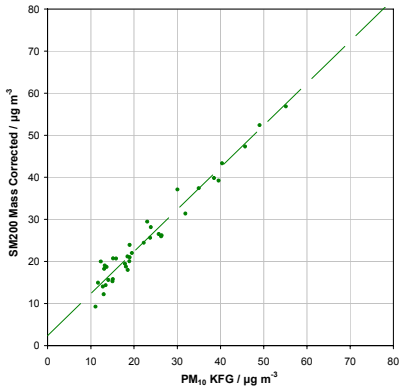
SM200 Mass Corrected	Dataset	Grubbs' Test		24 hour		Orthogonal Regression				Annual Limit Value of 40 µg m^3		Daily Limit Value of 50 µg m^3		
		n_G	n_{Gmax}	n_{bs}	u_{bs}	n_{c-s}	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{CM} / %	% > 50 % LV	W_{CM} / %	% > 50 % LV	(n_{ES},n_{EC})
Individual Campaigns	Birmingham Winter	-	-	-	-	-	-	- - -	- - -	-	-	-	-	-
	Birmingham Summer	0	0	31	2.54	22	0.968	1.057 +/- 0.042	-4.266 +/- 1.001	14.80	22.7	10.60	18.2	(1,1)
	Teddington Winter	-	-	-	-	-	-	- - -	- - -	-	-	-	-	-
	Teddington Summer	1	1	56	1.98	43	0.964	0.969 +/- 0.029	-1.817 +/- 0.688	18.51	25.6	15.97	20.9	(2,2)
	Bristol Summer	3	4	44	1.73	38	0.957	1.000 +/- 0.035	2.351 +/- 0.888	16.43	42.1	13.27	31.6	(1,2)
	Bristol Winter	2	2	51	1.69	37	0.958	0.973 +/- 0.034	1.825 +/- 0.883	12.60	45.9	9.98	35.1	(1,1)
	East Kilbride Summer	2	2	46	1.14	35	0.773	1.008 +/- 0.083	1.309 +/- 0.938	14.71	5.7	12.08	2.9	(0,0)
	East Kilbride Winter	1	1	46	1.15	29	0.889	0.987 +/- 0.063	-0.129 +/- 0.767	11.41	13.8	9.47	3.4	(0,0)
All Campaigns	All Data	-	-	274	1.73	204	0.932	1.007 +/- 0.018	-0.129 +/- 0.400	14.92	27.0	12.09	19.6	(5,6)
Annual Limit Value of 40 µg m^3	< 20 µg m^3	-	-	149	1.76	149	0.662	1.116 +/- 0.052	-1.423 +/- 0.698	21.61	-	-	-	-
	> 20 µg m^3	-	-	55	1.58	55	0.894	1.000 +/- 0.045	-0.100 +/- 1.583	17.72	-	-	-	-
Daily Limit Value of 50 µg m^3	< 25 µg m^3	-	-	164	1.73	164	0.740	1.147 +/- 0.045	-1.828 +/- 0.651	-	-	25.17	-	-
	> 25 µg m^3	-	-	40	1.67	40	0.895	1.054 +/- 0.055	-2.649 +/- 2.159	-	-	13.76	-	-

- Denotes Not Applicable.

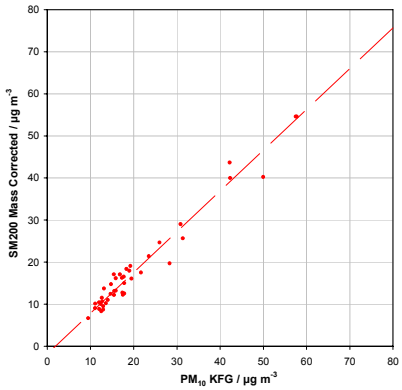
Figure D.11 Continued: Charts summarising the comparison of SM200 Mass Corrected and PM_{10} KFG.



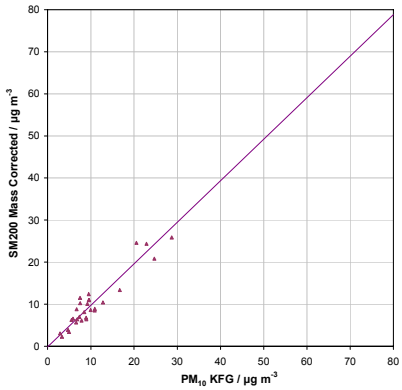
Birmingham Summer



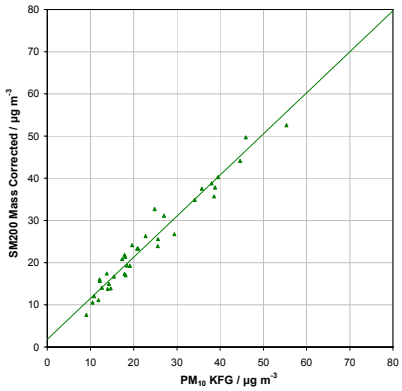
Bristol Summer



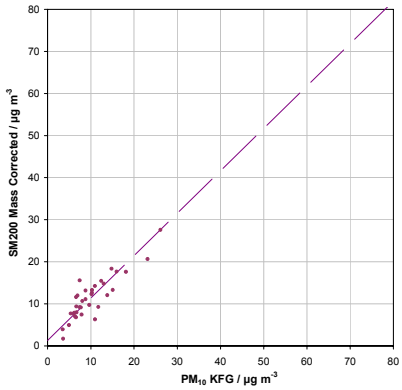
Teddington Summer



East Kilbride Winter

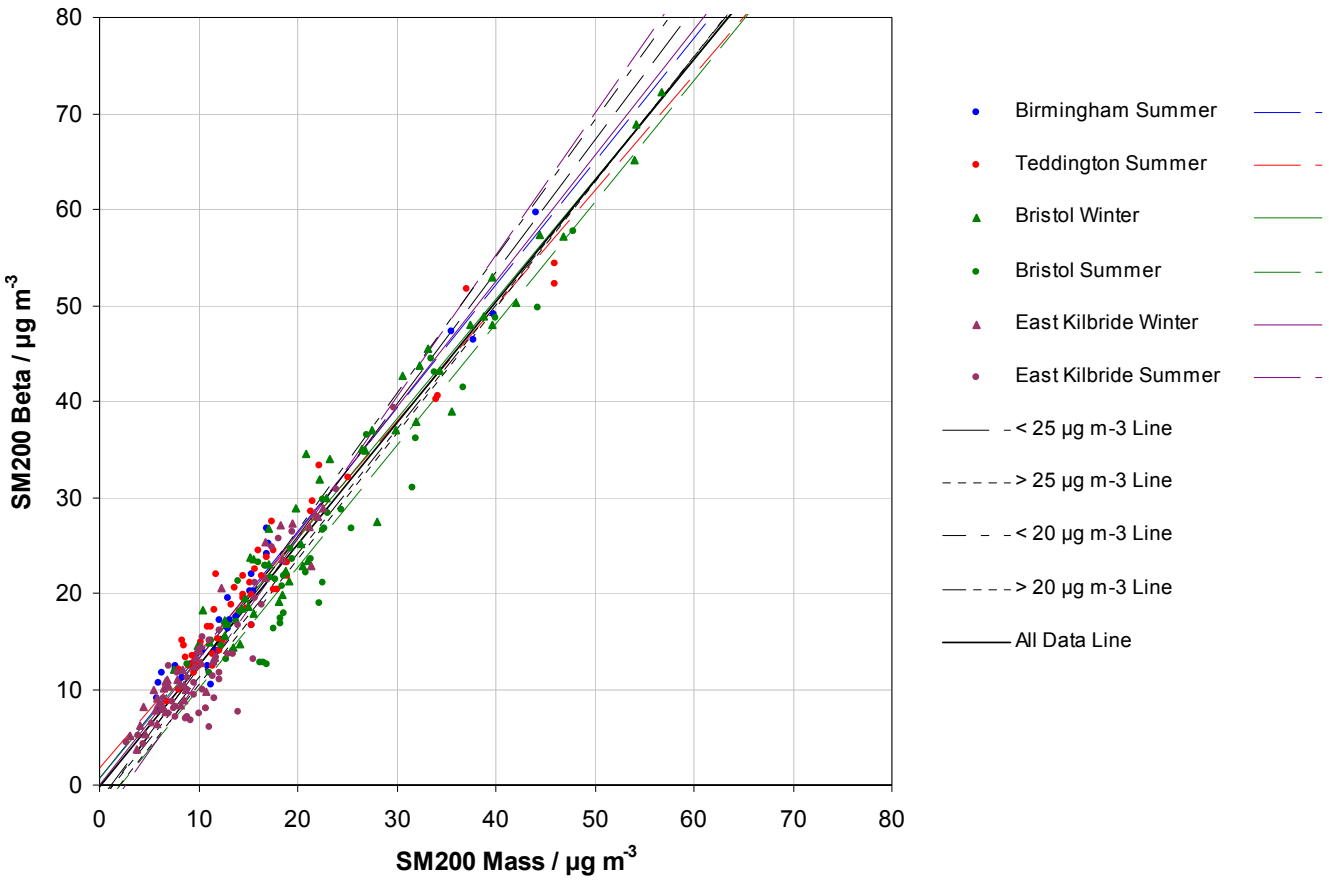


Bristol Winter



East Kilbride Summer

Figure D.12: Chart and Table summarising the comparison of SM200 Mass and SM200 Beta Candidate Methods. The terms and colours used in the Table are discussed in Section 4.2. a and u_a have units of µg m^{-3}.



SM200 Mass vs SM200 Beta	Dataset	Orthogonal Regression								
		n_{c-s}	r^2	Slope (b)	+/-	u_b	Intercept (a)	+/-	u_a
Individual Campaigns	Birmingham Winter	-	-	-	-	-	-	-	-
	Birmingham Summer	31	0.976	1.284	+/-	0.037	0.786	+/-	0.663
	Teddington Winter	-	-	-	-	-	-	-	-
	Teddington Summer	55	0.942	1.204	+/-	0.040	1.736	+/-	0.721
	Bristol Summer	44	0.908	1.269	+/-	0.059	-2.708	+/-	1.368
	Bristol Winter	50	0.961	1.247	+/-	0.036	0.736	+/-	1.002
	East Kilbride Summer	46	0.832	1.478	+/-	0.089	-3.971	+/-	1.085
	East Kilbride Winter	46	0.938	1.311	+/-	0.049	0.076	+/-	0.569
All Campaigns	All Data	272	0.946	1.264	+/-	0.018	-0.258	+/-	0.349
Annual Limit Value of 40 µg m^3	< 20 µg m^3	205	0.761	1.424	+/-	0.047	-1.981	+/-	0.590
	> 20 µg m^3	67	0.917	1.294	+/-	0.046	-1.772	+/-	1.499
Daily Limit Value of 50 µg m^3	< 25 µg m^3	230	0.813	1.375	+/-	0.038	-1.561	+/-	0.533
	> 25 µg m^3	42	0.892	1.310	+/-	0.067	-2.715	+/-	2.532

- Denotes Not Applicable.

Figure D.12 Continued: Charts summarising the comparison of SM200 Mass and SM200 Beta.

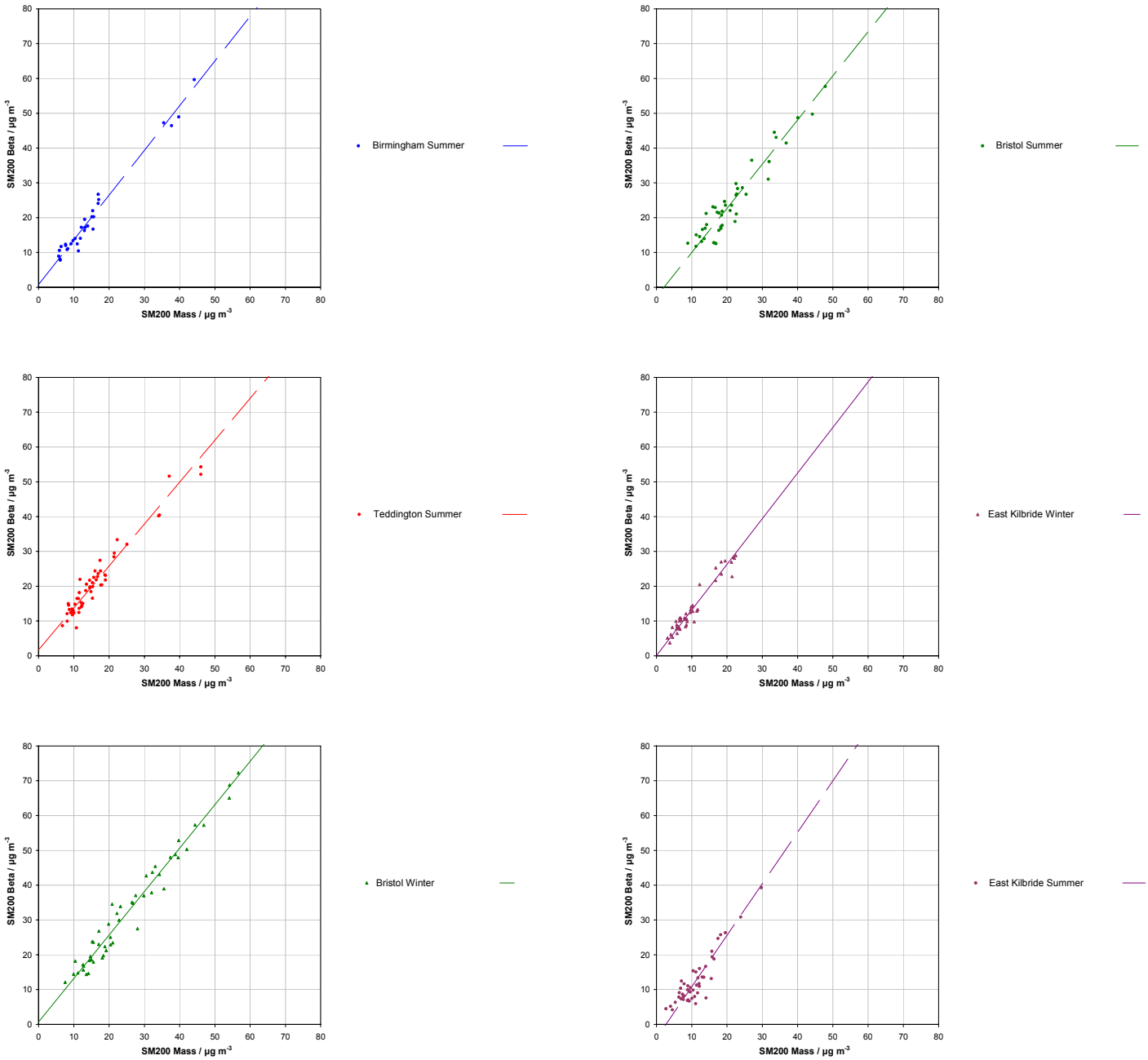
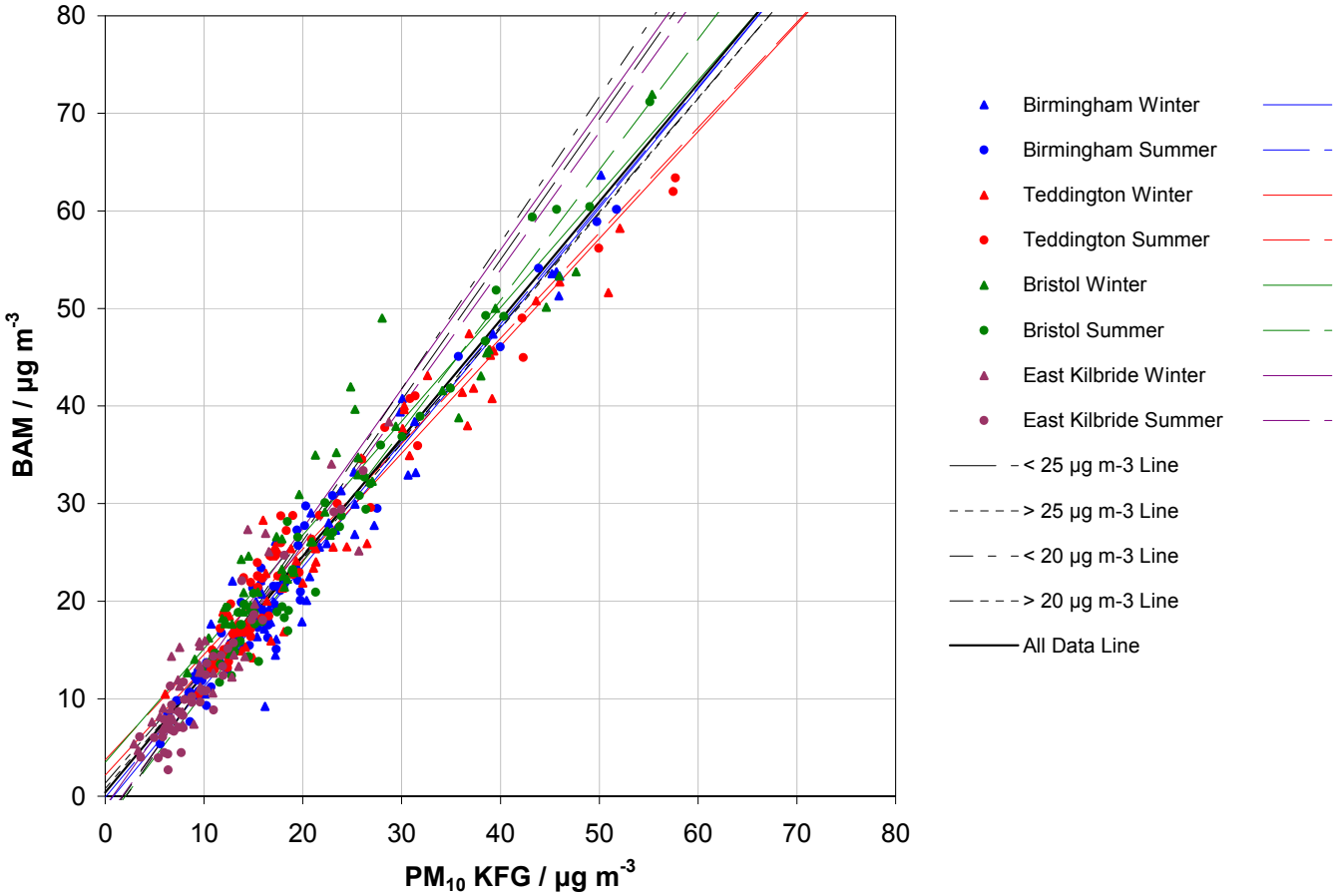


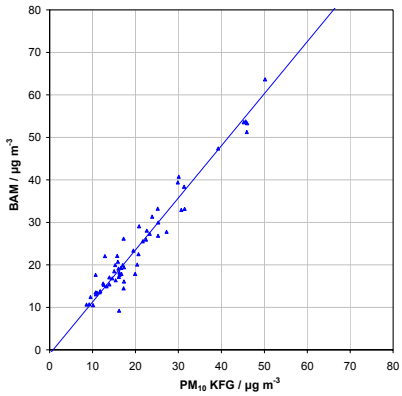
Figure D.13: Chart and Table summarising the comparison of BAM Candidate Method against PM_{10} KFG Reference Method. The terms and colours used in the Table are discussed in Section 4.2. u_{bs}, a and u_a have units of µg m^{-3}.

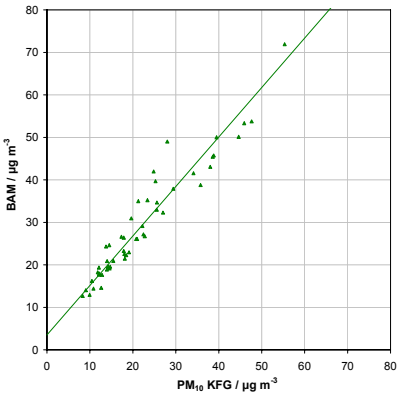


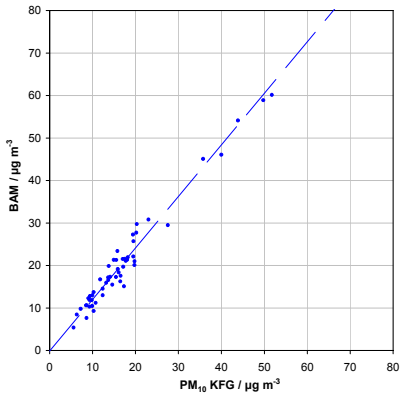
BAM	Dataset	1 hour		24 hour		Orthogonal Regression				Annual Limit Value of 40 µg m^3		Daily Limit Value of 50 µg m^3		
		n_{bs}	u_{bs}	n_{bs}	u_{bs}	n_{c-s}	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{CM} / %	% > 50 % LV	W_{CM} / %	% > 50 % LV	(n_{ES},n_{EC})
Individual Campaigns	Birmingham Winter	2670	4.53	111	2.75	59	0.942	1.225 +/- 0.039	-0.997 +/- 0.896	42.33	39.0	42.51	25.4	(1,5)
	Birmingham Summer	2680	3.86	110	2.14	54	0.965	1.213 +/- 0.032	-0.121 +/- 0.622	43.05	16.7	42.77	11.1	(1,3)
	Teddington Winter	2964	3.44	121	1.15	47	0.937	1.100 +/- 0.041	2.158 +/- 1.115	34.55	53.2	31.24	40.4	(2,4)
	Teddington Summer	2656	4.08	107	2.49	56	0.951	1.080 +/- 0.032	3.724 +/- 0.730	36.69	25.0	32.40	19.6	(2,3)
	Bristol Summer	1494	3.52	62	1.32	50	0.971	1.339 +/- 0.033	-2.722 +/- 0.829	55.38	42.0	57.61	32.0	(1,5)
	Bristol Winter	1982	3.91	82	2.31	51	0.920	1.165 +/- 0.047	3.490 +/- 1.172	53.75	47.1	49.23	31.4	(1,5)
	East Kilbride Summer	1583	3.59	64	1.63	46	0.924	1.409 +/- 0.058	-2.416 +/- 0.645	70.26	6.5	72.47	2.2	(0,0)
	East Kilbride Winter	1671	3.29	66	1.63	38	0.816	1.426 +/- 0.099	-1.059 +/- 1.173	81.90	7.9	82.25	5.3	(0,0)
All Campaigns	All Data	17700	3.84	723	2.06	401	0.943	1.211 +/- 0.014	0.380 +/- 0.315	46.58	30.4	45.31	21.4	(8,25)
Annual Limit Value of 40 µg m^3	< 20 µg m^3	8645	3.27	279	1.65	279	0.757	1.497 +/- 0.042	-3.173 +/- 0.571	84.77	-	-	-	-
	> 20 µg m^3	9055	4.31	124	2.32	122	0.896	1.171 +/- 0.034	1.342 +/- 1.155	44.80	-	-	-	-
Daily Limit Value of 50 µg m^3	< 25 µg m^3	11058	3.36	315	1.67	315	0.811	1.440 +/- 0.034	-2.625 +/- 0.506	-	-	78.45	-	-
	> 25 µg m^3	6642	4.53	88	2.49	86	0.868	1.179 +/- 0.046	0.794 +/- 1.737	-	-	41.73	-	-

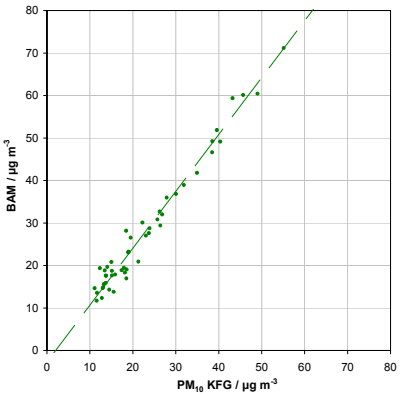
- Denotes Not Applicable.

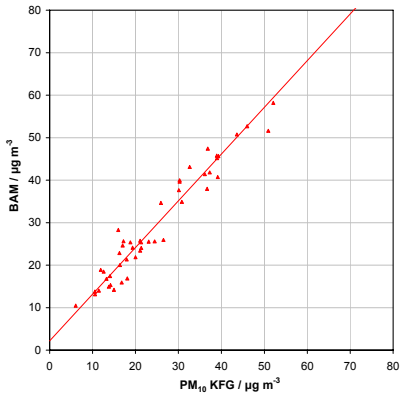
Figure D.13 Continued: Charts summarising the comparison of BAM and PM_{10} KFG.

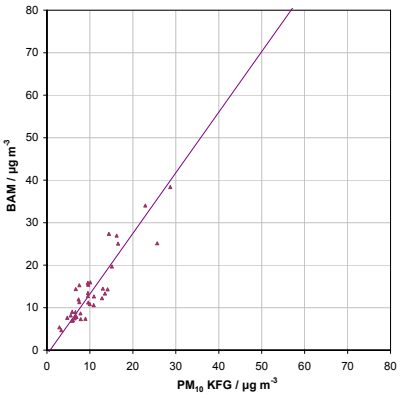


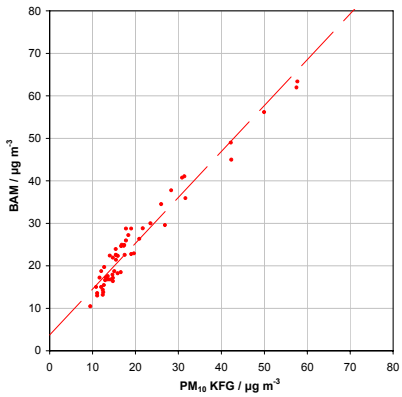












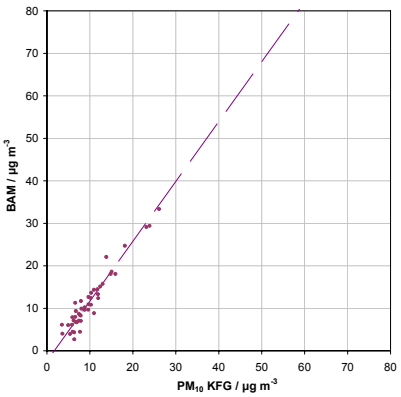
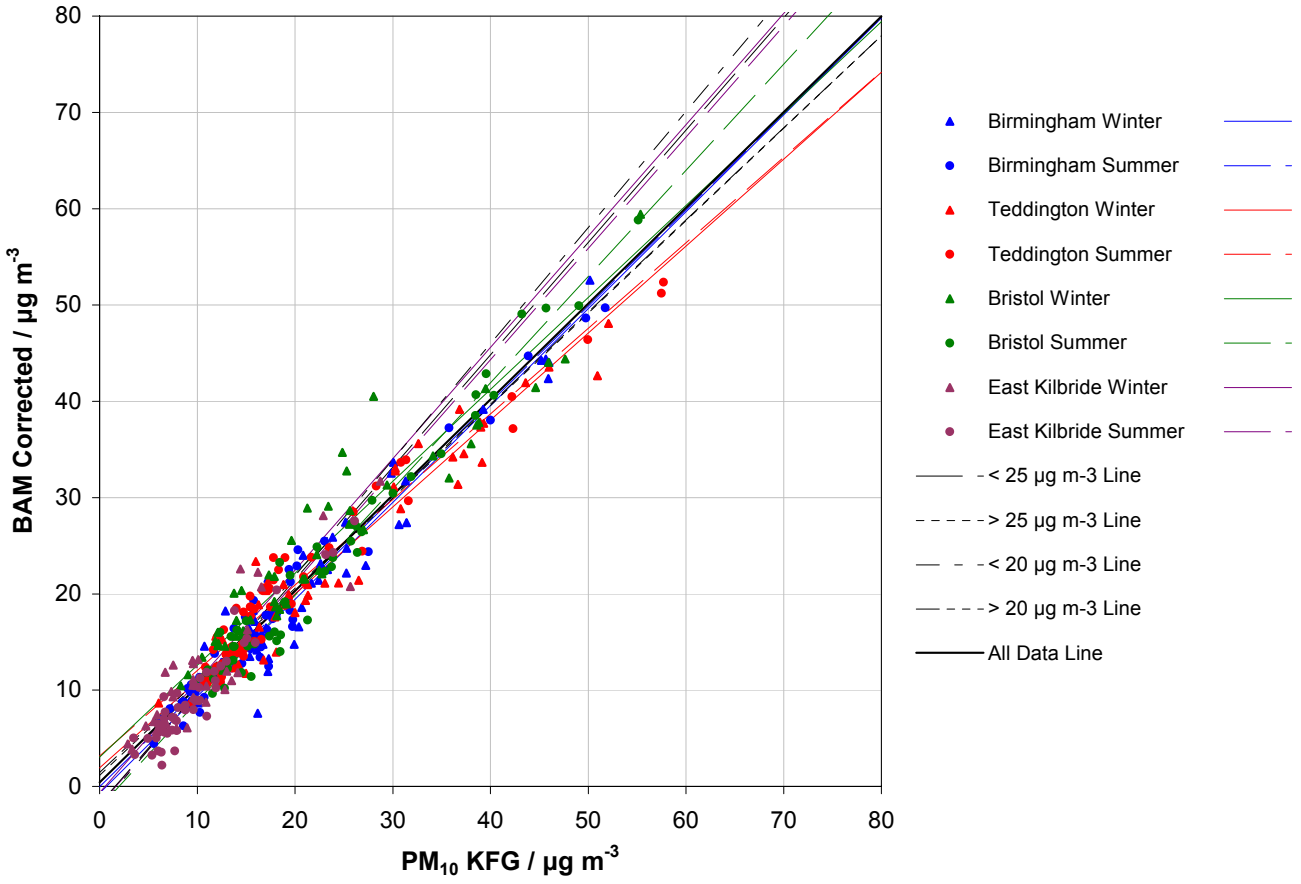


Figure D.14: Chart and Table summarising the comparison of Corrected BAM Candidate Method against PM_{10} KFG Reference Method. The terms and colours used in the Table are discussed in Section 4.2. u_{bs}, a and u_a have units of µg m^{-3}.

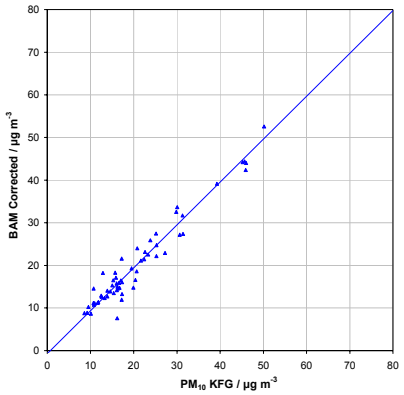
$$BAM_{Corrected} = \frac{BAM}{1.211}$$



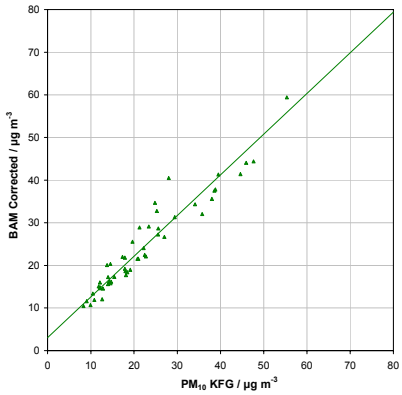
BAM Corrected	Dataset	1 hour		24 hour		Orthogonal Regression				Annual Limit Value of 40 µg m^{-3}		Daily Limit Value of 50 µg m^{-3}		
		n_{bs}	u_{bs}	n_{bs}	u_{bs}	n_{c-s}	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{CM} / %	% > 50 % LV	W_{CM} / %	% > 50 % LV	(n_{ES},n_{EC})
Individual Campaigns	Birmingham Winter	2670	3.74	111	2.27	59	0.942	1.006 +/- 0.032	-0.704 +/- 0.740	11.01	39.0	8.93	25.4	(1,1)
	Birmingham Summer	2680	3.19	110	1.77	54	0.965	0.998 +/- 0.026	-0.041 +/- 0.514	7.81	16.7	6.49	11.1	(1,0)
	Teddington Winter	2964	2.84	121	0.95	47	0.937	0.903 +/- 0.034	1.922 +/- 0.921	16.34	53.2	15.82	40.4	(2,0)
	Teddington Summer	2656	3.37	107	2.06	56	0.951	0.888 +/- 0.027	3.160 +/- 0.603	11.81	25.0	12.63	19.6	(2,2)
	Bristol Summer	1494	2.90	62	1.09	50	0.971	1.103 +/- 0.027	-2.180 +/- 0.685	13.68	42.0	14.25	32.0	(1,1)
	Bristol Winter	1982	3.23	82	1.91	51	0.920	0.954 +/- 0.039	3.057 +/- 0.968	16.72	47.1	12.93	31.4	(1,1)
	East Kilbride Summer	1583	2.96	64	1.35	46	0.924	1.156 +/- 0.048	-1.912 +/- 0.533	22.71	6.5	24.21	2.2	(0,0)
	East Kilbride Winter	1671	2.72	66	1.35	38	0.816	1.156 +/- 0.082	-0.640 +/- 0.969	31.52	7.9	30.92	5.3	(0,0)
All Campaigns	All Data	17700	3.17	723	1.70	401	0.943	0.994 +/- 0.012	0.420 +/- 0.260	12.55	30.4	10.17	21.4	(8,5)
Annual Limit Value of 40 µg m^{-3}	< 20 µg m^{-3}	10845	2.77	279	1.36	279	0.757	1.205 +/- 0.035	-2.207 +/- 0.471	32.04	-	-	-	-
	> 20 µg m^{-3}	6855	3.72	124	1.91	122	0.896	0.957 +/- 0.028	1.441 +/- 0.954	15.22	-	-	-	-
Daily Limit Value of 50 µg m^{-3}	< 25 µg m^{-3}	12934	2.83	315	1.38	315	0.811	1.167 +/- 0.028	-1.843 +/- 0.418	-	-	27.66	-	-
	> 25 µg m^{-3}	4766	3.96	88	2.06	86	0.868	0.960 +/- 0.038	1.146 +/- 1.435	-	-	12.98	-	-

- Denotes Not Applicable.

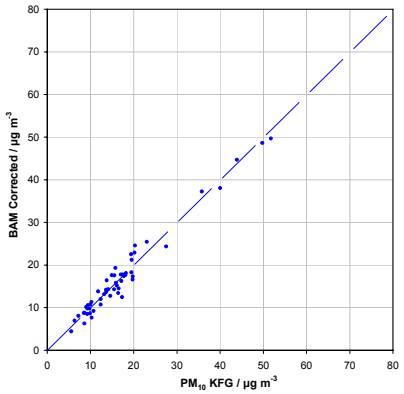
Figure D.14 Continued: Charts summarising the comparison of BAM Corrected and PM_{10} KFG.



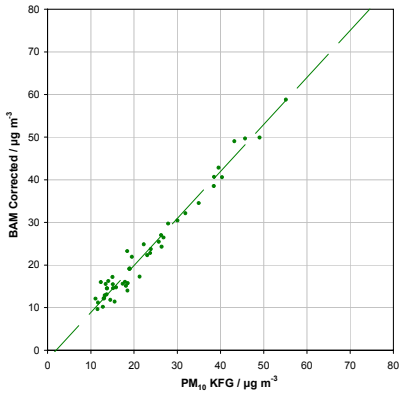
Birmingham Winter



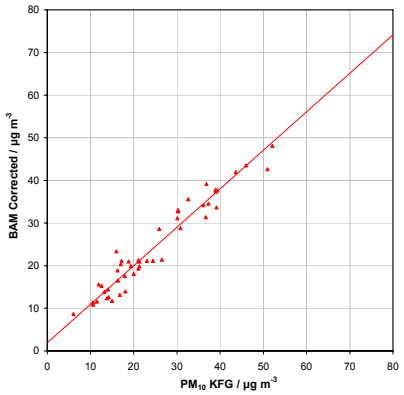
Bristol Winter



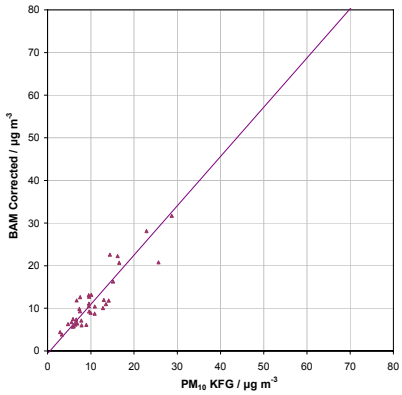
Birmingham Summer



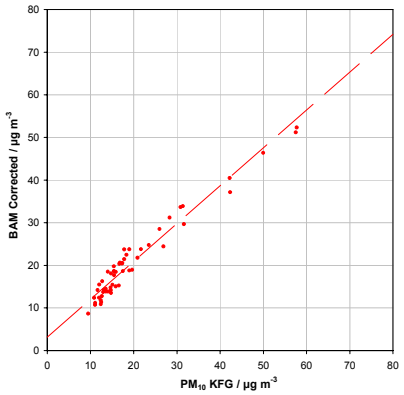
Bristol Summer



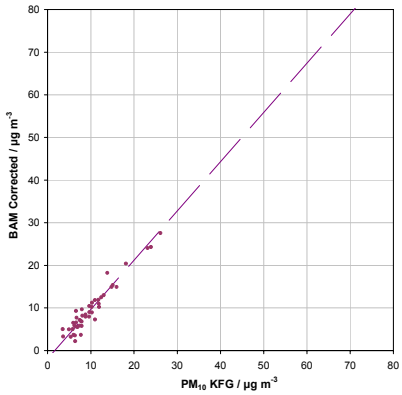
Teddington Winter



East Kilbride Winter

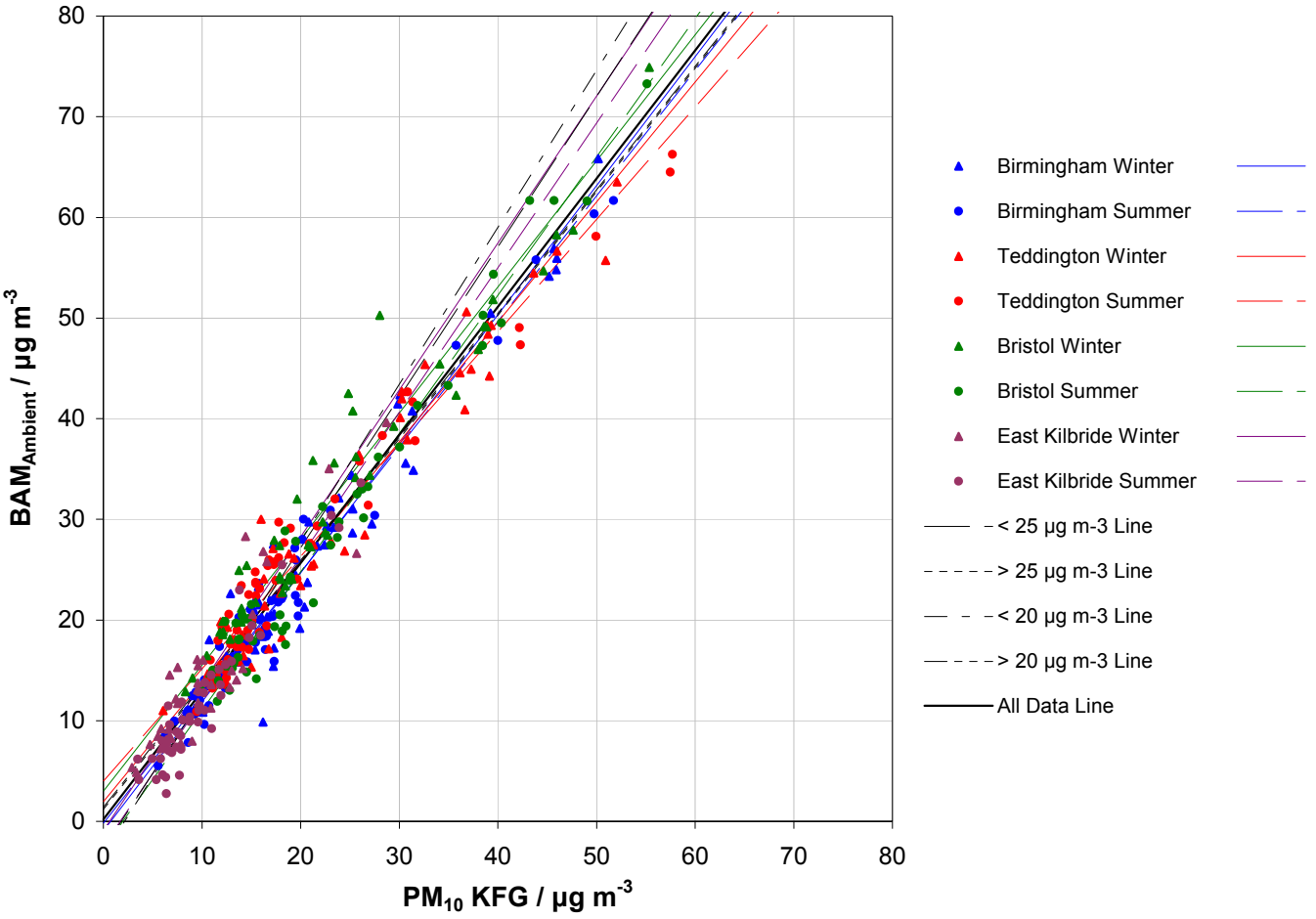


Teddington Summer



East Kilbride Summer

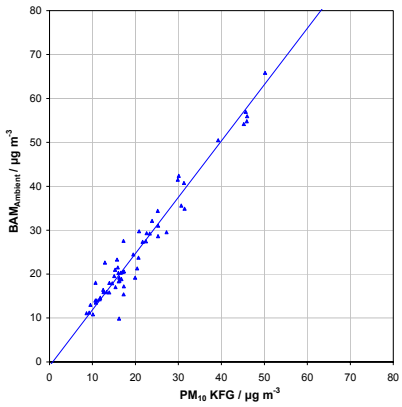
Figure D.15: Chart and Table summarising the comparison of $BAM_{Ambient}$ Candidate Method against PM_{10} KFG Reference Method. The terms and colours used in the Table are discussed in Section 4.2. u_{bs}, a and u_a have units of µg m^{-3}.



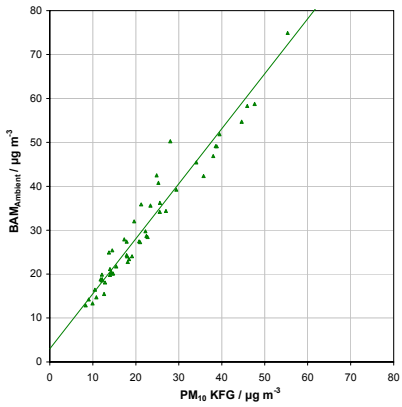
BAM Ambient	Dataset	1 hour		24 hour		Orthogonal Regression				Annual Limit Value of 40 µg m³		Daily Limit Value of 50 µg m³		
		n_{bs}	u_{bs}	n_{bs}	u_{bs}	n_{c-s}	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{CM} / %	% > 50 % LV	W_{CM} / %	% > 50 % LV	(n_{ES},n_{EC})
Individual Campaigns	Birmingham Winter	2670	4.77	111	2.89	59	0.948	1.282 +/- 0.038	-0.946 +/- 0.886	53.35	39.0	53.67	25.4	(1,6)
	Birmingham Summer	2680	3.95	110	2.20	54	0.969	1.246 +/- 0.030	-0.192 +/- 0.601	49.22	16.7	49.09	11.1	(1,3)
	Teddington Winter	2964	3.68	121	1.23	47	0.946	1.192 +/- 0.041	1.950 +/- 1.122	50.61	53.2	47.83	40.4	(2,5)
	Teddington Summer	2655	4.24	107	2.59	56	0.956	1.116 +/- 0.032	3.984 +/- 0.720	44.72	25.0	40.27	19.6	(2,3)
	Bristol Summer	1494	3.61	62	1.36	50	0.969	1.374 +/- 0.035	-2.712 +/- 0.882	62.57	42.0	64.78	32.0	(1,6)
	Bristol Winter	1982	4.16	82	2.48	51	0.944	1.253 +/- 0.042	2.982 +/- 1.056	67.57	47.1	63.90	31.4	(1,6)
	East Kilbride Summer	1583	3.66	64	1.67	46	0.921	1.436 +/- 0.060	-2.432 +/- 0.669	75.57	6.5	77.80	2.2	(0,0)
	East Kilbride Winter	1671	3.41	66	1.68	38	0.839	1.459 +/- 0.095	-0.935 +/- 1.125	88.80	7.9	89.15	5.3	(0,0)
All Campaigns	All Data	17699	4.01	723	2.15	401	0.950	1.273 +/- 0.014	0.183 +/- 0.309	57.57	30.4	56.69	21.4	(8,29)
Annual Limit Value of 40 µg m³	< 20 µg m³	8311	3.38	279	1.71	279	0.771	1.560 +/- 0.043	-3.378 +/- 0.577	96.11	-	-	-	-
	> 20 µg m³	9388	4.50	124	2.43	122	0.916	1.227 +/- 0.032	1.377 +/- 1.092	55.10	-	-	-	-
Daily Limit Value of 50 µg m³	< 25 µg m³	10761	3.49	315	1.73	315	0.825	1.495 +/- 0.034	-2.723 +/- 0.505	-	-	88.78	-	-
	> 25 µg m³	6938	4.71	88	2.62	86	0.891	1.227 +/- 0.044	1.207 +/- 1.647	-	-	52.19	-	-

- Denotes Not Applicable.

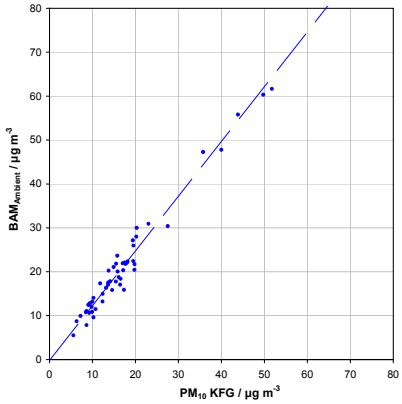
Figure D.15 Continued: Charts summarising the comparison of $BAM_{Ambient}$ and PM_{10} KFG.



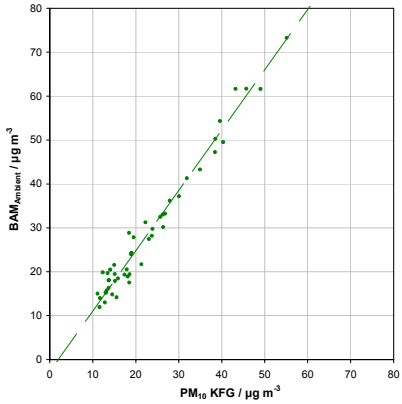
Birmingham Winter



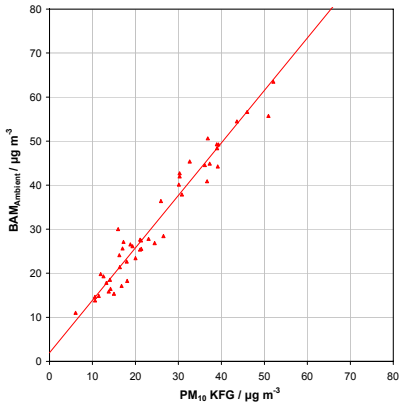
Bristol Winter



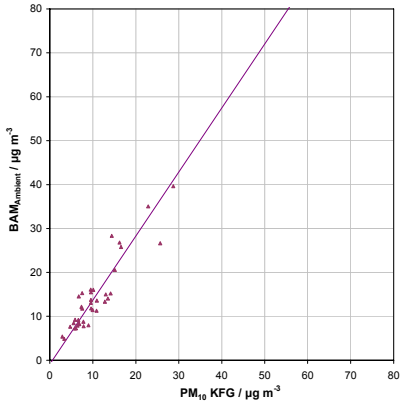
Birmingham Summer



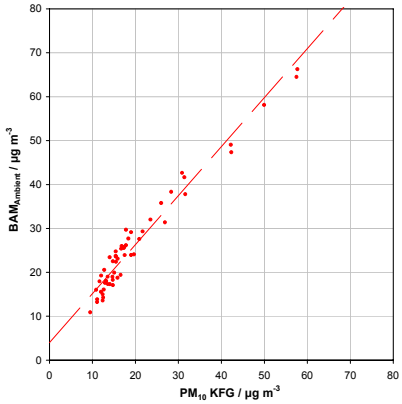
Bristol Summer



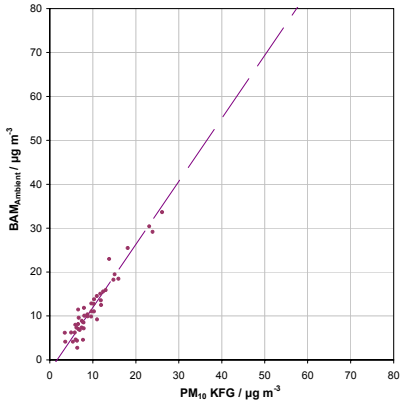
Teddington Winter



East Kilbride Winter



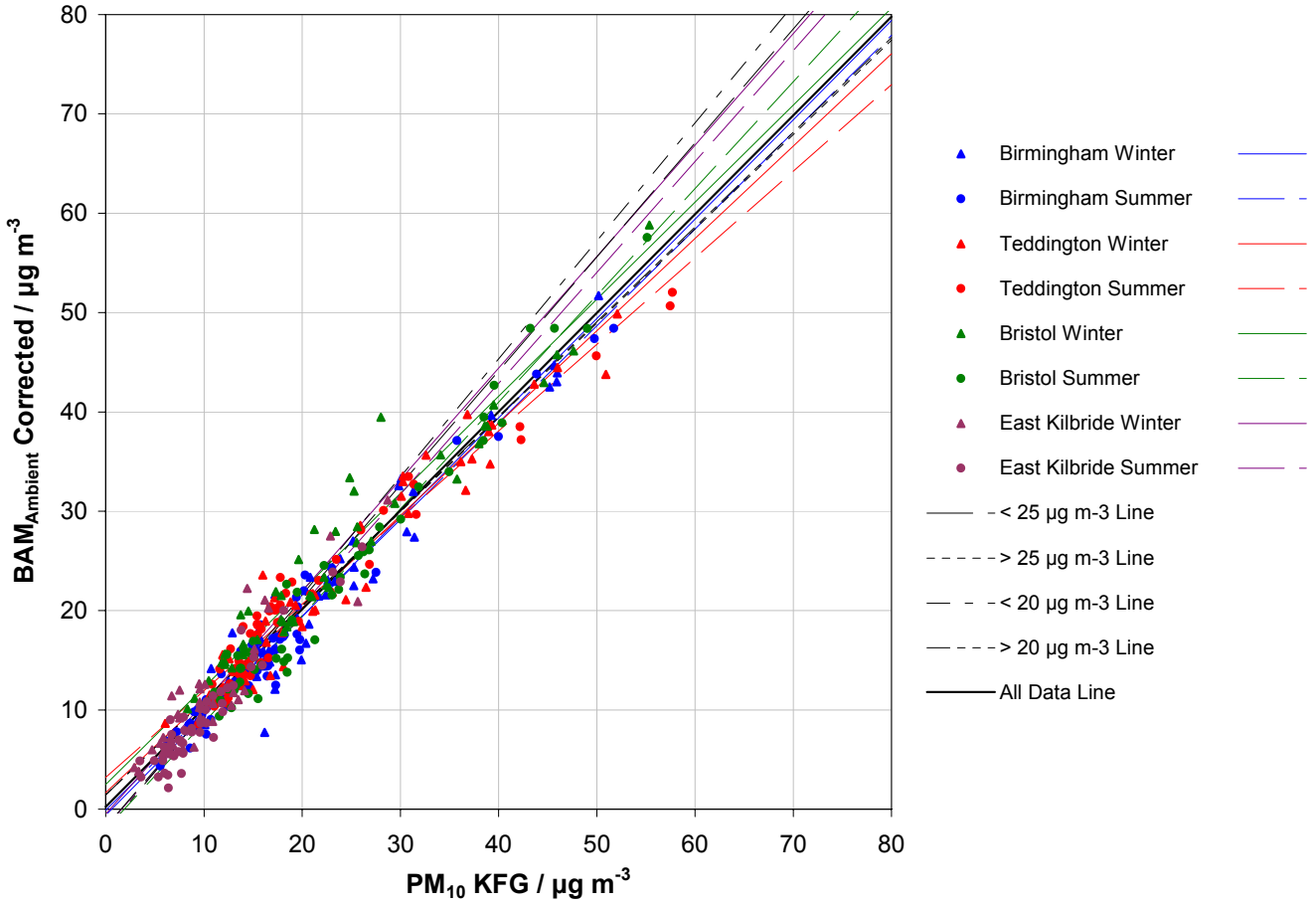
Teddington Summer



East Kilbride Summer

Figure D.16: Chart and Table summarising the comparison of Corrected $BAM_{Ambient}$ Candidate Method against PM_{10} KFG Reference Method. The terms and colours used in the Table are discussed in Section 4.2. u_{bs}, a and u_a have units of µg m^{-3}.

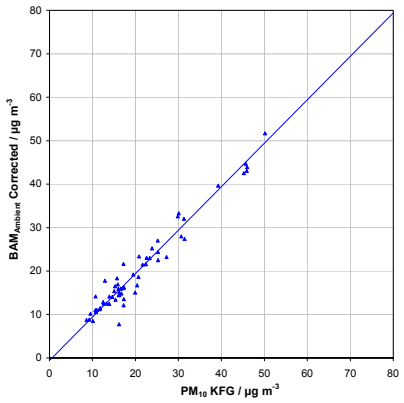
$$BAM_{Ambient\ \ Corrected} = \frac{BAM_{Ambient}}{1.273}$$



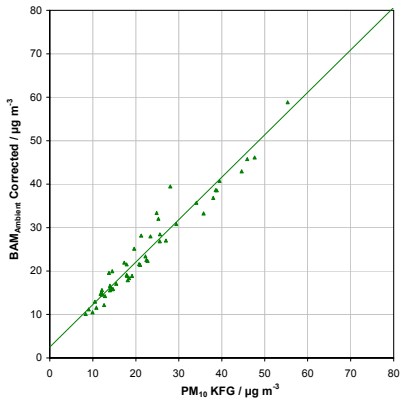
BAM Ambient Corrected	Dataset	1 hour		24 hour		Orthogonal Regression				Annual Limit Value of 40 µg m³		Daily Limit Value of 50 µg m³		
		n_{bs}	u_{bs}	n_{bs}	u_{bs}	n_{c-s}	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{CM} / %	% > 50 % LV	W_{CM} / %	% > 50 % LV	(n_{ES},n_{EC})
Individual Campaigns	Birmingham Winter	2670	3.94	111	2.27	59	0.948	1.000 +/- 0.030	-0.610 +/- 0.696	10.31	39.0	8.42	25.4	(1,1)
	Birmingham Summer	2680	3.26	110	1.73	54	0.969	0.975 +/- 0.024	-0.088 +/- 0.472	8.68	16.7	7.79	11.1	(1,0)
	Teddington Winter	2964	3.04	121	0.97	47	0.946	0.929 +/- 0.032	1.687 +/- 0.881	13.67	53.2	12.50	40.4	(2,0)
	Teddington Summer	2655	3.45	107	2.04	56	0.956	0.872 +/- 0.025	3.223 +/- 0.565	13.13	25.0	14.77	19.6	(2,2)
	Bristol Summer	1494	2.84	62	1.07	50	0.969	1.075 +/- 0.027	-2.038 +/- 0.693	10.94	42.0	10.57	32.0	(1,1)
	Bristol Winter	1982	3.27	82	1.95	51	0.944	0.977 +/- 0.033	2.495 +/- 0.829	15.41	47.1	12.01	31.4	(1,1)
	East Kilbride Summer	1583	2.88	64	1.31	46	0.921	1.117 +/- 0.047	-1.803 +/- 0.526	15.99	6.5	17.20	2.2	(0,0)
	East Kilbride Winter	1671	2.68	66	1.32	38	0.839	1.122 +/- 0.074	-0.486 +/- 0.884	25.68	7.9	24.92	5.3	(0,0)
All Campaigns	All Data	17699	3.25	723	1.69	401	0.950	0.994 +/- 0.011	0.260 +/- 0.243	11.56	30.4	9.40	21.4	(8,5)
Annual Limit Value of 40 µg m³	< 20 µg m³	10604	2.81	279	1.34	279	0.771	1.188 +/- 0.033	-2.175 +/- 0.453	28.83	-	-	-	-
	> 20 µg m³	7095	3.81	124	1.91	122	0.916	0.953 +/- 0.025	1.415 +/- 0.857	13.61	-	-	-	-
Daily Limit Value of 50 µg m³	< 25 µg m³	12684	2.87	315	1.36	315	0.825	1.147 +/- 0.027	-1.770 +/- 0.396	-	-	24.13	-	-
	> 25 µg m³	5015	4.06	88	2.06	86	0.891	0.950 +/- 0.034	1.446 +/- 1.293	-	-	11.94	-	-

- Denotes Not Applicable.

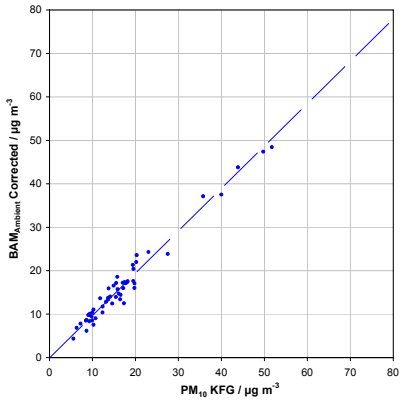
Figure D.16 Continued: Charts summarising the comparison of Corrected $BAM_{Ambient}$ and PM_{10} KFG.



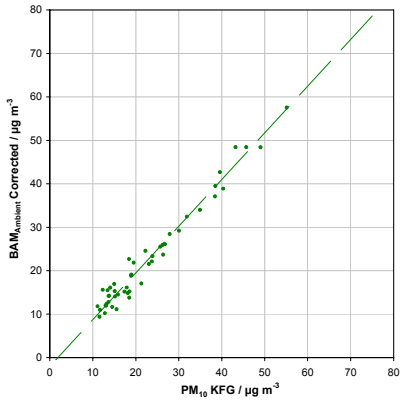
Birmingham Winter



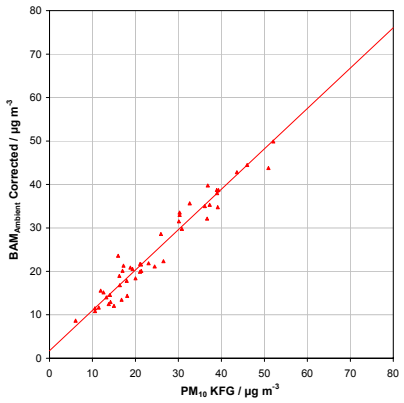
Bristol Winter



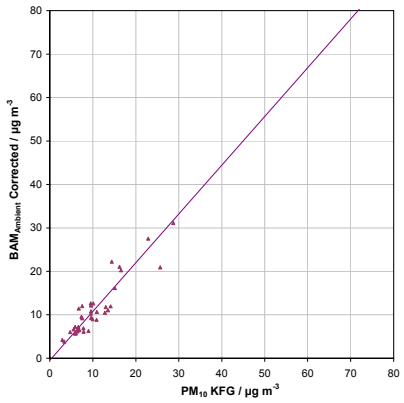
Birmingham Summer



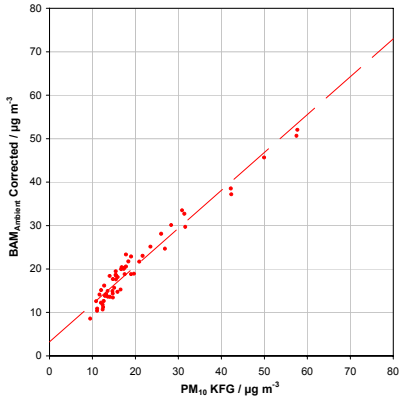
Bristol Summer



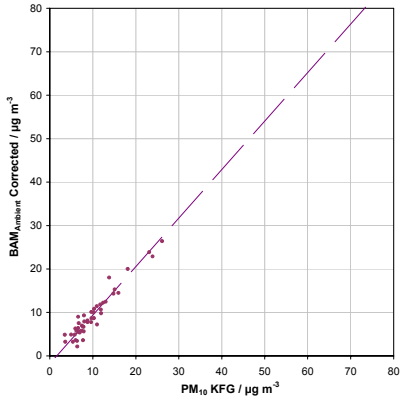
Teddington Winter



East Kilbride Winter

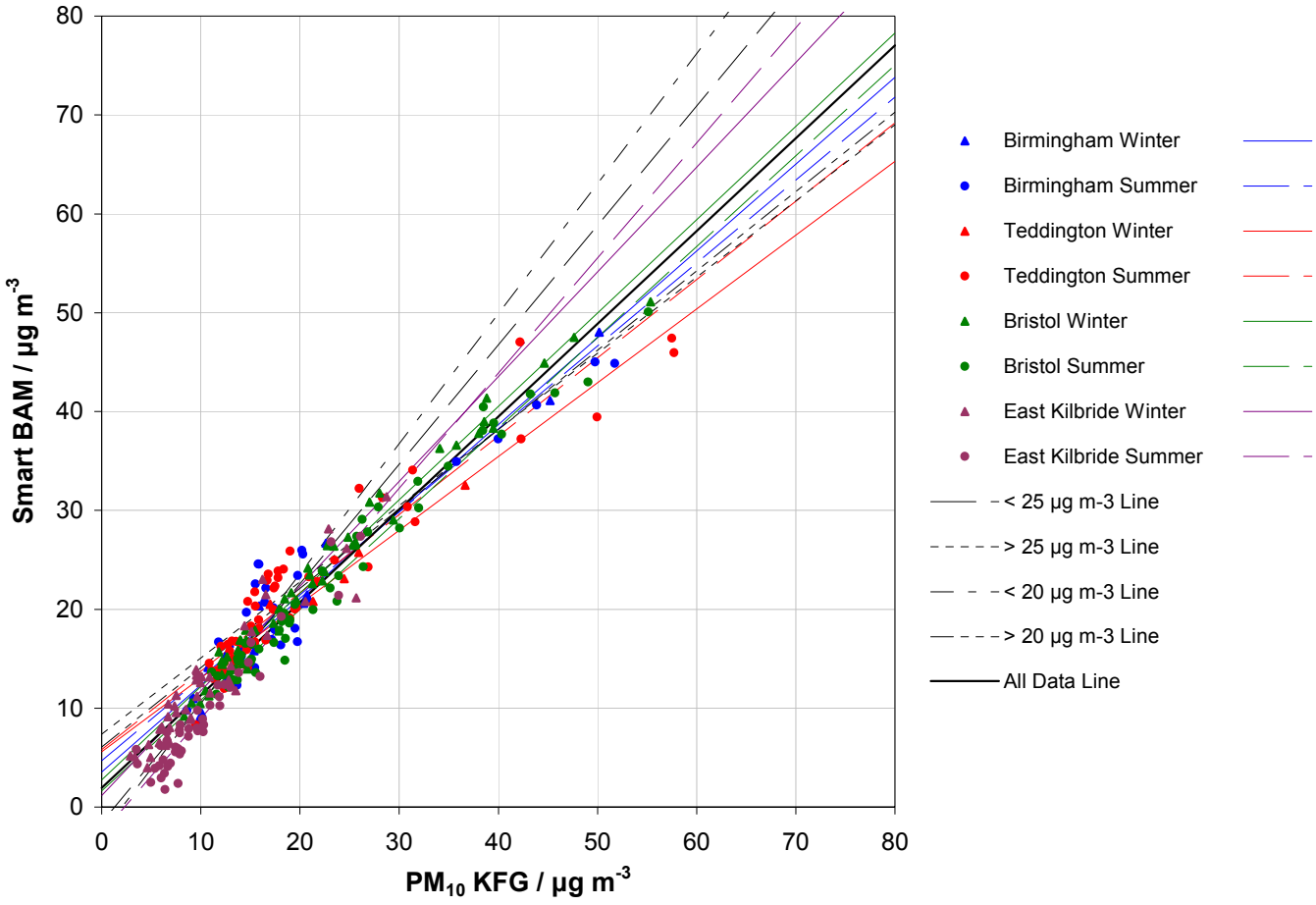


Teddington Summer



East Kilbride Summer

Figure D.17: Chart and Table summarising the comparison of Smart BAM Candidate Method against PM_{10} KFG Reference Method. The terms and colours used in the Table are discussed in Section 4.2. u_{bs}, a and u_a have units of µg m^{-3}.



Smart BAM	Dataset	1 hour		24 hour		Orthogonal Regression			
		n_{bs}	u_{bs}	n_{bs}	u_{bs}	n_{c-s}	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a
Individual Campaigns	60.00	952	3.60	39	1.79	15	0.973	0.878 +/- 0.040	3.540 +/- 0.914
	75.86	1782	4.28	72	2.34	29	0.892	0.839 +/- 0.054	4.690 +/- 1.269
	33.33	234	4.50	9	1.38	6	0.961	0.746 +/- 0.074	5.603 +/- 1.791
	75.86	2374	4.13	95	1.54	58	0.895	0.792 +/- 0.035	5.826 +/- 0.779
	56.86	1518	3.75	61	0.90	51	0.975	0.918 +/- 0.021	1.621 +/- 0.530
	54.00	2106	4.17	88	1.10	50	0.983	0.944 +/- 0.018	2.730 +/- 0.435
	93.33	1619	3.36	64	1.38	45	0.923	1.164 +/- 0.049	-2.692 +/- 0.549
	88.37	2094	3.37	84	0.99	43	0.902	1.059 +/- 0.052	1.152 +/- 0.641
All Campaigns	71.72	12679	3.87	512	1.48	297	0.934	0.939 +/- 0.014	1.944 +/- 0.296
Annual Limit Value of 40 µg m^3	< 20 µg m^3	7474	3.46	213	1.19	213	0.816	1.315 +/- 0.038	-2.713 +/- 0.502
	> 20 µg m^3	5205	4.40	86	1.48	84	0.910	0.803 +/- 0.027	6.056 +/- 0.898
Daily Limit Value of 50 µg m^3	< 25 µg m^3	9159	3.56	242	1.19	242	0.851	1.208 +/- 0.030	-1.584 +/- 0.434
	> 25 µg m^3	3520	4.60	57	1.62	55	0.875	0.770 +/- 0.038	7.373 +/- 1.448

Figure D.17 Continued: Charts summarising the comparison of Smart BAM and PM_{10} KFG.

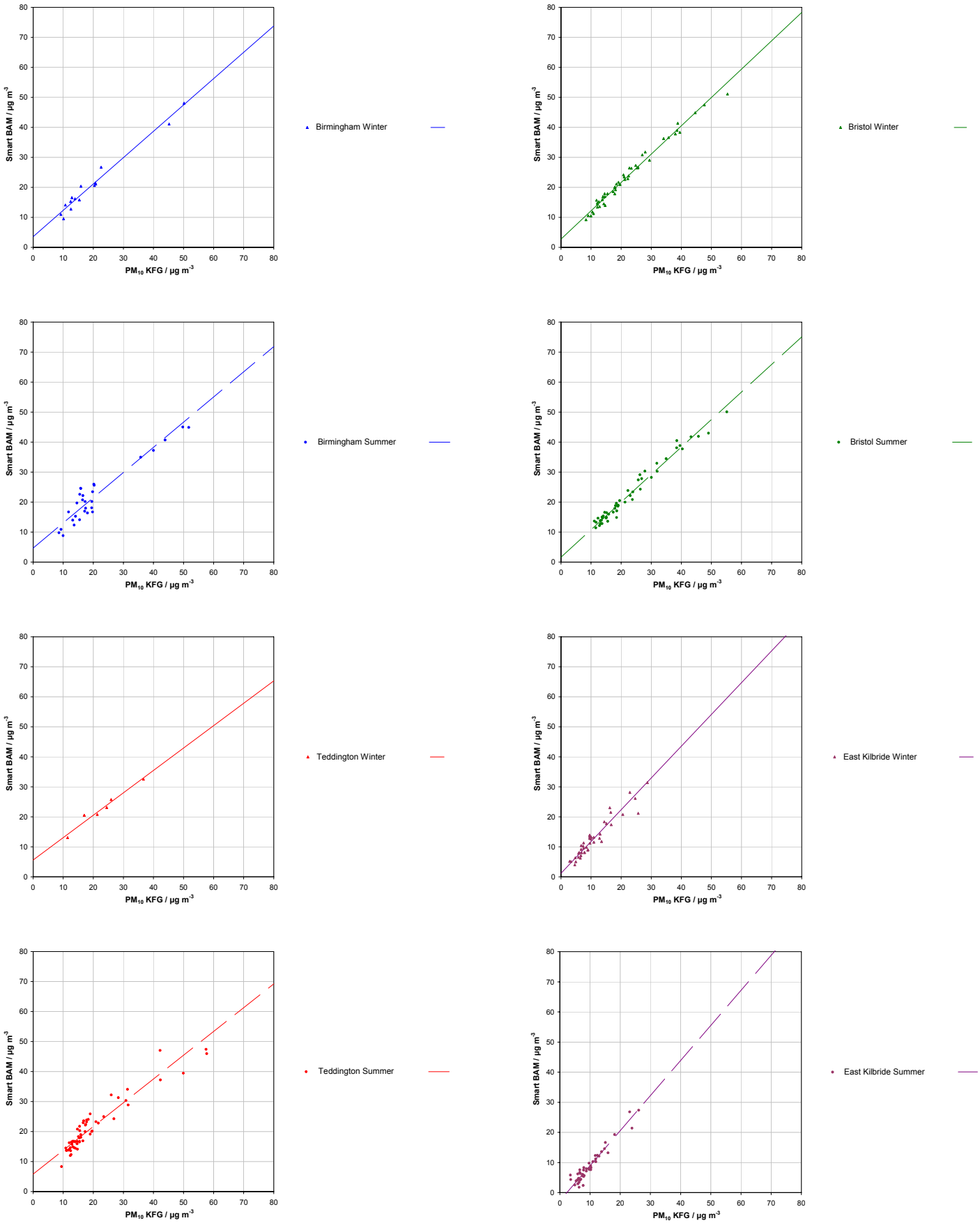
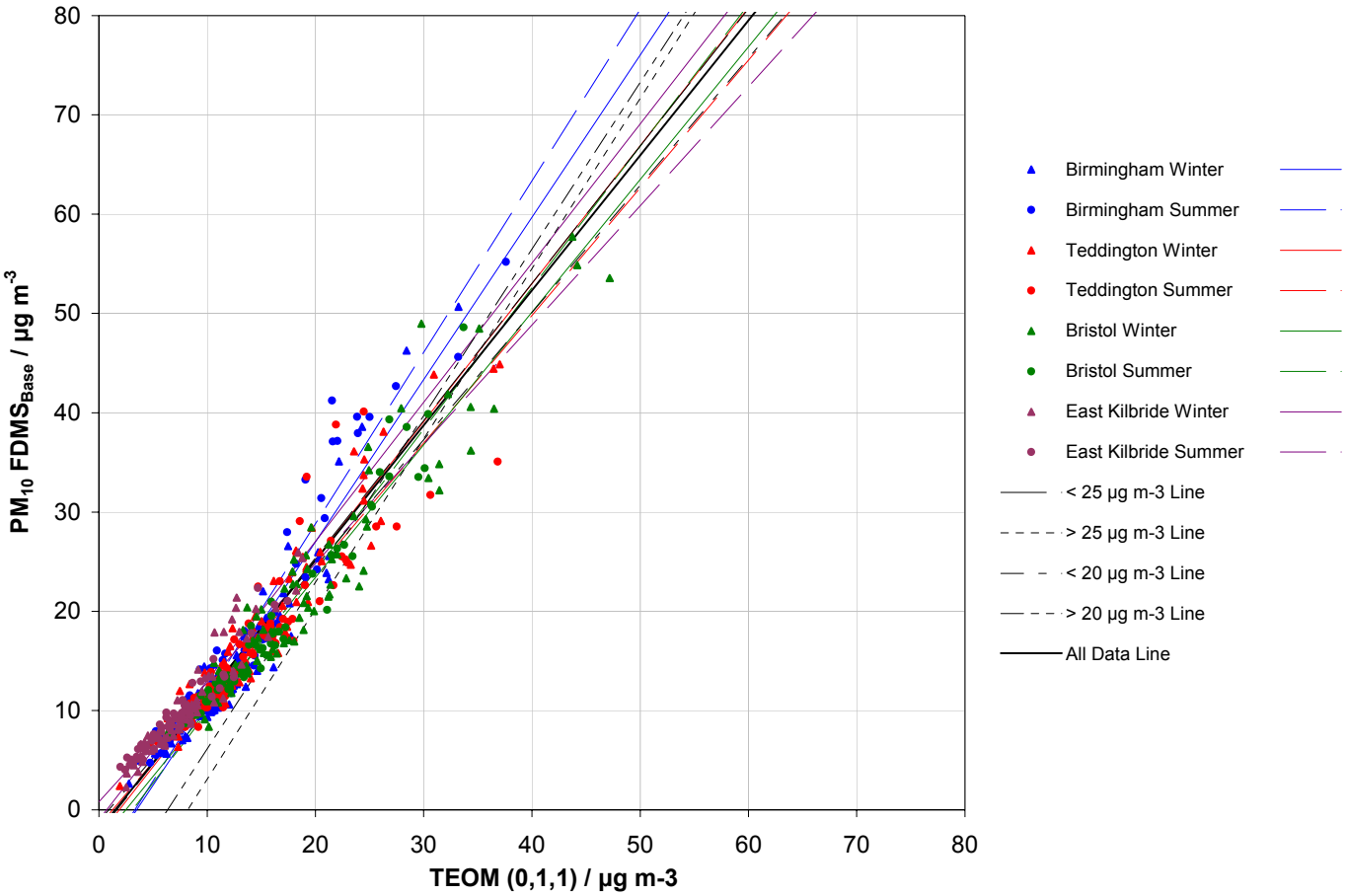


Figure D.18: Chart and Table summarising the comparison of PM_{10} $FDMS_{Base}$ against TEOM(0,1,1). The terms and colours used in the Table are discussed in Section 5.9. a and u_a have units of µg m^{-3}.



TEOM (0,1,1) vs PM_{10} $FDMS_{Base}$	Dataset	Orthogonal Regression				Annual LV	Daily LV
		n	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{F-T} / %	W_{F-T} / %
Individual Campaigns	Birmingham Winter	75	0.914	1.635 +/- 0.055	-5.696 +/- 0.755	99.28	104.64
	Birmingham Summer	70	0.926	1.727 +/- 0.056	-5.731 +/- 0.835	117.84	123.17
	Teddington Winter	85	0.931	1.390 +/- 0.040	-2.627 +/- 0.635	66.07	68.27
	Teddington Summer	82	0.822	1.286 +/- 0.059	-1.636 +/- 0.903	51.33	52.09
	Bristol Summer	53	0.950	1.425 +/- 0.044	-4.414 +/- 0.801	63.87	67.93
	Bristol Winter	82	0.917	1.336 +/- 0.043	-3.300 +/- 0.894	53.27	55.55
	East Kilbride Summer	54	0.934	1.200 +/- 0.043	0.819 +/- 0.335	44.51	43.58
	East Kilbride Winter	66	0.904	1.402 +/- 0.054	-1.010 +/- 0.502	75.77	76.63
All Campaigns	All Data	567	0.908	1.360 +/- 0.017	-2.061 +/- 0.263	63.35	64.77
Annual Limit Value of 40 µg m^{-3}	< 20 µg m^{-3}	478	0.856	1.281 +/- 0.022	-1.152 +/- 0.262	51.50	-
	> 20 µg m^{-3}	89	0.625	1.678 +/- 0.100	-10.635 +/- 2.692	88.01	-
Daily Limit Value of 50 µg m^{-3}	< 25 µg m^{-3}	528	0.866	1.383 +/- 0.022	-2.284 +/- 0.288	-	68.26
	> 25 µg m^{-3}	39	0.532	1.715 +/- 0.168	-14.069 +/- 5.371	-	90.57

- Denotes Not Applicable.

Figure D.18 Continued: Charts summarising the comparison of PM_{10} $FDMS_{Base}$ and TEOM(0,1,1).

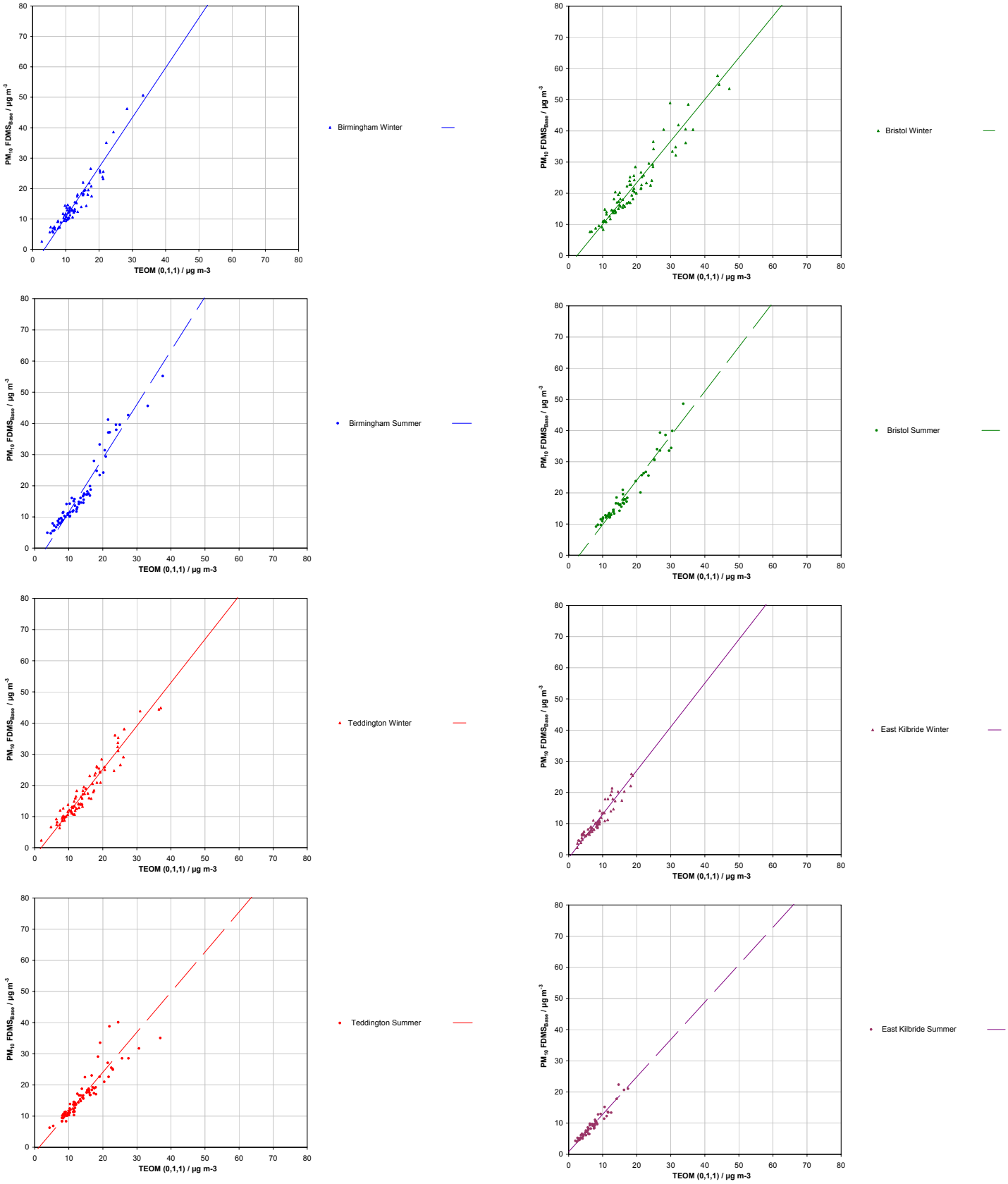
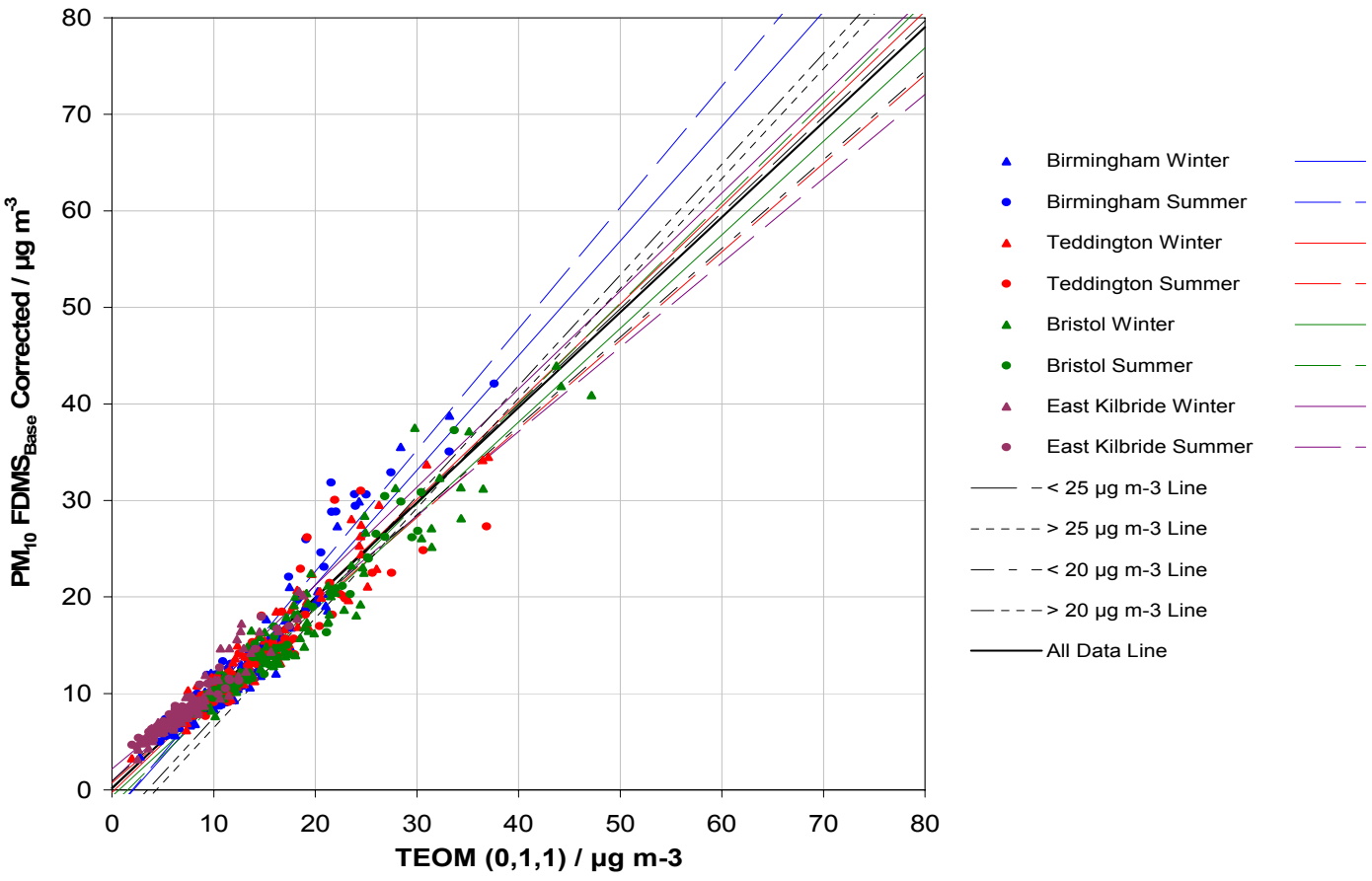


Figure D.19: Chart and Table summarising the comparison of Corrected PM_{10} $FDMS_{Base}$ against TEOM(0,1,1). The terms and colours used in the Table are discussed in Section 5.9. a and u_a have units of µg m^{-3}.

$$TEOM\,(0,1,1) = \left(\frac{\left(PM_{10} FDMS_{Base} + 2.061 \right)}{1.360} \right)$$



TEOM (0,1,1) vs PM_{10} $FDMS_{Base}$ Corrected	Dataset	Orthogonal Regression				Annual LV	Daily LV
		n	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{F-T} / %	W_{F-T} / %
Individual Campaigns	Birmingham Winter	75	0.914	1.187 +/- 0.040	-2.483 +/- 0.555	26.96	28.72
	Birmingham Summer	70	0.926	1.257 +/- 0.041	-2.524 +/- 0.614	40.63	42.50
	Teddington Winter	85	0.931	1.012 +/- 0.029	-0.257 +/- 0.467	9.58	8.00
	Teddington Summer	82	0.822	0.917 +/- 0.044	0.722 +/- 0.664	17.24	16.58
	Bristol Summer	53	0.950	1.040 +/- 0.032	-1.597 +/- 0.589	8.43	7.25
	Bristol Winter	82	0.917	0.969 +/- 0.031	-0.662 +/- 0.657	15.51	13.35
	East Kilbride Summer	54	0.934	0.874 +/- 0.031	2.183 +/- 0.246	15.30	17.21
	East Kilbride Winter	66	0.904	1.015 +/- 0.039	0.907 +/- 0.369	10.03	8.74
All Campaigns	All Data	567	0.908	0.985 +/- 0.013	0.199 +/- 0.193	11.29	9.38
Annual Limit Value of 40 µg m^{-3}	< 20 µg m^{-3}	478	0.856	0.920 +/- 0.016	0.923 +/- 0.193	14.02	-
	> 20 µg m^{-3}	89	0.625	1.147 +/- 0.073	-3.998 +/- 1.980	23.61	-
Daily Limit Value of 50 µg m^{-3}	< 25 µg m^{-3}	528	0.866	0.995 +/- 0.016	0.110 +/- 0.212	-	8.35
	> 25 µg m^{-3}	39	0.532	1.138 +/- 0.124	-4.960 +/- 3.950	-	19.80

- Denotes Not Applicable.

Figure D.19 Continued: Charts summarising the comparison of Corrected PM_{10} $FDMS_{Base}$ and TEOM(0,1,1).

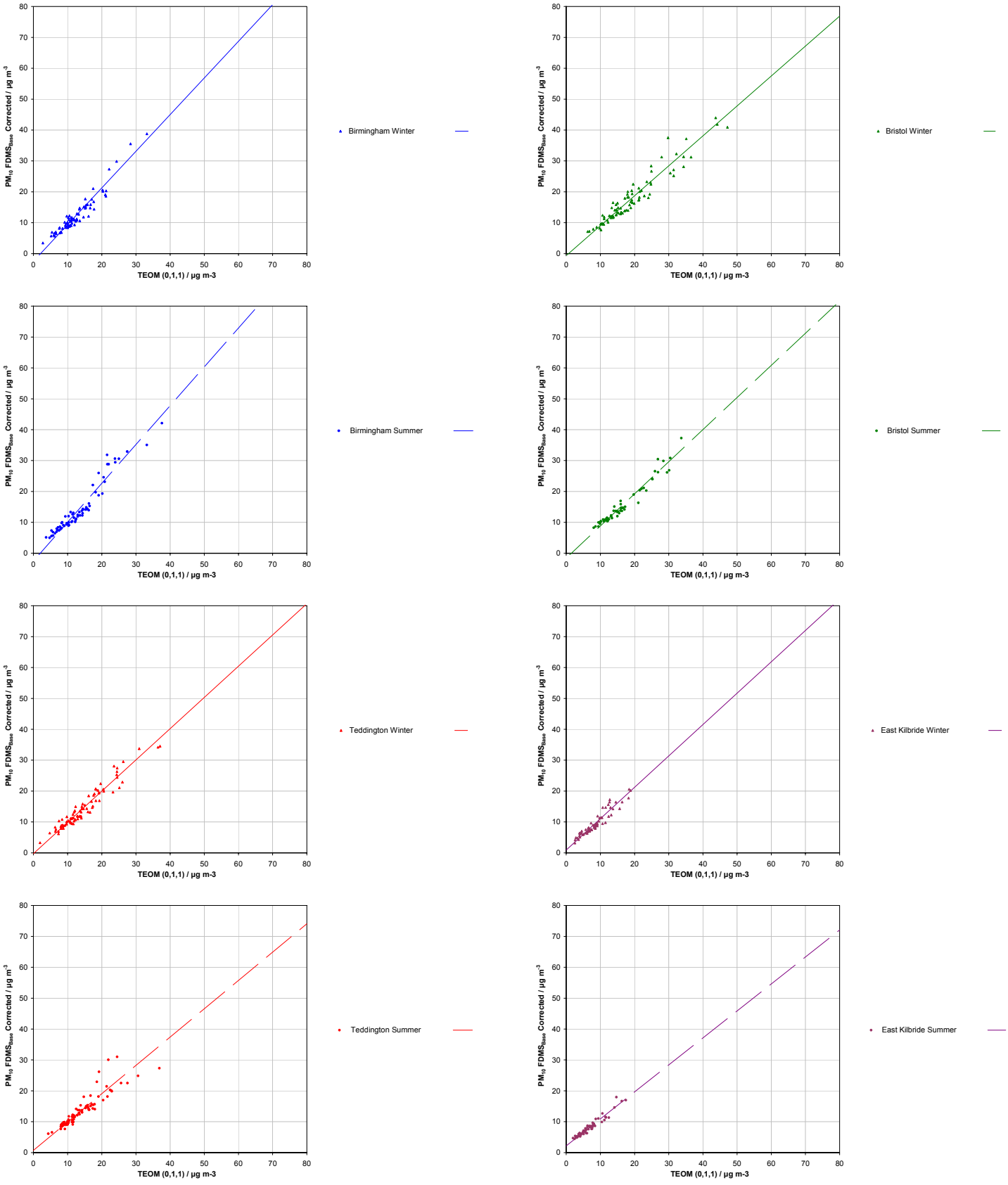
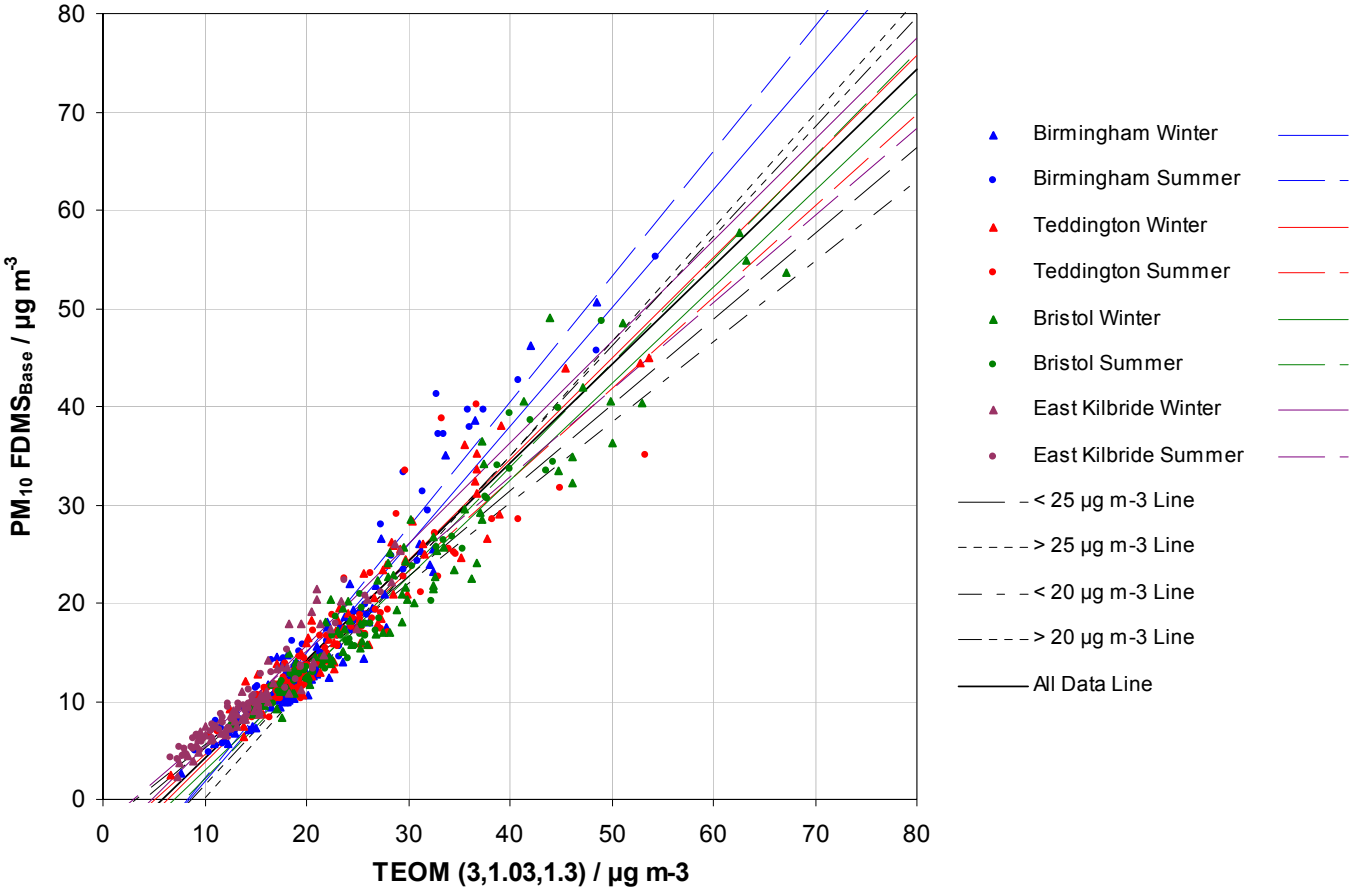


Figure D.20: Chart and Table summarising the comparison of PM_{10} $FDMS_{Base}$ against TEOM(3,1.03,1.3). The terms and colours used in the Table are discussed in Section 5.9. a and u_a have units of µg m^{-3}.



TEOM (3,1.03,1.3) vs PM_{10} $FDMS_{Base}$	Dataset	Orthogonal Regression				Annual LV	Daily LV
		n	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	W_{F-T} / %	W_{F-T} / %
Individual Campaigns	Birmingham Winter	75	0.914	1.206 +/- 0.041	-10.296 +/- 0.909	16.38	10.23
	Birmingham Summer	70	0.926	1.277 +/- 0.042	-10.638 +/- 0.988	15.60	17.89
	Teddington Winter	85	0.931	1.028 +/- 0.030	-6.550 +/- 0.745	29.69	22.74
	Teddington Summer	82	0.822	0.932 +/- 0.044	-4.852 +/- 1.070	40.48	34.93
	Bristol Summer	53	0.950	1.057 +/- 0.033	-8.487 +/- 0.926	32.73	24.04
	Bristol Winter	82	0.917	0.985 +/- 0.032	-6.936 +/- 1.012	40.92	33.28
	East Kilbride Summer	54	0.934	0.888 +/- 0.032	-2.662 +/- 0.453	36.17	33.39
	East Kilbride Winter	66	0.904	1.032 +/- 0.040	-4.982 +/- 0.651	19.97	14.80
All Campaigns	All Data	567	0.908	1.001 +/- 0.013	-5.826 +/- 0.309	32.20	25.71
Annual Limit Value of 40 µg m^3	< 20 µg m^3	279	0.794	0.820 +/- 0.023	-2.603 +/- 0.350	49.33	-
	> 20 µg m^3	288	0.840	1.117 +/- 0.026	-9.677 +/- 0.795	31.30	-
Daily Limit Value of 50 µg m^3	< 25 µg m^3	393	0.836	0.874 +/- 0.018	-3.484 +/- 0.321	-	39.65
	> 25 µg m^3	174	0.768	1.162 +/- 0.042	-11.554 +/- 1.447	-	23.22

- Denotes Not Applicable.

Figure D.20 Continued: Charts summarising the comparison of PM_{10} $FDMS_{Base}$ and TEOM(3,1.03,1.3).

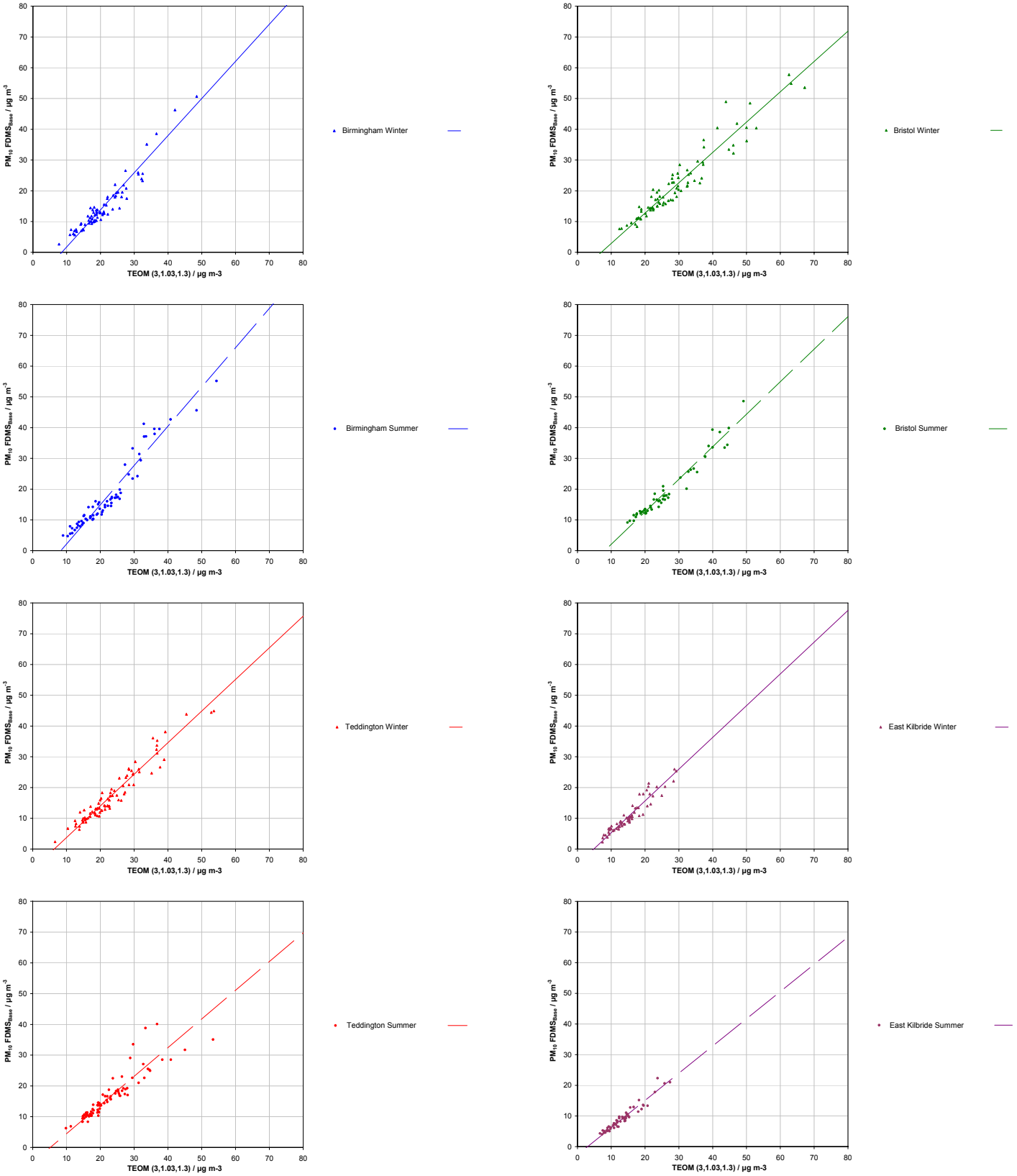
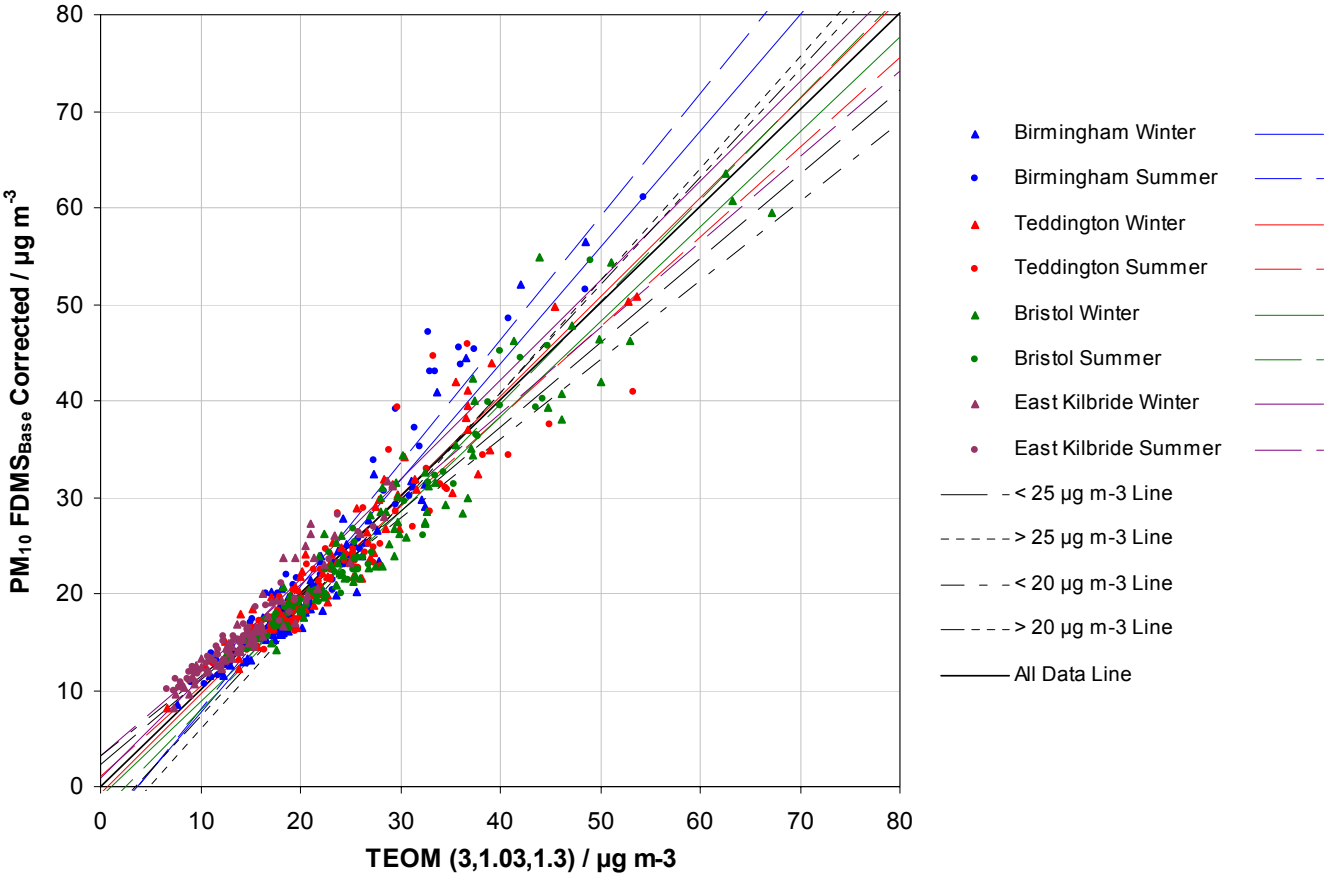


Figure D.21: Chart and Table summarising the comparison of Corrected PM_{10} $FDMS_{Base}$ against TEOM(3,1.03,1.3). The terms and colours used in the Table are discussed in Section 5.9. a and u_a have units of µg m^{-3}.

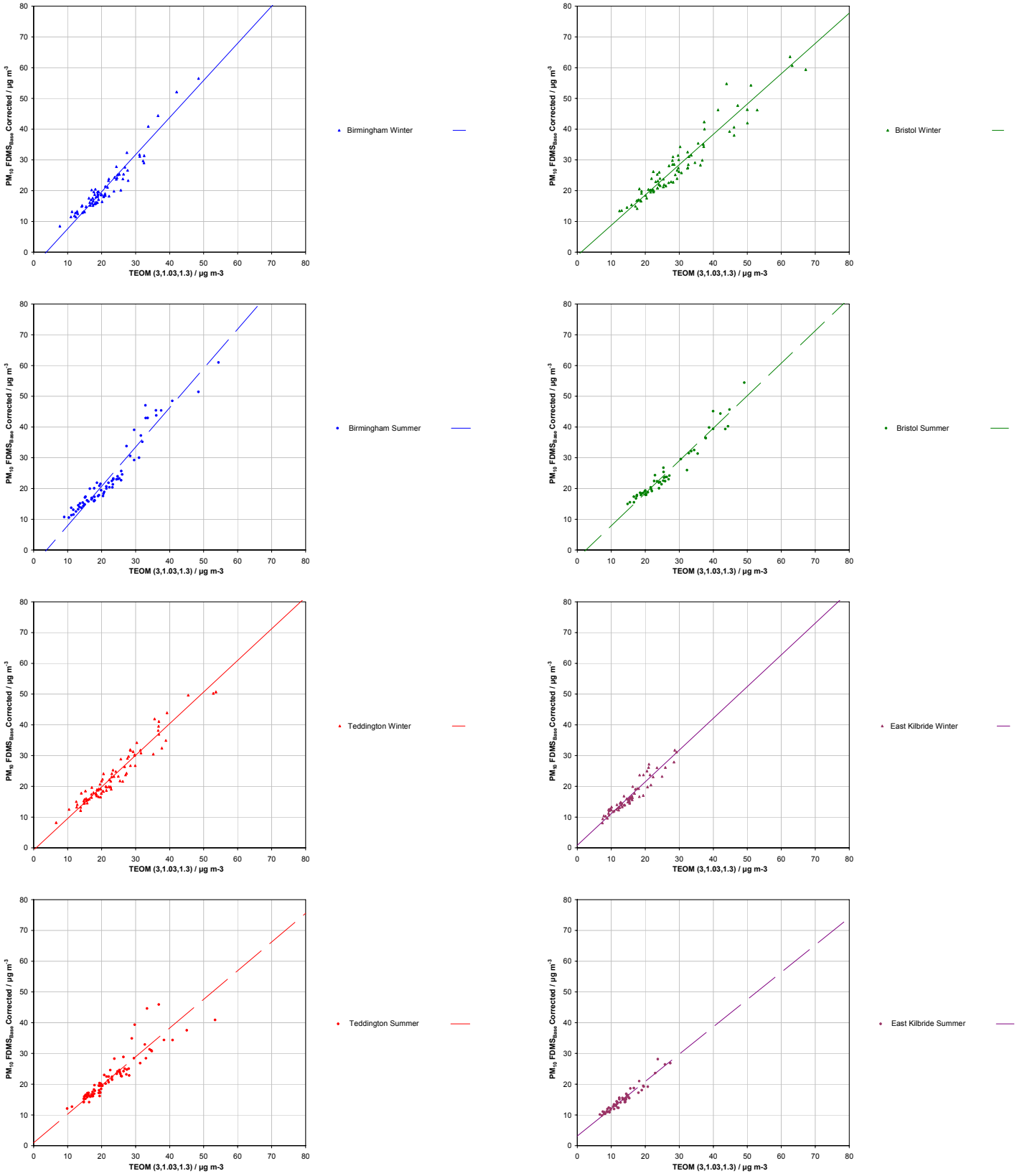
$$TEOM\,(3,1.03,1.3) = \left(PM_{10}FDMS_{Base} + 5.826\right)$$



TEOM (3,1.03,1.3) vs PM_{10} $FDMS_{Base}$ Corrected	Dataset	Orthogonal Regression				Annual LV	Daily LV
		n	r^2	Slope (b) +/- u_b	Intercept (a) +/- u_a	$W_{F\text{-}T}$ / %	$W_{F\text{-}T}$ / %
Individual Campaigns	Birmingham Winter	75	0.914	1.206 +/- 0.041	-4.470 +/- 0.909	22.88	25.55
	Birmingham Summer	70	0.926	1.277 +/- 0.042	-4.811 +/- 0.988	35.06	38.32
	Teddington Winter	85	0.931	1.028 +/- 0.030	-0.724 +/- 0.745	12.22	10.02
	Teddington Summer	82	0.822	0.932 +/- 0.044	0.974 +/- 1.070	16.98	15.14
	Bristol Summer	53	0.950	1.057 +/- 0.033	-2.660 +/- 0.926	10.62	8.39
	Bristol Winter	82	0.917	0.985 +/- 0.032	-1.109 +/- 1.012	18.22	14.86
	East Kilbride Summer	54	0.934	0.888 +/- 0.032	3.165 +/- 0.453	8.55	10.73
	East Kilbride Winter	66	0.904	1.032 +/- 0.040	0.844 +/- 0.651	13.03	11.48
All Campaigns	All Data	567	0.908	1.001 +/- 0.013	0.000 +/- 0.309	14.38	11.51
Annual Limit Value of 40 µg m^3	< 20 µg m^3	279	0.794	0.820 +/- 0.023	3.224 +/- 0.350	20.81	-
	> 20 µg m^3	288	0.840	1.117 +/- 0.026	-3.851 +/- 0.795	19.46	-
Daily Limit Value of 50 µg m^3	< 25 µg m^3	393	0.836	0.874 +/- 0.018	2.343 +/- 0.321	-	17.04
	> 25 µg m^3	174	0.768	1.162 +/- 0.042	-5.728 +/- 1.447	-	21.03

- Denotes Not Applicable.

Figure D.21 Continued: Charts summarising the comparison of Corrected PM_{10} $FDMS_{Base}$ and TEOM(3,1.03,1.3).



APPENDIX E

DEVIATIONS FROM THE GUIDANCE, EN12341 AND EN14907

E.1 Introduction

Throughout this report the authors have highlighted that it has been necessary to both interpret The Guidance on PM equivalence, and also to 'step outside' the current CEN standards for PM_{10} and $PM_{2.5}$. It is intended that the experience gained by the UK team in undertaking this programme will be fed back to EU Working Groups on particulate matter. As such, any future revisions to current Guidance and CEN standards can build upon these experiences and those derived from other equivalence-based programmes. It is emphasised that the application of the precise methodology set out within The Guidance is not mandatory, and that other approaches that are in broad compliance with the principles of ENV 13005 may be used, provided that the validity of the approach is adequately justified.

E.2 Summary of Deviations from EN12341

E.2.1. EN12341 only allows for quartz fibre filters to be used for the measurement of PM_{10}. Emfab filters were used in the current study. EN14907 allows for the use of any of Emfab; Teflon; quartz or glass fibre. It is expected that these four filter media will be allowed in future revision of PM standards.

E.3 Summary of Deviations from EN14907

E.3.1. EN14907 states: "The sampling system shall be made of an inert, non-corroding, electrically conducting material: preferably stainless steel or anodised aluminium or aluminium alloy". The units employed in this study were constructed of anodised aluminium (and as such conforms to EN14907), however, the manufacturer now manufactures the samplers from stainless steel.

E.3.2. EN14907 requires the filter be held in an environment with sheath air surrounding the inlet pipe work. The $PM_{2.5}$ samplers used as the reference method in the current study hold the filter outside (as with the PM_{10} reference sampler). Sunlight shining on the filter holder may therefore be a problem, however, the Europe wide CEN study for formulating EN14907 [12] tested both the samplers used in the current study and the sheath air cooled version, with no observed difference in the results. EN14907 was not finalised at the time the current study commenced, and there were no commercially available reference samplers conforming to EN14907 at project inception.

E.3.3. The glove box used for weighing was maintained at (20 ± 1) °C and (50 ± 5) % RH in line with EN14907. Occasions when the measured humidity fell outside the prescribed limits were noted. For a short period early in the Programme a series of filters was weighed with high relative humidity due to laboratory control problems. Where the effected weighings were post sampling weights, the filters were reweighed. Where the effected filters were pre sampling weights, the results were included, as it was not possible to reweigh them; they were weighed relative to a

tare filter kept in identical conditions; and the laboratory experiments had shown that the mass of un-sampled Emfab filters is essentially unaffected by relative humidity when the protocol is followed. Analysis of the finalised data indicated that there was no effect on the outcome of the equivalence tests when these filters were used.

E.3.4. EN14907 states that sampled filters may be stored for a maximum of 15 days before introduction to the weighing room, which was not always adhered to. However, all filters were kept refrigerated from the time that they were removed from the samplers. Tests by NPL had shown that ammonium nitrate would not evaporate from filters even at 50 ºC, and so this approach was considered to be valid. It is felt that as 15 days was impractical for a relatively small scale field study, it is less likely to be attainable if this methodology were adopted by a National or Regional network, and as such, the methodology employed herein is representative of how the reference samplers would be operated in practice.

E.3.5. EN14907 states that unloaded filters should be rejected if the difference between the masses of the two pre weighings is greater than 40 µg. Similarly, EN14907 states that sampled filters should be rejected if the difference between the masses of the two post weighings is greater than 60 µg. In practice, filters were not rejected based on these criteria, as this would severely impact data capture rate. The observed distributions of repeat mass measurements are shown in Section A.4, and are considered unlikely to have had a significant effect on the results.

E.4 Summary of Deviations from The Guidance

E.4.1. Significant outliers were sometimes observed when considering the intra-instrument comparison of filter mass based measurements (PM_{10} KFG; $PM_{2.5}$ Leckel; Partisol 2025; and SM200 Mass). It is thought that these outliers are associated with human error (for example through transporting or weighing filters, or problems related to filter identification), and are therefore representative of the methods employed by the operators and not the instrument itself. Particularly where significant ‘human error’ outliers occur for the reference sampler, leaving these outliers in will result in the failure of all candidate instruments, and so it was considered necessary to remove these outliers for filter mass based measurements.

The Guidance states that: “Indications of outlying data (pairs) may be obtained using Grubb’s tests on the individual single-period variances. Outlier tests are to be performed at the 99% level”. This statement is ambiguous as to whether and to what extent Grubbs’ Test should be used, and so the approach followed in the CEN $PM_{2.5}$ study [12] was adopted in the current study, whereby: “[Grubbs’ Test] was repeated until either the critical value was not exceeded, or at most 5% of the

data pairs were removed.". In order to standardise this procedure (and so remove any opportunity for bias in data interpretation), all outlying data pairs identified by Grubbs' Test were removed up to a maximum of three pairs in each dataset. Three outliers were chosen as being representative of the maximum 5% of pairs that were deleted in the CEN $PM_{2.5}$ study [12]. Grubbs' Test was applied only to pairs of results from nominally identical instruments. No data were removed because of differences between results from different types of instrument.

In applying the Grubbs' Test, a number of obvious outliers were removed. In addition, a number of less obvious outliers have been removed. It is felt that deleting these points that were not obviously outliers would not compromise the results of the tests for equivalence, so rather than introduce a subjective element into outlier removal; the stated procedure was always followed.

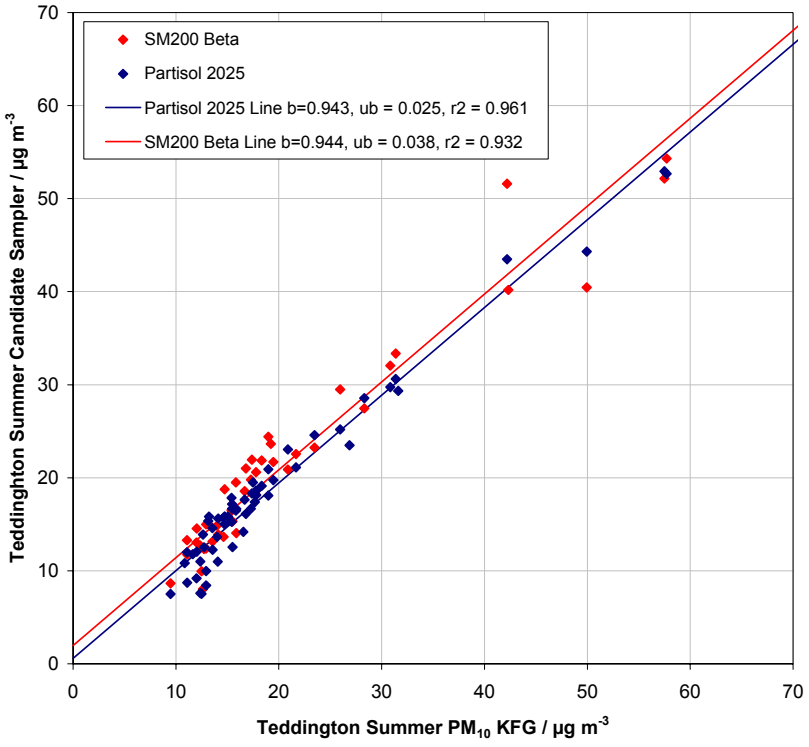
It should be noted that Grubbs' test identifies outliers that are significantly outside the rest of the dataset. For instruments where there is high reproducibility (such as $PM_{2.5}$ Leckel in the current study), a greater number of outliers are identified as a result of the 'tighter' agreement between instruments. This is because outliers due to small amounts of 'human error' were more easily identifiable than for other instruments where the general scatter of the instrument is of a similar magnitude to the 'human error'.

E.4.2. The Guidance states that a precondition for acceptance of a dataset is that the slope or intercept should be 'insignificantly different' from 1 and zero respectively for any of the individual or combined datasets based on two standard deviations. These criteria have the effect of punishing instruments with low scatter, while rewarding instruments whose results contain a relatively large amount of scatter (though not enough scatter that they fail on the random term element of the expanded uncertainty calculations). For example, consider the Teddington Summer data for the Partisol 2025 ($b = 0.943$; $u_b = 0.025$; $r^2 = 0.961$) and SM200 Beta ($b = 0.944$; $u_b = 0.038$; $r^2 = 0.932$). Both instruments have a near identical slope (b) against the reference method, however as the Partisol 2025 has less scatter, the uncertainty in the slope (u_b) is lower, and therefore the slope of the Partisol 2025 is significant (based on two standard deviations), whereas the SM200 Mass is not. According to The Guidance, as two of the slopes for the Partisol 2025 are significant, the entire dataset 'may' be corrected by the slope of the regression of the entire dataset comprised of all campaigns together. For the Partisol 2025, the slope of all the data was 1.003, and so correcting for slope would be ill advised. We therefore concluded that these criteria were inappropriate in practice.

Instead, the authors have elected to remove this ambiguity in The Guidance and proceed by an alternative approach. Data were corrected only if the slopes of the

datasets were all greater or all less than 1, and/or the intercepts of the datasets were all greater or all less than zero. This was shown to be a highly consistent and pragmatic approach.

Figure E.1: Chart summarising the comparison of SM200 Beta and Partisol 2025 Candidate Methods for Teddington Summer Data. Both have near identical slopes, yet when implementing the criteria suggested in The Guidance, only the Partisol 2025 slope is statistically significant based on two standard deviations.



E.4.3. For the purpose of this study, where a candidate instrument was found to fail on W_{CM} (expanded uncertainty) for the <50 % Limit Value dataset alone (either before or after slope and/or intercept correction), this was not considered sufficient evidence for a candidate instrument to be excluded. Rather, it reflects the problems associated with regression calculations where there is significant scatter on data that are restricted to within a narrow range (*i.e.* low PM concentrations).

This approach has also been followed at East Kilbride, where measured concentrations (particularly for $PM_{2.5}$) were very low. Whilst these data have been included in the tests applied to the combined datasets, the individual East Kilbride datasets have been treated with caution. Failure of a candidate instrument to meet the W_{CM} criterion for this site alone was not considered suitable justification for rejection. The Guidance states that a minimum of four datasets are required to declare that the equivalence criteria are met. It is important to note that whilst eight datasets were collected in the current study, it was not considered appropriate to exclude individual datasets simply because they did not conform to desired

criteria. By treating the East Kilbride datasets with caution (on the basis that ambient concentrations were very low and that this compromises the orthogonal regression), the authors believe that the most rigorous approach has been adhered to.

E.4.4. The equations used in the uncertainty calculations are the same as those used in The Guidance. However, the nomenclature has been changed slightly in order to remove ambiguity. For example, in equation E C.16 (based on Equation 9.6 in The Guidance), the number 100 has been added to clarify that the uncertainty should be converted to a percentage; and also y_i has been replaced by LV as the denominator of the equation as the former is confusing to non-statisticians.

E.4.5. The Guidance available at time of writing (Version 3), states that datasets should be split to those greater and less than 50 % of the Data Quality Objective. This is an error, and datasets should be split to be greater and less than 50 % of the Limit Value. The authors of The Guidance have been notified of this error.

E.4.6. In the current study, the $PM_{2.5}$ FDMS was shown to fail the 25 % expanded uncertainty criteria for the Birmingham Winter dataset. This was attributed to the lower Limit Value for $PM_{2.5}$ instruments compared to that for PM_{10}. At lower Limit Values, a non-zero intercept becomes statistically more significant in the calculation of the expanded uncertainty. As the Limit Value for $PM_{2.5}$ has yet to be finalised, the candidate instrument was deemed to meet the criteria for equivalence.

E.4.7. Owing to difficulties in obtaining valid concurrent paired data for candidate and reference samplers, some datasets have fewer than 40 data-pairs. It is recommended that future studies operate three of each instrument.