



The King's College London
Volatile Correction Model for PM₁₀
Development, Testing and Application

**Prepared for Department for Environment, Food and Rural Affairs (Defra),
the Scottish Executive, the Welsh Assembly Government and the DoE in
Northern Ireland**

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King's College London

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SUMMARY

This report details the derivation, testing and application of a model to correct measurements of PM₁₀ by the Tapered Element Oscillating Microbalance (TEOM) such that they can be used to measure PM₁₀ for assessment against the EU Limit Value in the UK.

The First Daughter Directive (1999/30/EC) set Limit Values for PM₁₀ and also stipulated that PM₁₀ should be measured gravimetrically as laid out in EN12341 (CEN, 1998). There is however a conflict between the requirement to measure PM₁₀ gravimetrically and the requirement for rapid public reporting, and many member states, including the UK, rely on non-gravimetric techniques to measure PM₁₀. In the UK the majority of PM₁₀ measurements are made using the TEOM. In 2006, the UK PM₁₀ Equivalence Programme showed that the TEOM did not meet the equivalence criteria. The implied need to upgrade or replace TEOMs with an equivalent automated measurement technique has significant cost implications for DEFRA, the Devolved Administrations and for local authorities.

The KCL Volatile Correction Model (VCM) was based on analysis of daily mean measurements of PM₁₀ by Filter Dynamics Measurement System (FDMS) and TEOM at sites in the UK Equivalence Programme and at sites in the London Air Quality Network (LAQN). The model used the FDMS purge measurement (a measure of the volatile component of PM₁₀, which is expressed as a negative concentration) to correct for differences in the sensitivity to volatile PM₁₀ between the TEOM and the EU reference method. The model equation for the correction of TEOM PM₁₀ measurements is:

$$\text{Reference Equivalent PM}_{10} = \text{TEOM} - 1.87 \text{ FDMS purge}$$

The FDMS purge concentration may be measured at a remote site, allowing the possibility of using a single FDMS instrument to correct the PM₁₀ measurements made by several TEOMs in a defined geographical area.

Three data analysis 'experiments' were undertaken to test the equivalence of the model to the EU reference method and to determine the maximum distance over which a FDMS purge measurement could correct measurements from TEOM instruments. The model was assessed against the criteria for the EC Working Group's Guidance for the Demonstration of Equivalence of Ambient Air Monitoring Methods: the 'Guidance'. Overall 772 equivalence tests were undertaken. The model passed the Guidance equivalence criteria at the sites used in the UK Equivalence Programme and can therefore be considered an equivalent method.

Further, the model passed the equivalence criteria using remote FDMS purge measurements over a maximum distance of approximately 200 km (22 out of 23 tests at less than 200 km passed the equivalence criteria, the single failure was marginal). This proves that the model is a viable tool for correcting measurements from TEOM instruments on the national and local government networks using FDMS purge measurements from a more limited network of sites.

The FDMS and the model were also tested against measurements at AURN sites. The AURN sites were outside the UK Equivalence Programme and employed slightly different measurement methodologies, although they did conform to the relevant CEN standard for PM₁₀ measurement. In most circumstances, the FDMS failed the equivalence criteria when tested against the AURN measurements. The model was derived from FDMS measurements and therefore unsurprisingly it also failed in many of these circumstances.

It was concluded that the failure of the FDMS and the model to pass the equivalence criteria at these sites was primarily due to the differences in measurement methodology at the AURN sites from that employed in the UK Equivalence Programme. For this reason, it is recommended that the measurement methodology at the AURN sites is brought into line with that used during the UK Equivalence Programme as far as is practically possible.

To enable the model to be applied to the TEOM measurements made routinely in the UK the configuration of the TEOMs should be changed to be the same as that used in the UK

Equivalence Programme. This necessitates removing the software correction factors and reporting measurements at atmospheric temperature and pressure.

The current and planned installation of FDMS instruments in the UK was found to provide adequate coverage for the model to be applied in all locations in the UK except parts of Scotland and Northern Ireland, where three additional FDMS instruments would be required. Additional FDMS instruments were also recommended in East Anglia, the northeast, the northwest, Kent and the south coast to enhance the coverage in England.

A method of testing one FDMS instrument against another distant FDMS instrument was developed to ensure that any future FDMS network remains representative of purge measurements around the UK, without the need to undertake detailed ongoing measurement method comparisons. Using the measurements from the UK Equivalence Programme, a threshold of $1.5 \mu\text{g m}^{-3}$ in the uncertainty between these purge measurements was calculated. This value can be used to test whether the model can be applied to the area between two AURN sites.

GLOSSARY

ATP	Atmospheric Temperature and Pressure.
DEFRA	Department for Environment Food and Rural Affairs.
Emfab	Teflon-coated glass fibre filters.
EN 12341	Standard for the reference measurement of PM ₁₀ concentration
Equivalence	Equivalent PM ₁₀ measurement method to EN12341 according to the criteria in the Guidance.
EU	European Union.
FDMS	Filter Dynamics Measurement System.
FDMS purge	Mass concentration obtained from the FDMS at 30°C with sample having passed through dryer and 4°C chilled filter. Confusingly, termed FDMS Reference by the manufacturer.
FDMS Base	Mass concentration obtained from the FDMS at 30°C with sample having passed through a dryer.
Guidance, the	EC (2005). Demonstration of Equivalence of Ambient Air Monitoring Methods, EC Working group on Guidance for the Demonstration of Equivalence.
KCL	King's College London.
KFG	Klienfiltergerrat PNS-X8 a European Reference sampler for the measurement of PM ₁₀ .
NPL	National Physical Laboratory.
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
MS SQL	Microsoft Structured Query Language.
OS	UK Ordinance Survey.
PM ₁₀	Fraction of airborne particulate that passes through a size selective inlet with a 50 % collection efficiency at an aerodynamic diameter of 10 µm.
Partisol 2025	A sampler for the measurement of PM ₁₀ . Harrison 2006 found this sampler to be equivalent to the EU reference method.
TEOM	Tapered Element Oscillating Microbalance.
U _{BS}	Between sampler uncertainty.
U _{purge}	Between FDMS purge uncertainty.
W _{CM}	Relative expanded uncertainty at the limit value.

1 INTRODUCTION

The UK's EU obligations regarding air quality are set out in The Air Quality Framework Directive (96/62/EC) and in four Daughter Directives. These directives set Limit and Target Values for individual air pollutants along with data quality requirements with respect to 'accuracy' and data capture.

The First Daughter Directive (1999/30/EC) included Limit Values for PM₁₀ and also stipulated that PM₁₀ should be measured gravimetrically as laid out in EN12341 (CEN, 1998). There is however a conflict between the requirement to measure PM₁₀ gravimetrically and the requirement for rapid public reporting due to the time between sampling, weighing and reporting the data, which can be up to 21-28 days after the sample was taken. Many member states therefore rely on automated techniques to measure PM₁₀.

In the UK the majority of PM₁₀ measurements are made using the TEOM automated method. The TEOM has the widely acknowledged disadvantage of driving off semi-volatile material such as ammonium nitrate and organic aerosols (Ruppecht E. *et al.*, 1992; Allen and Reiss, 1997; Salter and Parsons, 1999; Soutar *et al.*, 1999; Green *et al.*, 2001; Josef *et al.*, 2001; Charron *et al.*, 2003). A 'correction' factor of 1.3 was therefore recommended in the UK for comparison of TEOM PM₁₀ measurements with the EU Directive (DETR, 2000).

Comparing the performance of the reference gravimetric technique with other PM₁₀ measurement techniques is not simple. This is due to the lack of a standard reference material for airborne particulate and due to the nature of the pollutant itself; different measurement techniques have different sensitivity to both the semi-volatile constituents of PM₁₀ and to the confounding effects of relative humidity. Guidance for the demonstration of equivalence has been proposed by the EC Working Group for the Demonstration of Equivalence (the 'Guidance').

During 2004 DEFRA embarked upon a programme to determine the equivalence of several automated and non-automated PM₁₀ and PM_{2.5} measurement techniques (Harrison, 2006). Several instruments proved equivalent to the European PM₁₀ reference method: Partisol 2025, FDMS, Opsis SM200 Beta Attenuation Monitor (BAM), Opsis SM200 sampler (with slope and intercept correction) and the Met One Beta BAM (with slope correction). Importantly, the TEOM did not meet the equivalence criteria and is therefore not suitable for reporting PM₁₀ and for analysis against the EU limit values. The implied need to upgrade or replace TEOMs with an equivalent automated measurement technique has significant cost implications for DEFRA, the Devolved Administrations and for local authorities.

During 2003 King's College London (KCL) instigated a FDMS monitoring programme in conjunction with the London Boroughs (Green and Fuller, 2004; Green and Fuller, 2006). Arising from this programme, Green and Fuller (2006) proposed a relationship utilising FDMS purge measurements to maintain 'continuity' between measurements of PM₁₀ made using the FDMS and those made using the TEOM.

Given that a relationship could be derived to achieve continuity between TEOM and FDMS, and that the FDMS is equivalent to the EU reference gravimetric method, it should be possible to correct TEOM measurements so that they can meet the equivalence criteria. Further, the 'continuity' relationship proposed by Green and Fuller (2006) implies the possibility of a regionally derived correction factor; correcting several TEOMs in a region based on the measurements from a single FDMS. Initial tests of this hypothesis (the KCL Volatile Correction Model) proved encouraging and Defra therefore commissioned KCL to carry out a detailed appraisal to inform the future PM₁₀ monitoring strategy for the UK.

This report details the results of a series of 'experiments' using ambient air pollution measurements from several UK monitoring programmes. The report follows a progressive approach to testing the hypothesis. In each case the results from the KCL Volatile Correction Model were compared to the criteria in the Guidance which was used as the arbiter of the efficacy of the correction model. The staged approach is summarised below

A) Derivation of the KCL Volatile Correction Model.

B) The model was then tested in three experiments:

Experiment 1) The model was tested using collocated FDMS and TEOM measurements and compared to the reference method measurements from the UK Equivalence Programme. In this experiment sufficient measurements were available to subject the results to the full equivalence tests. The objective of the experiment was to prove the equivalence of the model excluding the regional aspects.

Experiment 2) The TEOM measurements made in the UK Equivalence Programme were 'corrected' using FDMS measurements from distant sites and compared to the reference method measurements. Again sufficient measurements were available to subject the results to the full equivalence tests. The experiment had two objectives; to prove the equivalence of the model including the regional aspects and to begin to determine the model's spatial applicability.

Experiment 3) The TEOM measurements at other UK sites were 'corrected' using FDMS measurements from distant sites and compared to the Partisol measurements. Results were judged in terms of the equivalence criteria. This experiment aimed to further determine the model's spatial applicability.

C) The results from B) were used to determine the required spatial distribution of FDMS instruments to enable the model to be applied to all AURN TEOMs.

2 METHOD

This section details the measurement methods used, the measurement programmes that supplied data, model derivation, statistical comparisons used, the coding of the model and the design of the experiments.

2.1 Measurement Methods

Four methods were used for measurement of the mass concentration of PM₁₀ or chemical speciation; these methods are described in sections 2.1.1 to 2.1.4. Given the purpose of the study, the TEOM and FDMS methods are described in greater detail.

2.1.1 Gravimetric Measurement of PM₁₀

The gravimetric method for the measurement of PM₁₀ mass concentration forms the basis of the European and US gravimetric reference methods when used in association with defined operating parameters governing the choice of sampler, filter and method of laboratory (EPA, 1997; CEN, 1998; CEN, 2003); these are summarised in Table 1. The gravimetric samplers collected particulate matter onto a pre-weighed filter. The filter was then re-weighed under standardised conditions to determine the mass of particulate collected on the filter. Using measurements of sample volume, a mass concentration of particulate matter in the air was calculated.

	EU PM ₁₀	EU PM _{2.5}	US EPA PM ₁₀	US EPA PM _{2.5}
Sampling Period	24 h	24 h (±1 h)	24 h	24 h
Filter Media	Quartz Fibre	Quartz Fibre, Glass Fibre, PTFE, Emfab	Not Specified	PTFE
Filter Conditioning Temperature	20 °C (±1 °C)	20 °C (±1 °C)	15-30 °C (±3 °C)	15-30 °C (±3 °C)
Filter Conditioning Humidity	50% RH (±3% RH)	50% RH (±5% RH)	20-45% RH (±5% RH)	20-45% RH (±5% RH)
Minimum Filter Equilibration Time	48 h	48 h	24 h	24 h
Reporting Conditions	0 °C, 101.3 kPa	Ambient	Ambient	Ambient

Table 1: Specifications for the EU and US EPA Reference Methods

Two gravimetric sampling methods were used to measure PM₁₀ in this study, the Leckel Klienfiltergerrat PNS-X8 (KFG) and the Partisol 2025. The KFG is a European reference sampler for the measurement of PM₁₀. The Partisol 2025 was found to be equivalent to the reference sampler for the measurement of PM₁₀ in the UK using Teflon-coated glass fibre (Emfab) filters (Harrison 2006). The Partisol 2025 was used as the reference sampler in the French Equivalence Programme, using quartz filters (Ampe *et al.*, 2005). Quartz filters are required for the measurement of PM₁₀ under the current legislation (CEN, 1998). However, Brown *et al.* (2006) found that the choice of filter media could impact on the repeatability of measurement due to the loss of filter integrity, the loss of sampled material during storage and transport and the degree to which of temperature and humidity during conditioning affect the mass measurement. It was expected at the onset of the UK Equivalence Trials, that Emfab would be included in the revised PM₁₀ standard as they are included in EN14907. Consequently, the Equivalence Programme used Emfab filters, while the AURN used (and continues to use) quartz fibre filters, in accordance with EN12341. Stricter protocols for storage, transport, conditioning and weighing were also used in the Equivalence Programme as proposed in Brown *et al.* (2006) and in EN14907. These included chilled storage and transport, additional conditioning time pre and post exposure, tighter temperature and relative humidity controls and the reweighing of unloaded and loaded filters to ensure repeatability (leading to discarding of filters).

2.1.2 Tapered Element Oscillating Microbalance (TEOM)

The TEOM is a real time particulate mass monitor, its mass measurement method relies on a microbalance, which consists of a hollow glass tapered tube, clamped at one end and free to oscillate at the other; an exchangeable filter is placed on the free end. The frequency of

oscillation was measured and recorded by a microprocessor at two-second intervals. A schematic of the entire system is shown in Figure 4. The filter and the air stream passing through it were heated to 50 °C to reduce the interferences from particle bound water and to minimise thermal expansion of the tapered element, which may affect the oscillating frequency. This has the widely acknowledged disadvantage of driving off semi-volatile material such as ammonium nitrate and organic aerosols (Rupprecht E. *et al.*, 1992; Allen and Reiss, 1997; Salter and Parsons, 1999; Soutar *et al.*, 1999; Green *et al.*, 2001; Josef *et al.*, 2001; Charron *et al.*, 2003). However, the TEOM has received US EPA certification as an equivalent method for PM₁₀ monitoring (Rupprecht & Patashnick Co., 2003).

To enable a valid comparison between the measurement methods, adjustments were made to the TEOM measurements. The first corrected for the US EPA Correction Factor in the TEOM (TEOM = 3.0 µg m⁻³ + 1.03 Raw TEOM), which was included to account for the relative underestimation when compared to the US EPA reference method (Rupprecht E. *et al.*, 1992). The second corrected for the reporting conditions of the TEOM, which default to 25 °C, and 1 atmosphere pressure, and was the US EPA requirement prior to 1997. These are referred to as standard temperature and pressure (STP) and atmospheric temperature and pressure (ATP). The TEOM is reported at atmospheric temperature and pressure unless stated otherwise.

2.1.3 The Filter Dynamics Measurement System (FDMS)

The FDMS aims to measure the mass concentration of airborne particulate matter and quantify the mass changes of the filter due to evaporative and condensation processes that will affect the measurements. This system was based on TEOM technology, using the same microbalance. The FDMS sampled air through an R&P PM₁₀ inlet, and then used a dryer to remove water from the sample; this allowed the mass to be measured at 30 °C rather than 50 °C. After passing through the dryer, measurement was alternated between two cycles (base and purge), switching between them every six minutes; the different configurations of these cycles are shown in Figure 5. The change in mass on the filter was measured by the microbalance during both cycles.

A total particulate matter concentration measured by the FDMS was calculated as:

$$FDMS = FDMS\ base - FDMS\ purge$$

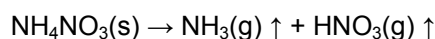
2.1.3.1 Base Measurement

The change in mass of the filter was measured by the microbalance after size selection and passing through the dryer. This provided a mass concentration of PM₁₀ analogous to that measured by the TEOM; the difference being the dryer and the reduced sampling temperature.

2.1.3.2 Purge Measurement (referred to as Reference in manufacturers literature)

During the purge cycle a filter, chilled to 4 °C, removed particulate matter and volatile organic compounds from the sample stream. This purged air was passed through the microbalance filter and the change in mass of filter measured.

During the purge measurement cycle, the mass lost due to the evaporation of volatile particulate matter tended to exceed the mass gained due to any condensation of gaseous material onto the filter. This resulted in a predominately negative purge measurement and increased the FDMS mass measurement above the base measurement. The dominant process during this cycle is therefore evaporation due to the volatile nature of many of the components of particulate matter (such as ammonium nitrate and organic compounds). The evaporation of ammonium nitrate into nitric acid and ammonia is shown in the equation below. However, positive measurements were also made, indicating that adsorption was occurring during certain conditions.



A study in the USA (Hering *et al.*, 2004) found a 1:1 relationship between the mass change during the FDMS purge cycle and measurements of nitrate in PM_{2.5} i.e. ammonium nitrate

accounted for the vapourisation from the filter measured during the purge cycle. A similar relationship has been found at Marylebone Road in London (Green, 2004) and is shown in Figure 1.

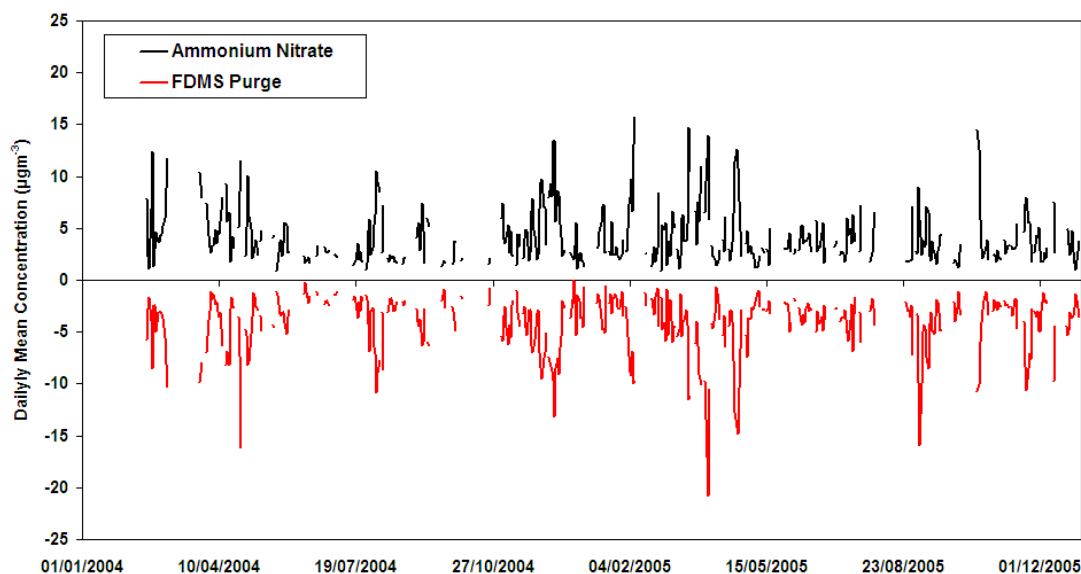


Figure 1: Time series of R&P 8400N daily mean ammonium nitrate measurements and daily mean FDMS purge measurements made at Marylebone Road during 2004

When examined at an hourly time resolution the relationship between the two metrics becomes increasingly clear. Figure 2 shows the hourly FDMS purge and ammonium nitrate measurements at Marylebone Road during April 2004. This month was chosen because the relatively low temperatures and prevalence of long range transport of secondary particulate matter during the spring leads to some of the highest particulate ammonium nitrate concentrations found in London each year. The FDMS purge and ammonium nitrate measurements shown in Figure 2 correlate fairly well ($r^2 = 0.50$). However a closer examination reveals a small lag between the peak concentration of ammonium nitrate and the maximum FDMS purge measurement. An example is shown on the inset graph in Figure 2, which highlights the hourly measurements from Marylebone Road between 16th April and 18th April (the highest concentrations during that month). The dotted line shows the time of the maximum ammonium nitrate concentration; $23 \mu\text{g m}^{-3}$ at 6:00 am on 17th April. The maximum FDMS purge concentration was measured one hour later. This was consistent with previous studies, which showed that the lag time between the ammonium nitrate concentration measurement and vaporisation was between 40 minutes and 100 minutes (Hering *et al.*, 2004). Indeed, if the time of the FDMS purge measurements during April is lagged by two hours, the r^2 increases to 0.62.

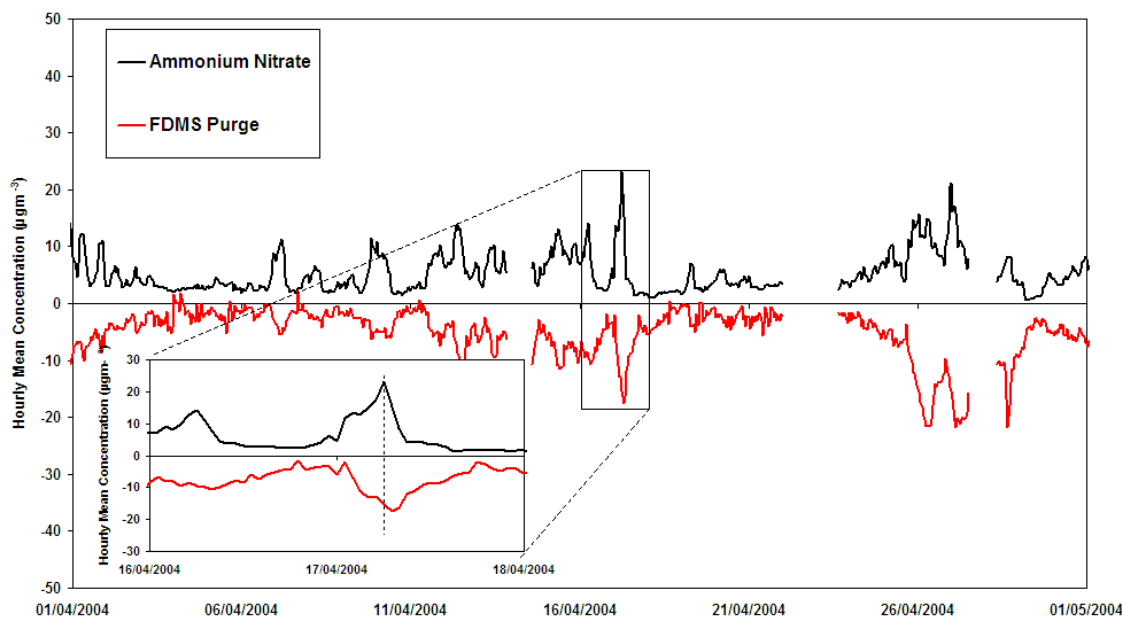


Figure 2: Time series of R&P 8400N hourly mean ammonium nitrate measurements and hourly mean FDMS purge measurements made at Marylebone Road during April 2004. The inset graph highlights the peak concentrations (shaded) measured on 17th April.

Orthogonal regression analysis of the more limited collocated ammonium nitrate and FDMS purge measurements at Harwell and Belfast are shown in Figure 3 alongside those from Marylebone Road. Strong correlations were found, however, slopes varied between 0.5 (Harwell) to 1.99 (Belfast), the Marylebone Road slope was 1.08. All the intercepts were close to zero. The relationship between the FDMS purge measurement and ammonium nitrate concentration therefore appears to vary at different locations where it is measured in the UK. However, as discussed a near 1:1 relationship has been demonstrated in London and at several sites in the USA and the reason for this differing relationship at other sites in the UK clearly requires further investigation.

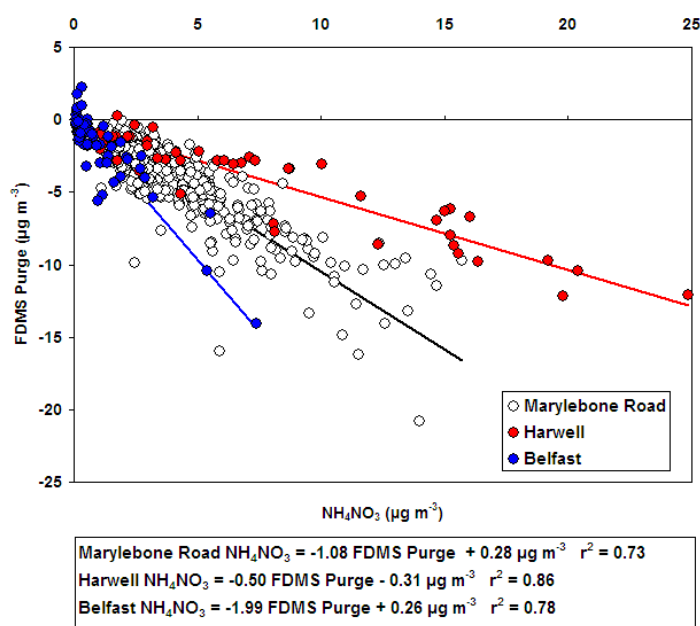


Figure 3: Orthogonal regression analysis between the NH_4NO_3 concentration in $PM_{2.5}$ and the FDMS purge measurements at Marylebone Road between 17th February 2004 and 31st December 2005.

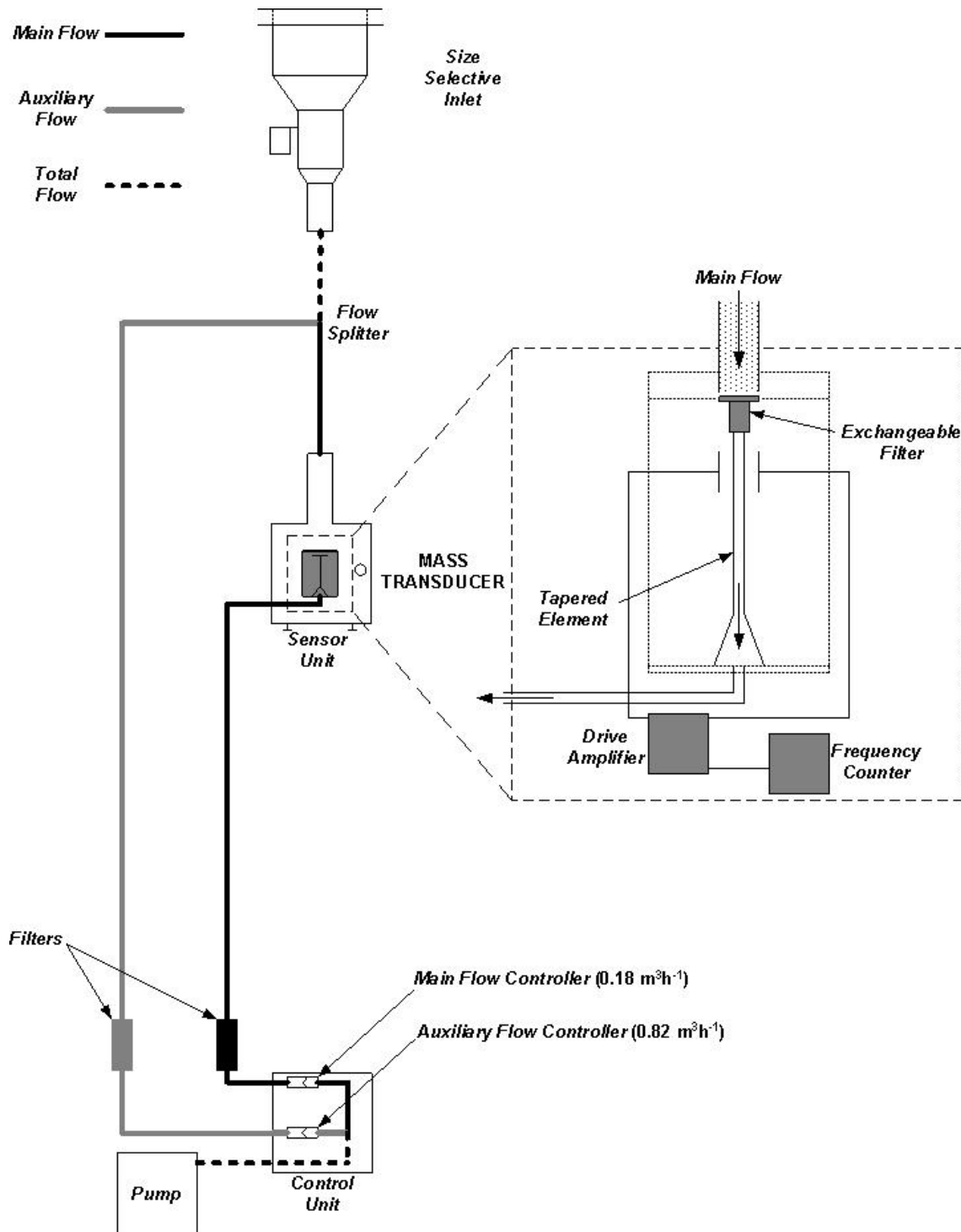


Figure 4: Schematic of the TEOM

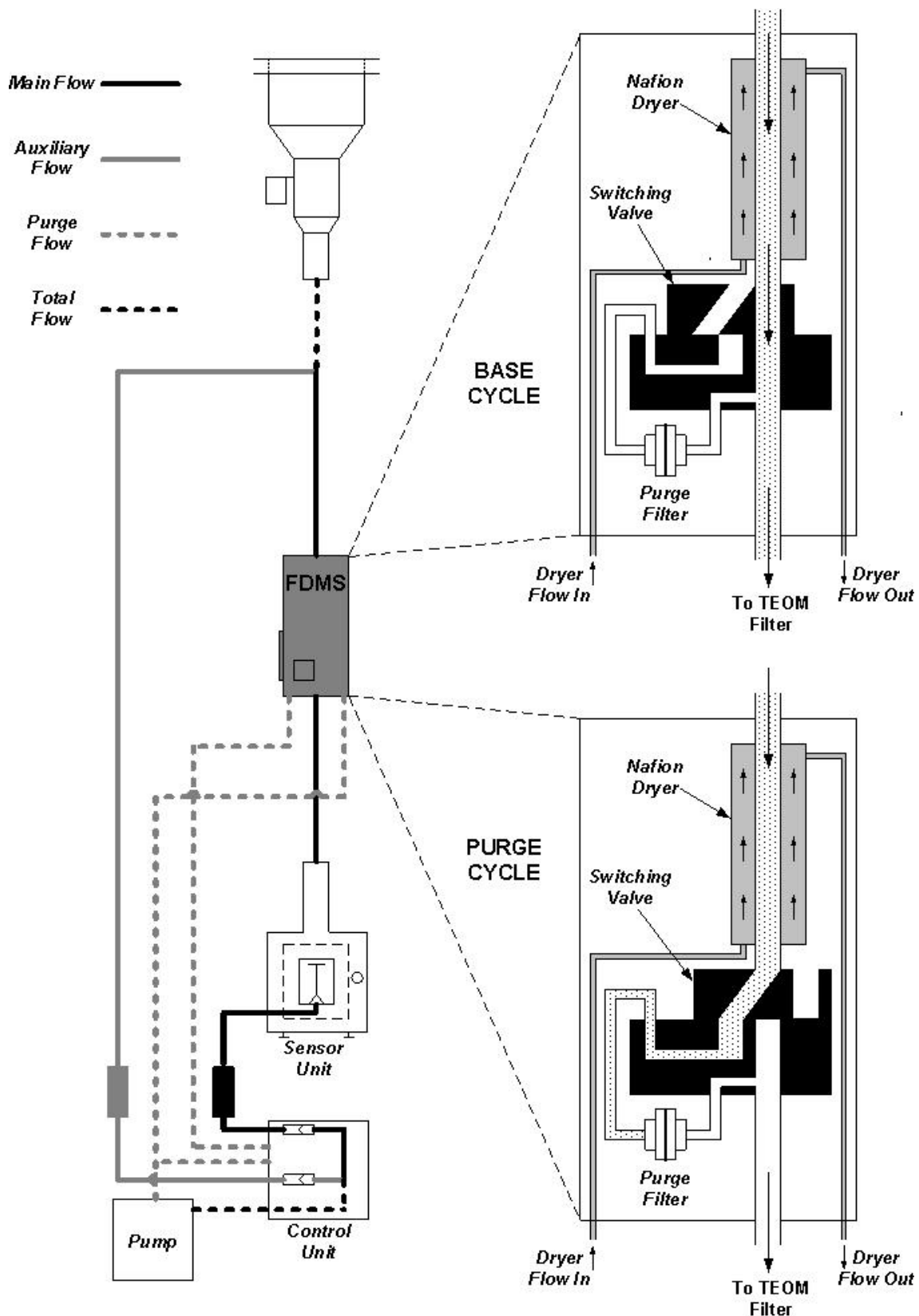


Figure 5: A schematic of the FDMS system. Base cycle (top) and purge cycle (bottom) configurations are shown separately.

2.1.4 Nitrate measurement

Nitrate measurements were made using the Rupprecht & Patashnick (R&P) Nitrate Monitor 8400N. The R&P 8400N is a near real-time particulate nitrate monitor, measuring the inorganic nitrate composition of PM_{2.5}. It consists of two instruments: a C3 pulse generator and a NO_x pulse analyser. The instrument was operated at default settings, although the cycle time was set to 15 minutes so that it could be directly compared to the TEOM instruments (before May 2005 at Harwell and Belfast this was 10 minutes). Every 15 (or 10) minutes, collected particles were flash-volatilised in a nitrogen atmosphere by resistive heating of the NiChrome strip. The NO_x pulse analyser measured the resulting pulse of NO_x.

2.2 Measurement Programmes

Measurements were obtained from four measurement programmes.

2.2.1 UK Equivalence Programme

The Defra funded UK Equivalence Programme (Harrison 2006) was a bespoke measurement programme designed to test the equivalence of seven candidate instruments to the EU reference methods for the measurement of PM₁₀ and PM_{2.5} concentration. The programme was managed by Bureau Veritas and included the operation of instruments at four locations in the UK; Teddington (suburban London), Bristol, Birmingham and East Kilbride. Measurements from the four locations were divided into separate summer and winter deployments to provide eight field campaigns from late 2004 to early 2006.

The candidate instruments included paired TEOM and FDMS for the measurement of PM₁₀, as well as other beta attenuation and sampler instruments not used in this study. The reference instrument for PM₁₀ measurement was the KFG. Filters were changed daily at 10h, 11h or 15h GMT.

Gravimetric measurements were made using Teflon-bonded glass fibre (Emfab) (Pall Corp., NY, USA; Type: EMFAB TX40HI20-WW; Part No.: 7221). As discussed in section 2.1.1, Emfab filters were chosen after extensive investigation of the properties of various filter media by the National Physical Laboratory (NPL)(Brown *et al.*, 2006).

NPL were responsible for the provision of quality assured gravimetric PM measurements and AEA Energy and Environment undertook audits of each reference and candidate instrument. Prior to the full equivalence trial FDMS instruments were also briefly deployed at Belfast (urban centre) and Harwell (rural).

All measurements from the UK Equivalence Programme have been made available online and can be obtained from:

www.airquality.co.uk/archive/reports/cat05/0607131442_UK_Equivalence_Trials_Data.xls

and entered into the KCL air quality database.

2.2.2 The London Air Quality Network

The London Air Quality Network (LAQN) was formed in 1993 and comprises of over 100 local authority funded monitoring sites in London and the Home Counties. The network is managed by KCL.

During 2003 KCL instigated a FDMS monitoring programme with the following objectives:

- Establishing field operation protocols, audit and ratification procedures for the FDMS.
- Comparing the measurements of PM₁₀ made using the FDMS, TEOM and gravimetric methods.

- Investigating the concentrations of volatile PM, which were facilitated by the FDMS purge measurement cycle.
- Deriving relationships to maintain continuity between measurements of PM₁₀ made using the FDMS and those made using the TEOM.

By the end of 2006 London Boroughs had supported the installation of FDMS instruments at eight sites as shown in Figure 6; further details can be found in Table 2. The FDMS sites are managed by KCL. FDMS sample flow rates and K₀ factors were subject UKAS accredited audits by NPL and measurements were ratified by KCL. Further details of the LAQN FDMS programme can be found in (Green and Fuller, 2004; Green and Fuller, 2006).

Measurements from these sites were obtained from the KCL air quality database. These measurements were processed to create 24-hour mean concentrations commensurate with gravimetric filter change times. A 90% hourly data capture was required to create a valid 24-hour mean concentration. Collocated measurements of ambient temperature and pressure were used to convert reported TEOM measurements to ambient temperature and pressure.

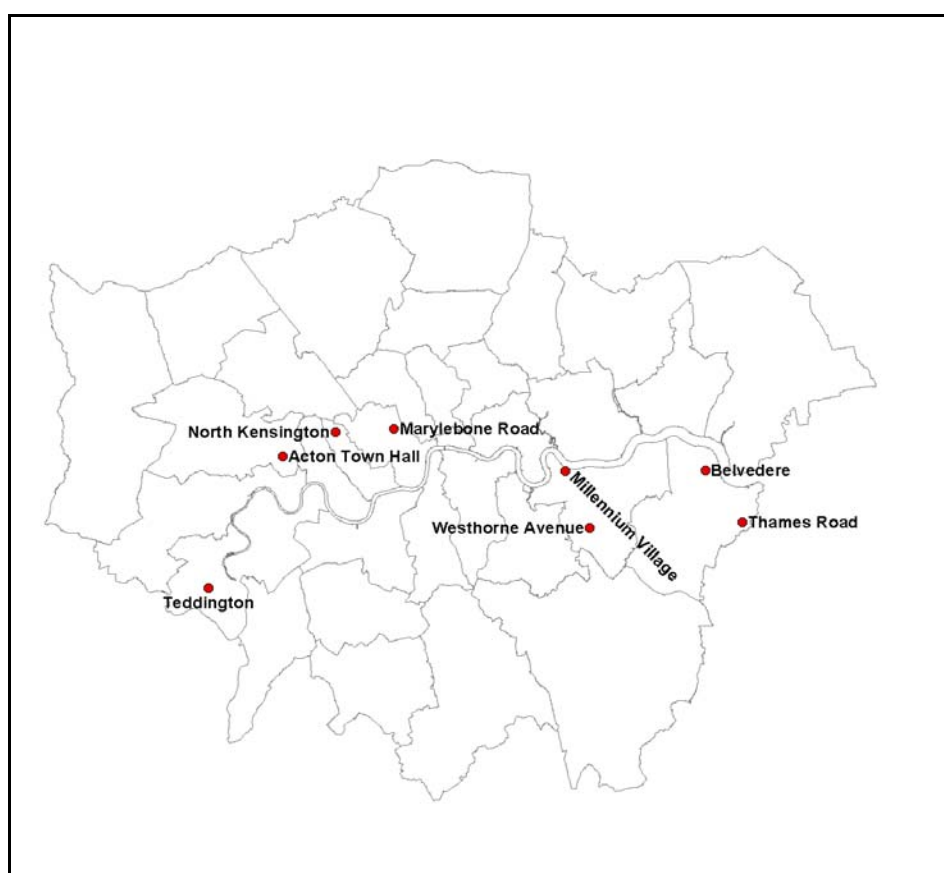


Figure 6: FDMS monitoring sites in the LAQN

2.2.3 The UK Automatic Urban and Rural Network (AURN)

The AURN was formed in 1998 from the combination of Defra's automated urban and rural measurement programmes. The network comprised of 127 sites during 2006. Collocated measurements of PM₁₀ using TEOM and gravimetric methods took place at eight sites.

The TEOM flow and microbalance K₀ factors were subject to UKAS accredited audit and AEA Energy and Environment ratified the measurements.

Gravimetric sampling was undertaken at Northampton using the Partisol 2025 onto quartz filters. Filters were retained in the samplers for a maximum of two weeks. Filters were changed

each midnight and filter weighing was carried out by Bureau Veritas according to the conditions in EN12341(CEN, 1998). Sample flow rates were subject to UKAS accredited audits and measurements were ratified by AEA Energy and Environment. Measurements were obtained from www.airquality.co.uk. TEOM measurements were processed to create 24-hour mean concentrations commensurate with gravimetric filter change times. A 90% hourly data capture was required to create a valid 24-hour mean concentration. Temperature and pressure measurements for the conversion of reported TEOM measurements to ambient temperature and pressure were obtained from the Belfast City Council for the Belfast site and Hertfordshire and Bedfordshire Air Pollution Monitoring network site at Luton, Bedfordshire, UK (OS 506500 222700, Lat: 51.892687N Long: 0.453770W, Datum: WGS84) for the other sites.

2.2.4 Other Defra Gravimetric Measurements

Other gravimetric measurements were also undertaken using the Partisol 2025 onto quartz filters. Filter handling and weighing was identical to that described in section 2.2.3. Sample flow rates were subject to UKAS accredited audits by AEA Energy and Environment and measurements were ratified by Bureau Veritas. Measurements were kindly supplied by David Harrison.

2.2.5 Defra Airborne Particle Concentration and Numbers Network

The Airborne Particle Concentration and Numbers Network measures concentrations of particle nitrate, sulphate, chloride, carbon and particle numbers at eight urban and one rural site in the UK. Measurements of nitrate in PM_{2.5} were made at three sites as listed in Table 2. From May 2005, operational management of these instruments was undertaken by KCL with audit and the measurements ratification undertaken by NPL. Prior to May 2005 site management and ratification of the R&P 8400N at the Marylebone Road site was undertaken by KCL and Bureau Veritas undertook these responsibilities for the remaining instruments and sites.

2.2.6 Drax Power Measurements

Two FDMS instruments were operated by Drax Power Ltd around their power station in Yorkshire (Anwyl, 2005). The instruments were subject to 3 monthly flow calibration. Measurements were collected and fault checked by Phil Anwyl of AQMS Ltd. Measurements were placed in the KCL database and subject to screening ratification checks.



Figure 7: FDMS and Partisol sampling locations used in this study in UK, further detail of the London sites is shown in Figure 6.

Site	Type	Gravimetric	Filter Type	TEOM	FDMS	NO ₃	OS Grid	Lat Long (Datum: WGS84)
Acton Town Hall	Roadside			Y	Y		520300 180050	Lat: 51.506586N Long: 0.268023W
Belfast	Urban Centre	Partisol	Quartz	Y	Y	Y	146231 529911	Lat: 54.600443N Long: 5.930566W
Belvedere	Suburban			Y	Y		550000 179070	Lat: 51.490685N Long: 0.159205E
Birmingham	Urban Background	KFG / Partisol	Emfab	Y	Y		404927 284168	Lat: 52.455443N Long: 1.928922W
Birmingham Centre	Urban Centre	Partisol	Quartz	Y			406342 286862	Lat: 52.479648N Long: 1.908049W
Bristol	Roadside	KFG / Partisol	Emfab	Y	Y		359469 172424	Lat: 51.449341N Long: 2.584642W
East Kilbride	Suburban	KFG / Partisol	Emfab	Y	Y		263975 653470	Lat: 55.755416N Long: 4.169038W
Glasgow Centre	Urban Centre	Partisol	Quartz	Y			258902 665028	Lat: 55.857731N Long: 4.255800W
Drax Hemingborough	Rural				Y		466999 430099	Lat: 53.762953 Long: 0.985131W
Drax Barlow	Urban Background				Y		465300 428700	Lat: 53.750587 Long: 1.011211W
Harwell	Rural	Partisol	Quartz	Y	Y	Y	447400 186300	Lat: 51.573582N Long: 1.317437W
Manchester Piccadilly	Urban Centre	Partisol	Quartz	Y			384310 398325	Lat: 53.481409N Long: 2.237894W
Marylebone Road	Kerbside	Partisol	Quartz	Y	Y	Y	528120 182000	Lat: 51.522393N Long: 0.154700W
Millennium Village	Urban Background				Y		540175 179000	Lat: 51.492575N Long: 0.017756E
North Kensington	Urban Background	Partisol	Quartz	Y	Y		524040 181740	Lat: 51.520967N Long: 0.213568W
Northampton	Urban Background	Partisol	Quartz	Y			476111 264524	Lat: 52.273610N Long: 0.885950W
Teddington	Suburban	KFG / Partisol	Emfab	Y	Y		515115 170778	Lat: 51.424331N Long: 0.345714W
Thames Road	Roadside				Y		552616 175415	Lat: 51.457146N Long: 0.195279E
Westhorne Avenue	Roadside				Y		541883 175016	Lat: 51.456350N Long: 0.040744E

Table 2: Summary of measurement sites. Sites shown in bold were used in the UK Equivalence Programme

2.3 Model Derivation

The KCL Volatile Correction Model was derived from four key principles developed from measuring PM₁₀ in London and from the measurements and conclusions of the UK Equivalence Programme.

2.3.1 FDMS Demonstrates Equivalence in the UK Equivalence Programme

In the UK Equivalence Programme report Harrison (2006) used the Guidance to demonstrate that the FDMS met the equivalence criteria and could therefore be considered equivalent to the reference method. The statistical comparisons in the Guidance were designed to show that the candidate method is capable of fulfilling the data quality objectives specified in the First Daughter Directive (see section 2.4).

2.3.2 FDMS Measurement Equation

As described in section 2.1.3 the FDMS measurement equation (FDMS = FDMS Base - FDMS purge) formed the basis for the model development. Figure 15 shows how each of the terms was substituted to derive a reference equivalent PM₁₀ measurement.

2.3.3 Linear Relationship Between the FDMS Purge Measurement and the Difference Between the FDMS Base and the TEOM

As described in sections 2.1.2 and 2.1.3, the TEOM and the FDMS elevated their sample temperatures to 50 °C and 30 °C respectively. This provided stable thermal conditions for the mass balance (Chung *et al.*, 2001). A temperature of 50 °C also provided a low sample relative humidity for the TEOM, which reduced the impact of water on the measurement. The FDMS maintained low sample relative humidity using a diffusion dryer. Therefore, other than the difference in temperature the FDMS base measurement and the TEOM could be considered analogous.

Differences in the mass concentrations measured by the FDMS base cycle and the TEOM have been reported in previous studies (Green, 2004; Harrison, 2006). Green and Fuller (2006) estimated that the difference between the mass concentration measured by the FDMS base cycle and the TEOM to be approximately equal to the FDMS purge measurement. If the FDMS purge measurement were an assessment of the evaporation of ammonium nitrate from the measurement filter, as shown in 2.1.3.2, the difference between the FDMS base and TEOM measurements seems to be related to the evaporation of ammonium nitrate at 50 °C but not at 30 °C.

An example of the relationship between the FDMS base and TEOM daily mean concentrations is shown in Figure 8. The correlation between the two metrics is very good ($r^2 = 0.72$) and the slope is very close to 1. This good correlation was also observed in the hourly mean measurements as shown in Figure 9; the r^2 of the correlation was 0.53. However, if as described in section 2.1.3.2 a lag of two hours between collection of ammonium nitrate and subsequent evaporation is taken into account; the r^2 increases to 0.65.

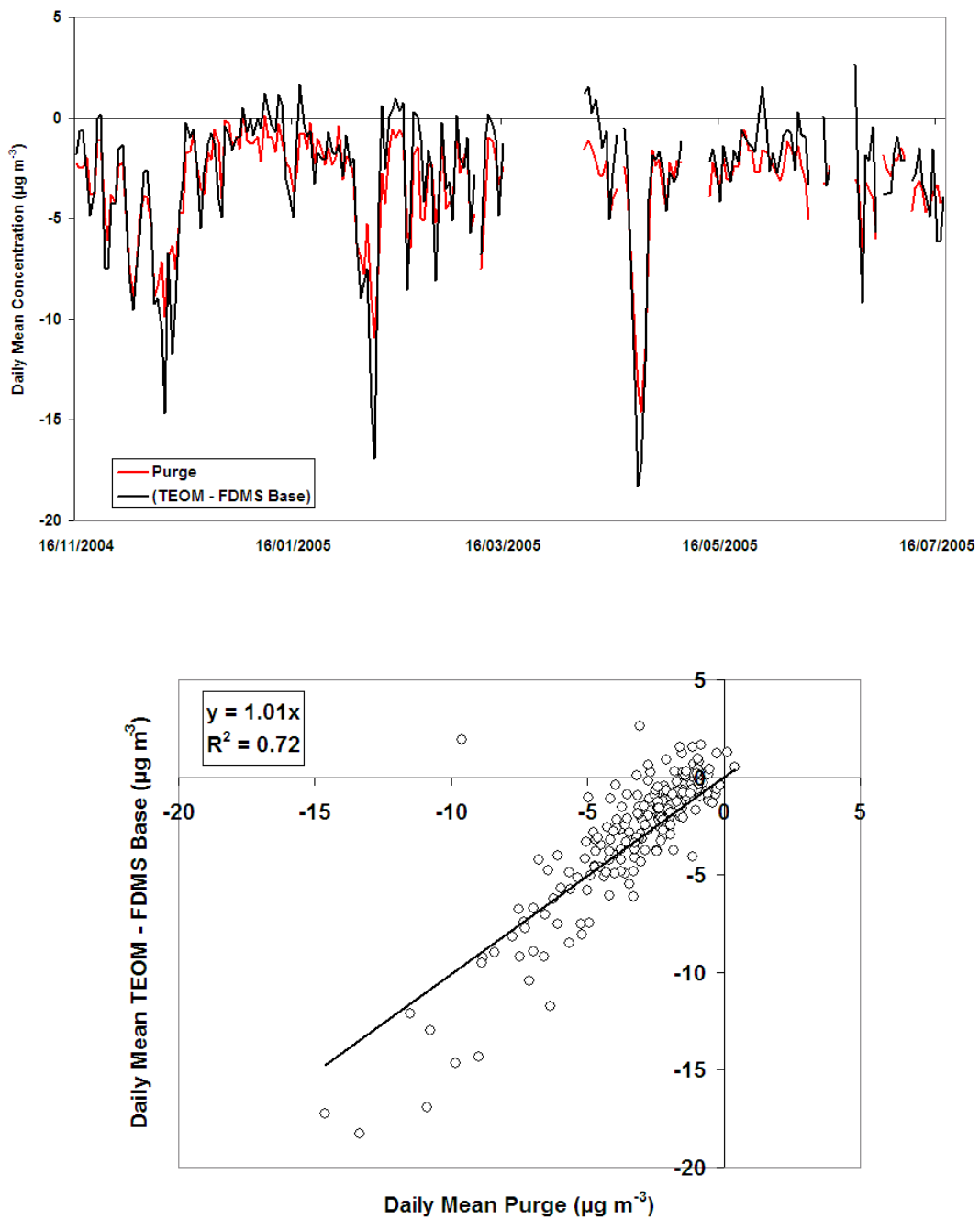


Figure 8: Relationship between the FDMS purge measurement and the (TEOM-FDMS Base) measurement at Teddington between November 2004 and July 2005 as a times series (top) and as a correlation with the orthogonal regression statistics (bottom)

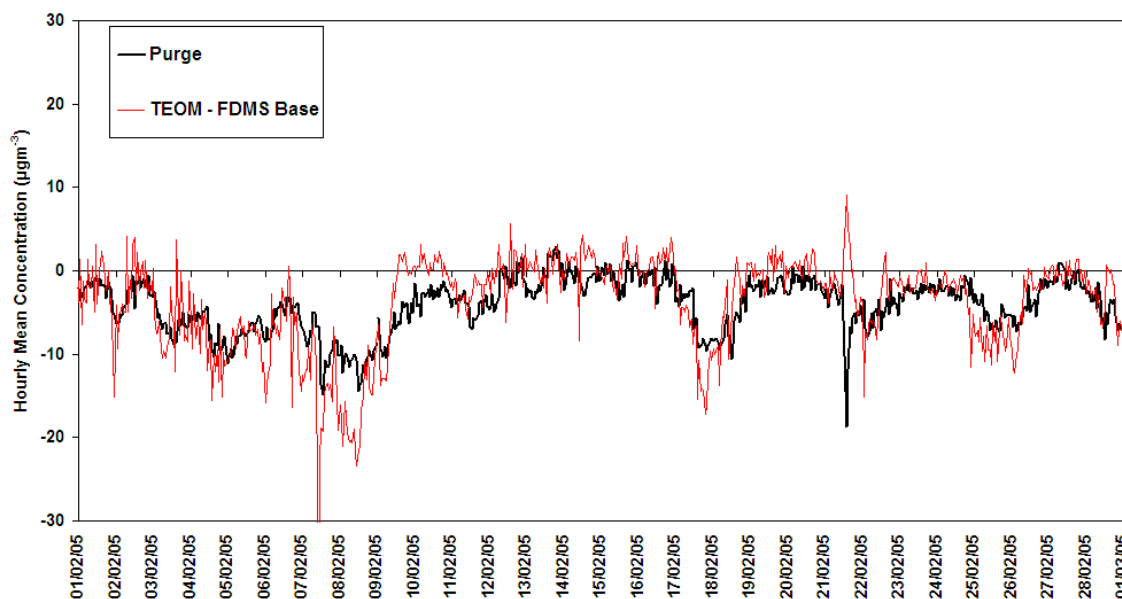


Figure 9: Hourly mean TEOM minus hourly mean FDMS base measurements and hourly mean FDMS purge measurements made at Teddington during February 2005.

To provide an input for the model, linear regression analysis (forced through zero) of the difference between FDMS base and TEOM daily mean measurements and the FDMS purge measurements, including those made during the UK Equivalence Programme, was undertaken for this study and is summarised in Figure 10. This shows the slopes ranged from 1.12 to -0.06.

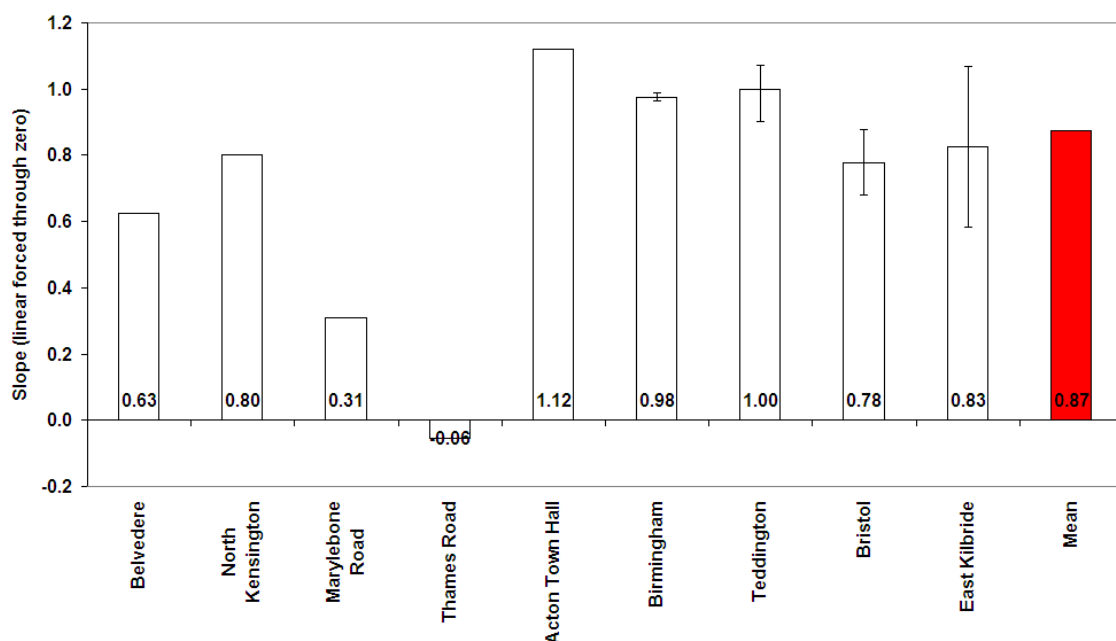


Figure 10: Slope of the linear regression analysis between the FDMS purge measurements (x) and (TEOM-FDMS Base) measurements (y) from each of the sites in London and those in the UK Equivalence Programme. The UK Equivalence Programme sites are shown as the mean of the four potential combinations of the paired instruments (2 TEOMs and 2 FDMS, i.e. TEOM1-FDMS1, TEOM1-FDMS2, TEOM2-FDMS1, TEOM2-FDMS2); error bars shown for these sites indicate the maximum and minimum of the four combinations. The mean on the right excludes Marylebone Road and Thames Road.

It was assumed that the FDMS Purge and the TEOM - FDMS Base were both influenced by ammonium nitrate. This is fairly uniform over a regional area; a relatively constant relationship across all sites was therefore expected. Examining the results, there was no consistent site type or regional differences, however, the two locations where low regression slopes were measured could be considered unusual.

- Thames Road experienced substantial construction work very close to the monitoring site during the measurement period that could have biased the instrument which was closer. The hourly mean measurements at Thames Road are shown in Figure 11. The correlation between the metrics is most clear during elevated FDMS purge concentrations. However, there appears to be a relatively consistent difference between them at other times, this is consistent with a bias between the instruments. Thames Road was therefore excluded from the model derivation.
- Marylebone Road is a heavily trafficked environment. There was a large degree of hourly variation when compared to both Thames Road and Teddington; this is clear when comparing Figure 9, Figure 11 and Figure 12. The correlation between the metrics is also clear at Marylebone Road but was masked by the hourly variation, which in turn impacted on the calculated regression slope. This is indicative of an ambient environment that is not well mixed or subject to rapid changes in the concentration of volatile particulate matter and therefore not representative of atmospheric conditions in the surrounding area. It was felt that this heavily trafficked environment would confound of the wider geographical application of the model and it was also excluded from the model derivation.

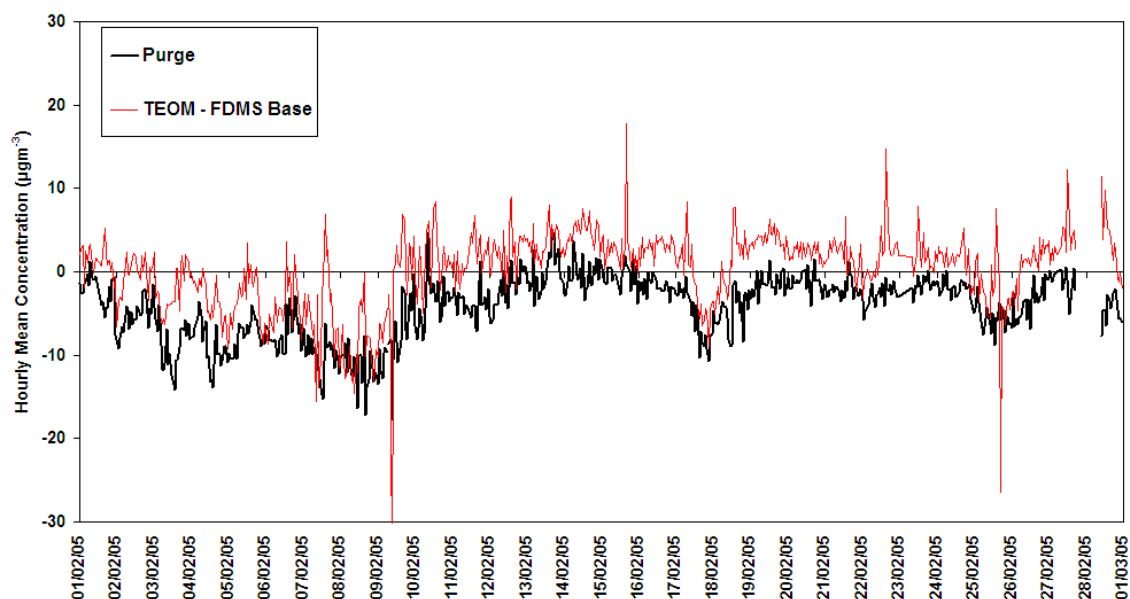


Figure 11: Hourly mean TEOM minus hourly mean FDMS base measurements and hourly mean FDMS purge measurements made at Thames Road during February 2005.

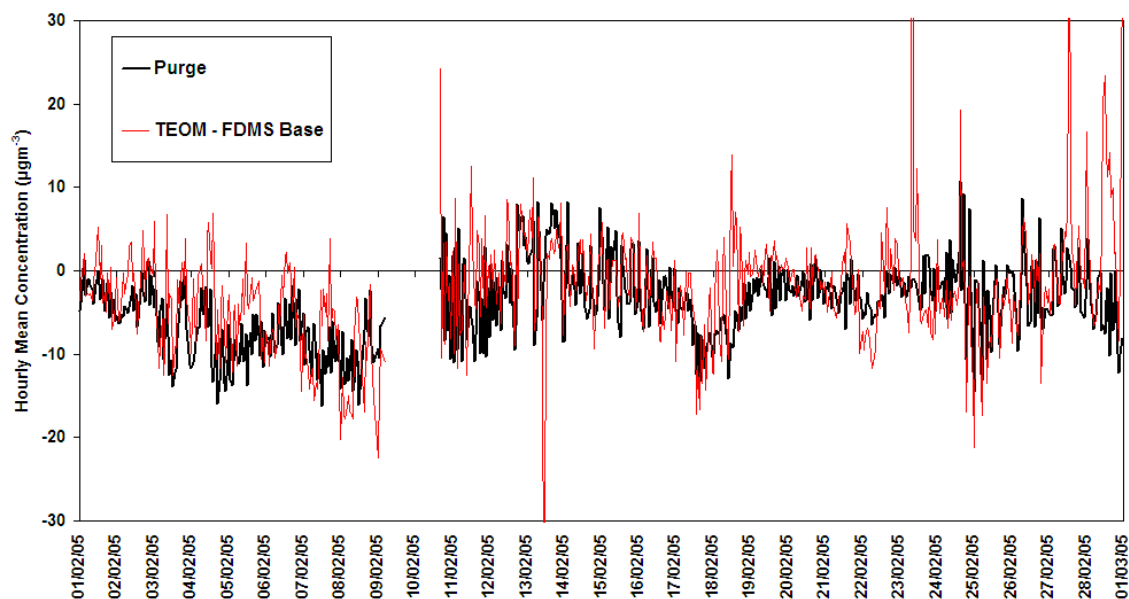


Figure 12: Hourly mean TEOM minus hourly mean FDMS base measurements and hourly mean FDMS purge measurements made at Marylebone Road during February 2005.

The mean linear regression slope shown in Figure 10 was therefore calculated excluding the results from Marylebone Road and Thames Road to provide a value of 0.87, including Marylebone Road and Thames Road it would have been 0.71. The FDMS Base concentration was therefore be represented by the following equation:

$$FDMS\ base = TEOM - 0.87FDMS\ purge$$

An alternative model parameterisation was investigated using slope and intercept regression coefficients resulting from orthogonal regression analysis. This better reflected the non-zero intercept evident in the relationships at some of the sites; however, it did not perform as well as the simple slope correction model in terms of relative combined expanded uncertainty. This and other model parameterisations are detailed in section 8.1.

2.3.4 Uniform Regional FDMS Purge Concentrations

Table 3 shows the mean summer and winter FDMS purge concentrations across the capital, this demonstrates a regional uniformity in these measurements. There is no distinction between roadside and background sites and no consistent difference between summer and winter. The maximum difference is 1.2 $\mu\text{g m}^{-3}$ between Marylebone Road and Acton Town Hall during the summer. This concentration is similar to the expected between sampler uncertainty 1.1 $\mu\text{g m}^{-3}$ for the daily mean FDMS purge measurements during the UK equivalence trial. The mean difference across all sites and seasons is 0.2 $\mu\text{g m}^{-3}$.

Site 1 (Serial #)	Site 2 (Serial #)	Mean Site 1 ($\mu\text{g m}^{-3}$)		Mean Site 2 ($\mu\text{g m}^{-3}$)	
		Summer	Winter	Summer	Winter
Teddington (#24447)	Marylebone Road	-3.7	-3.6	-4.1	-4.6
Teddington (#24431)	Marylebone Road	-3.2	-3.6	-4.1	-4.7
Teddington (#24447)	North Kensington	-3.7	-3.5	-4.1	-4.1
Teddington (#24431)	North Kensington	-3.2	-3.5	-4.1	-4.3
Teddington (#24447)	Teddington (#24431)	-3.6	-3.6	-3.2	-3.5
Marylebone Road	North Kensington	-4.0	-3.8	-4.0	-3.5
Marylebone Road	Acton Town Hall	-4.2	-4.0	-3.0	-3.6
North Kensington	Acton Town Hall	-3.3	-3.3	-2.9	-3.5

Table 3: FDMS purge paired data means from monitoring sites in London between January 1st 2004 and 31st December 2005

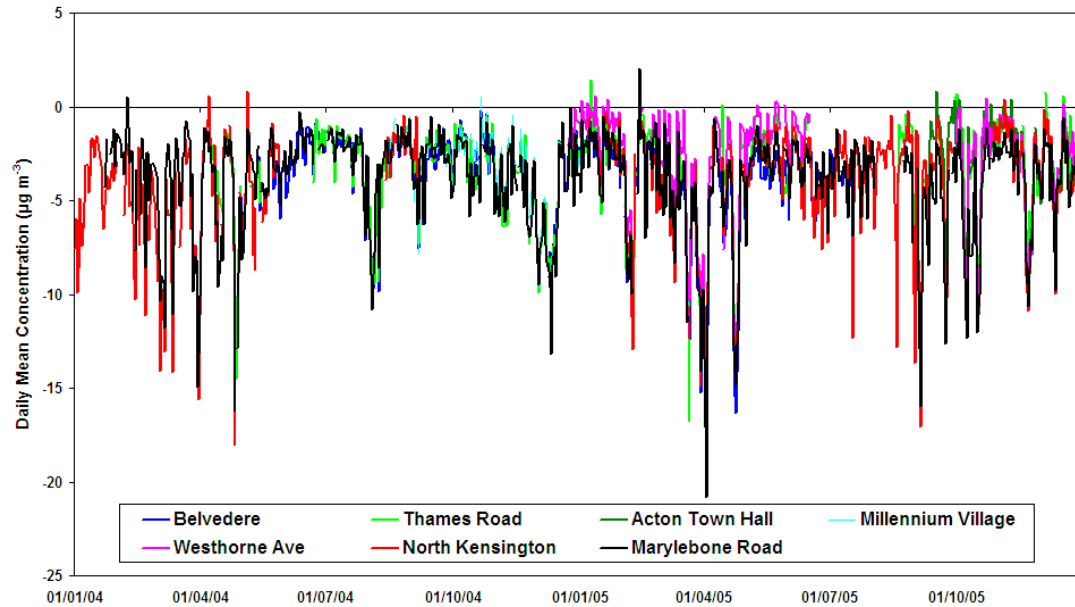


Figure 13: Daily mean FDMS purge measurement made in the London between 1st January 2004 and 31st December 2005

Figure 13 shows the time series of daily mean FDMS purge measurements made in London during 2004 and 2005, which clearly exhibit a similar daily variation. The daily mean FDMS purge concentrations from all the FDMS sites in the UK are also shown graphically in Appendix 8.7, these were correlated against each other using orthogonal regression to provide a correlation coefficient for each pair of sites. The correlation coefficient was compared to the distance between sites, where there are 40 or more daily mean pairs, the results are shown in Figure 14. It is clear from this figure that the correlation coefficients between daily mean FDMS purge concentrations reduce with increasing distance. It was therefore reasonable to assume that a single FDMS purge daily mean measurement was representative of a regional area. The extent of that area needed to be determined in model testing to establish at what distance the FDMS purge concentration causes the model to fail the equivalence criteria described in section 2.4.

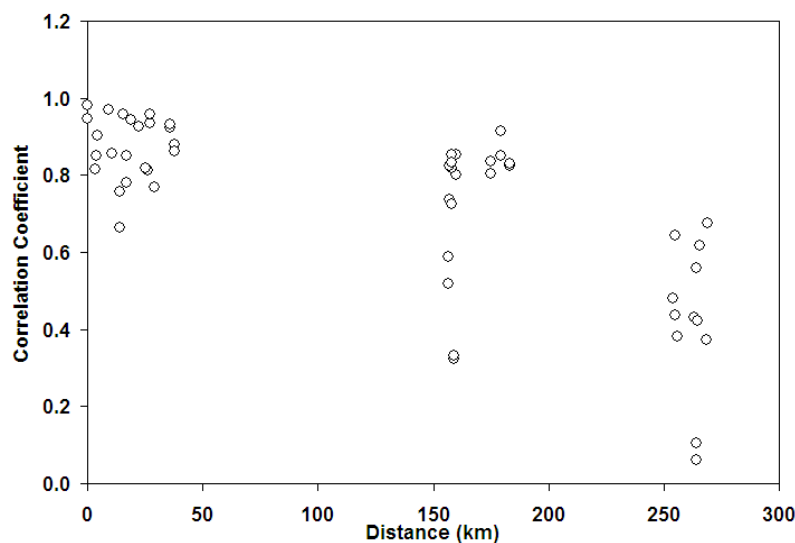


Figure 14: Correlation coefficients from orthogonal regression analysis of paired FDMS purge measurements (where $n \geq 40$) with increasing distance in the UK.

2.3.5 Model Summary

The model derivation is shown graphically in Figure 15.

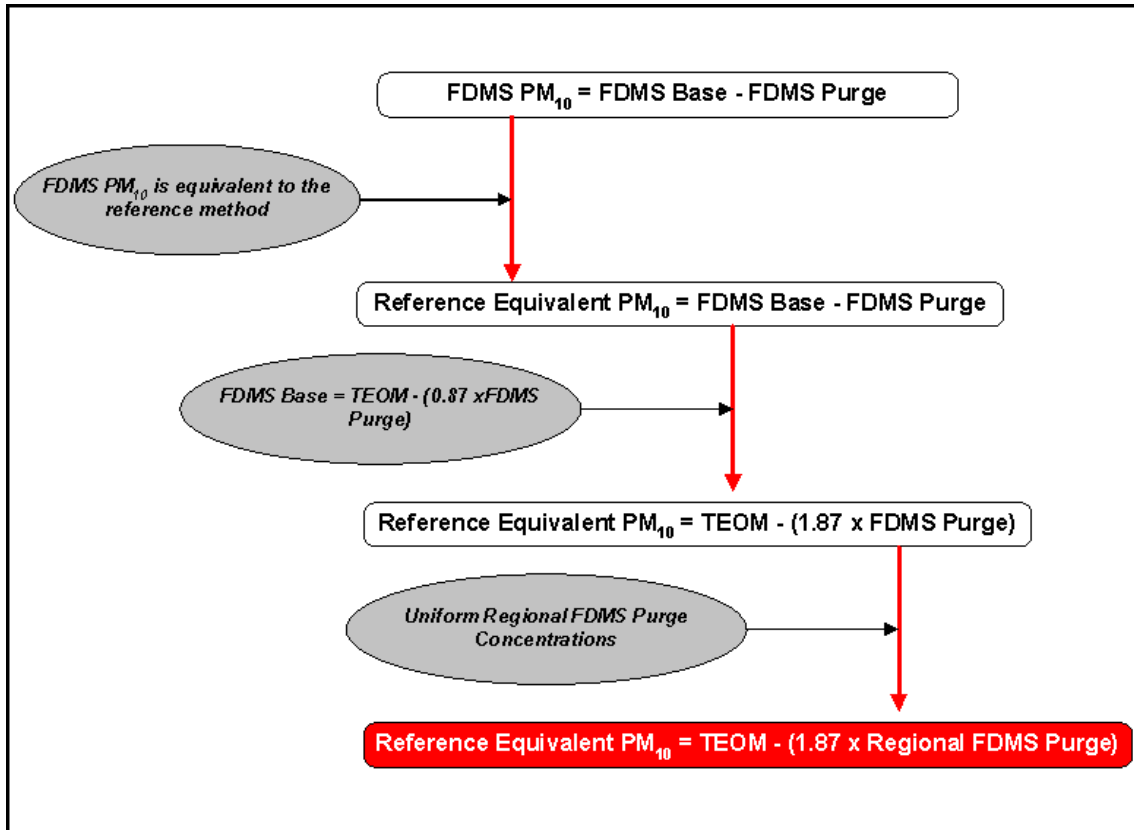


Figure 15: Model summary

2.4 Statistical Comparisons

The field test procedure for the demonstration of equivalence was determined by EC Working Group on Guidance for the Demonstration of Equivalence (EC, 2005), the Guidance and is also summarised in (Harrison, 2006). The Guidance involves four statistical tests for the evaluation of field measurements to determine equivalence. The calculations for these tests are detailed in the Guidance and are not repeated here. All tests were undertaken on daily mean concentrations. The statistical tests are summarised below and their application to this study are detailed.

2.4.1 Suitability of the Measurements

For a valid demonstration of equivalence four field tests are required, each with a minimum of 40 contemporaneous daily mean measurements for both the sampler and candidate instruments. At least 20% of these daily mean measurements should be greater than the daily mean limit value concentration the EU Daughter Directive.

2.4.2 Between Sampler / Instrument Uncertainty (U_{bs})

The Guidance requires that paired reference samplers and paired candidate samplers / instruments are deployed during the field tests. The between sampler uncertainty is a measure of the paired samplers / instruments ability to measure the same 24 hourly mean concentration. The between sampler uncertainty for both the reference must be less than 2 $\mu\text{g m}^{-3}$ and the between sampler uncertainty for the candidate must be less than 3 $\mu\text{g m}^{-3}$ for the evaluation to proceed. If this test is met the paired daily mean concentrations are averaged for use in the remainder of the test procedure.

However, in this study only single reference and candidate 'instruments' are available at several locations. In these cases the between sampler uncertainty was assumed to be the mean found by Harrison (2006) and the remainder of the evaluation was conducted using the daily mean concentrations from the single 'instrument', see Section 2.6.3.

The application of between sampler uncertainty in this study has also been used as a measure of the difference between the daily mean concentration of FDMS purge between instruments and locations.

2.4.3 Regression Analysis

It is assumed that the relationship between the daily mean concentrations measured by the reference and candidate samplers / instruments can be described by a linear relationship of the form:

$$y_i = a + bx_i$$

This relationship is determined by an orthogonal regression technique that allows for the symmetrical treatment of both variables and also estimates the uncertainty associated with the slope and intercept. The resulting slopes and intercepts are compared for each of the four field tests, the whole data sets and for the subset of daily mean concentrations greater or equal to 50 % of the upper assessment threshold in the Daughter Directive.

If regression slopes are significantly greater or less than 1 a slope correction can be applied to the measurements from the candidate instrument. If all intercepts are significantly greater or less than zero an intercept correction may be applied. If both these conditions occur the combination of slope and intercepts can be applied. Here we have followed the recommendations of Harrison (2006); that corrections only need to be applied where all slopes were greater or less than 1 or / and all intercepts were greater or less than zero

2.4.4 Combined Relative Expanded Uncertainty at the Limit Value (W_{CM})

The uncertainty in the measurements of the candidate from the reference were calculated as a function of the sum of the relative residuals from the orthogonal regression, the concentration from the original regression equation at the Limit Value and the between sampler uncertainty of the reference method. If a slope, intercept or slope and intercept correction factor was derived from the orthogonal regression, the uncertainty in this correction factor was included as an additional term in the uncertainty calculation.

The uncertainty (W_{CM}) should be calculated for each field test, the whole data set and for the subset of daily mean concentrations greater or equal to 50 % of the upper assessment threshold in the Daughter Directive.

The uncertainty in the measurements of the candidate from the reference (W_{CM}) for each subset of measurements was expressed relative to the Limit Value concentration with a coverage factor $k=2$ to approximate to a 95% confidence interval. The maximum value of W_{CM} must be less than the expanded uncertainty data quality objective of 25 % stipulated in the Daughter Directive.

Here we have departed from the Guidance in two respects, following the recommendations of Harrison (2006):

- The candidate was not deemed to fail the equivalence test on the sole basis of W_{CM} exceeding 25 % for the data set of measurements < 50 % of the Limit Value.
- Due to the low PM₁₀ concentrations measured at East Kilbride, the candidate was not deemed to fail the equivalence test on the sole basis of this deployment. This 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).

2.4.5 Summary of Relevant Equivalence Criteria

Criteria	Symbol	Value
Number of daily mean measurements	$n_{c,s}$	≥ 40
Number of daily mean measurements ≥ 50 % of limit value		≥ 25%
Between reference sampler uncertainty	U_{ref}	≤ 2 µg m ⁻³
Between candidate sampler uncertainty	U_{bs}	≤ 3 µg m ⁻³
Combined relative expanded uncertainty at the Limit Value	W_{CM}	≤ 25 %

Table 4: Summary of relevant equivalence criteria

2.5 Coding

A matrix was created to describe the different combination of site tests carried out in this study. MS SQL code was created to read the matrix and carry out two functions:

1. Extraction of concentration measurements from the KCL air quality database including:
 - a. Correction of automated measurements to atmospheric temperature and pressure.
 - b. The aggregation of hourly mean measurements from the automated instruments to form daily mean measurements commensurate with the manual filter change times.
 - c. Measurements were disaggregated into seasons where appropriate. Summer constituted 1st April - 30th September, winter constituted 1st October - 31st March. This differs from that used in Harrison (2006) where summer started on 23rd March and winter on 13th October.
2. Perform the calculations required by the equivalence test criteria. The calculations duplicated those in the Guidance and the associated spreadsheet circulated by CEN

(received from Paul Quincey (NPL) on 24/12/2004). Additional parameters that aided interpretation were also reported.

The code was tested using the spreadsheet supplied by CEN and the results in Harrison (2006); more detail can be found in Appendix 8.3 and 8.4. The SQL code may be found in Section 8.2.

2.6 Testing the Model Against the Equivalence Criteria

The model was then tested in three 'experiments'. Each 'experiment' used measurements made in the monitoring programmes listed in Section 2.2. In each case the model was tested against the criteria in the Guidance.

2.6.1 Experiment 1

Experiment 1 was designed to test the equivalence of the KCL Volatile Correction Model against the equivalence criteria, excluding the regional aspects.

Experiment 1 used measurements from collocated pairs of reference, FDMS and TEOM instruments from the UK Equivalence Programme. If we consider each equivalence site as having two TEOMs (A and B) and two FDMS (C and D) we have four possible pairs of modelled daily mean time series to test at each site:

$$\text{Modelled PM}_{10} 1A = \text{TEOM A} - 1.87 \text{ FDMS purge C}$$

$$\text{Modelled PM}_{10} 1B = \text{TEOM B} - 1.87 \text{ FDMS purge C}$$

$$\text{Modelled PM}_{10} 2A = \text{TEOM A} - 1.87 \text{ FDMS purge D}$$

$$\text{Modelled PM}_{10} 2B = \text{TEOM B} - 1.87 \text{ FDMS purge D}$$

$$\text{Modelled PM}_{10} 3A = \text{TEOM A} - 1.87 \text{ FDMS purge C}$$

$$\text{Modelled PM}_{10} 3B = \text{TEOM B} - 1.87 \text{ FDMS purge D}$$

$$\text{Modelled PM}_{10} 4A = \text{TEOM A} - 1.87 \text{ FDMS purge D}$$

$$\text{Modelled PM}_{10} 4B = \text{TEOM B} - 1.87 \text{ FDMS purge C}$$

Each pair of modelled PM₁₀ 24 hour mean time series were subject to the full equivalence test criteria.

2.6.2 Experiment 2

Experiment 2 was designed to test the equivalence of the KCL Volatile Correction Model against the equivalence criteria, including the regional aspects.

Experiment 2 used measurements from the collocated pairs of reference and TEOM instruments from the UK Equivalence Programme. The TEOM measurements were corrected using FDMS purge measurements from remote sites.

If we consider each equivalence site as having two TEOMs (A and B), which we seek to 'correct' using the model with input from a distant FDMS (Z), we can produce the following modelled daily mean time series to test for each distant FDMS for each of the equivalence deployments.

$$\text{Modelled PM}_{10} 1A = \text{TEOM A} - 1.87 \text{ FDMS purge Z}$$

$$\text{Modelled PM}_{10} 1B = \text{TEOM B} - 1.87 \text{ FDMS purge Z}$$

The pair of modelled PM₁₀ 24 hour mean time series were then subject to the full equivalence test criteria. To aid the determination of the spatial applicability of the model the distance between each remote FDMS site and the equivalence site was also calculated.

2.6.3 Experiment 3

This experiment aimed to further determine the model's spatial applicability.

Experiment 3 planned to use Partisol and TEOM measurements from Defra's AURN network and correct these using FDMS purge measurements from remote sites. This differed from the experiment 2 in several respects; the measurement methodology, the use of paired measurements and the use of the Grubbs' test. These differences are summarised in Table 5.

Parameter	UK equivalence	AURN	Notes
Filter media	Teflon coated glass fibre	Quartz	(Brown <i>et al.</i> , 2006; Harrison, 2006)
Filter storage in sampler	0 days	0.5 to 14 days	
Weighing criteria	EN 14907 modified	EN 12341	(Brown <i>et al.</i> , 2006)
Filter storage and transport	Chilled	Uncontrolled	(Harrison, 2006)
Grubbs' test	Yes	No	Removed 3 % of samples in UK Equivalence Programme
EU Reference sampler	Yes (KFG)	No (Partisol)	Partisol W _{CM} = 8% at 50 ug _m -3 (Harrison 2006)
Mean of paired measurements	Yes	No	
TEOM and FDMS reported at ATP	Measurements reported at local ATP	Measurements corrected using best available meteorological measurements	See section 2.2.3

Table 5: Differences in methodology between UK Equivalence Programme and the AURN

2.6.3.1 Experiment 3i

Experiment 3i aimed to quantify the change to W_{CM} due to the different equivalence test approach as summarised in Table 5; the lack of paired measurements at the AURN sites and the use of a non-reference (Partisol) sampler. Where no between reference uncertainty (U_{ref}) could be calculated (i.e. where only a single KFG or Partisol was used). The mean U_{ref} value for the reference methods during the Equivalence Programme was therefore used in these calculations (1.05 µg m⁻³ for KFG and 1.21 µg m⁻³ for Partisol).

Part 1 – KCL Volatile Correction Model

Difference in W_{CM} of the model due to the modified equivalence test was assessed by examining two sets of model comparisons using the measurements made during the UK Equivalence programme:

1. Firstly, W_{CM} was calculated between two KFG reference measurements and the model, which was based on two TEOMs and a single FDMS purge measurement.
2. Secondly, the gravimetric sampler was changed to a single Partisol rather than paired reference KFG samplers. W_{CM} was calculated between a single Partisol and the model, which used a single TEOM and a single FDMS purge measurement. This is analogous to modified equivalence test approach required at the AURN sites.

Part 2 – 'Equivalence' of FDMS PM₁₀ measurements at AURN sites.

Differences between the PM₁₀ concentrations measured by FDMS and by AURN Partisol were observed in a previous study (Green and Fuller, 2006). It was therefore necessary to quantify the difference between FDMS and by AURN Partisol, in terms of W_{CM}, before the KCL Volatile Correction Model could be tested at the AURN sites.

2.6.3.2 Experiment 3ii

Having considered the results from 3i it was then possible to test the equivalence of the model at each of the AURN sites. If we consider each AURN site as having a single Partisol (S) and a TEOM (R) which we seek to 'correct' with a remote FDMS (Z) we can produce a single modelled daily mean time series that can be compared to Partisol S:

$$\text{Modelled PM}_{10} = \text{TEOM R} - 1.87 \text{ FDMS purge Z} \approx \text{Partisol S}$$

2.7 Required Spatial Distribution of FDMS Instruments

This part of the report determined if Defra's planned 2007 FDMS deployment would allow the KCL Volatile Correction Model to be applied to all current UK AURN TEOM instruments. The distance between the AURN TEOM sites and the nearest 3 FDMS sites in Defra's planned 2007 deployment were compared to the results from experiment 2.

The analysis so far was concerned with demonstrating that the model produced daily and annual mean concentrations that had an expanded uncertainty of less than 25% when compared to the UK Equivalence Programme measurements. However, it is not intended that the Equivalence Programme should operate on an on-going basis. An alternative method was therefore required to demonstrate that the FDMS network would continue to maintain sufficient coverage to allow the model to operate at all AURN sites.

The model assumed that the FDMS purge concentration at the distant site was representative of the concentration at the site that we sought to correct. To quantify the changes in FDMS purge concentrations with distance, the concept of between sampler uncertainty was applied to the FDMS purge concentrations. The between purge uncertainty (u_{purge}) was calculated using the FDMS purge measurements from the local and distant sites by modifying the between sampler uncertainty calculation (Harrison, 2006) as follows:

$$u_{\text{purge}} = \sqrt{\frac{\sum_{i=1}^{n_{\text{bs}}} (p_{i,1} - p_{i,2})^2}{2n_{\text{purge}}}}$$

Where:

$p_{i,1}$ is the local purge measurement for a single 24 hour mean

$p_{i,2}$ is the distant purge measurement for a single 24 hour mean

n_{purge} = the number of 24 hour means present for both FDMS instruments

The between purge uncertainty was then compared to the expanded uncertainties calculated in experiment 2 to derive a between purge uncertainty at which the 25 % data quality objective would be breached.

3 RESULTS AND DISCUSSION

This section reports the results of the model testing. Further information on alternative model parameterisation test results can be found in section 8.1.

3.1 Experiment 1

The model was tested at the UK Equivalence Programme sites (Birmingham, Bristol, East Kilbride and Teddington) by correcting the TEOM daily mean measurements with the FDMS purge daily mean measurements using the model described in section 2.6.1.

The performance of the model in experiment 1 is summarised in Table 6. For completeness, datasets with an $n_{c,s}$ of less than 40 days are reported, however, these results should be treated with caution.

The model performance in terms of the equivalence procedure as set out in section 2.4 is as follows:

1. The 24-hour between sampler uncertainty ($0.88 \mu\text{g m}^{-3}$) was less than $3 \mu\text{g m}^{-3}$, and as such, the model in experiment 1 is suitable for consideration as a candidate method.
2. The slopes of the individual and combined datasets are both greater and less than 1 (winter range: 0.84 to 1.26, summer range: 0.93 to 1.06), and the intercepts are both greater and less than zero (winter range: -1.05 to 3.37, summer range: -0.21 to 4.50). 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 four combinations at East Kilbride in the summer.

In line with the recommendations of Harrison (2006) (section 2.4.4) the candidate was not deemed to fail the equivalence test on the basis of the data set of measurements < 50 % of the Limit Value or the individual deployments East Kilbride.

The KCL Volatile Correction Model was therefore deemed to meet the criteria for the equivalence employed in the UK Equivalence Programme.

Dataset				Distance Between Sites	Reference Mean	Modelled Mean	24 hour		Orthogonal Regression				Annual Limit Value (40 µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)		
Reference Site	FDMS 1 Serial #	FDMS 2 Serial #	Season				n _{bs}	u _{bs}	n _{c,s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	WCM (%)	%> 20 µg m ⁻³	WCM (%)	%> 25 µg m ⁻³	(n _{ES} / n _{EC})
Birmingham	04443	04443	S	0	18	19	60	0.38	39	0.96	0.94 +/- 0.03	2.00 +/- 0.64	9	18	8	15	(1,1)
Birmingham	04443	25053	S	0	18	19	60	1.03	39	0.96	0.95 +/- 0.03	2.69 +/- 0.66	10	18	7	15	(1,2)
Birmingham	25053	04443	S	0	18	19	60	1.33	39	0.96	0.95 +/- 0.03	2.69 +/- 0.66	10	18	7	15	(1,2)
Birmingham	25053	25053	S	0	18	20	69	0.38	41	0.95	0.95 +/- 0.04	3.58 +/- 0.73	14	20	10	15	(1,2)
Birmingham	04443	04443	W	0	19	18	84	0.15	47	0.91	0.96 +/- 0.04	0.20 +/- 0.87	12	32	11	15	(1,1)
Birmingham	04443	25053	W	0	19	18	84	0.81	47	0.91	0.96 +/- 0.04	-0.12 +/- 0.85	13	32	11	15	(1,1)
Birmingham	25053	04443	W	0	19	18	84	0.82	47	0.91	0.96 +/- 0.04	-0.12 +/- 0.85	13	32	11	15	(1,1)
Birmingham	25053	25053	W	0	21	19	106	0.17	59	0.95	0.95 +/- 0.03	-0.21 +/- 0.67	15	39	14	25	(1,1)
Bristol	24431	24431	S	0	22	25	44	0.38	36	0.96	1.04 +/- 0.04	2.01 +/- 0.90	21	39	19	25	(0,1)
Bristol	24431	24447	S	0	22	24	44	1.12	36	0.96	1.05 +/- 0.04	1.08 +/- 0.88	19	39	17	25	(0,1)
Bristol	24447	24431	S	0	22	24	44	1.24	36	0.96	1.05 +/- 0.04	1.08 +/- 0.88	19	39	17	25	(0,1)
Bristol	24447	24447	S	0	22	23	44	0.38	36	0.96	1.06 +/- 0.04	0.12 +/- 0.88	16	39	15	25	(0,1)
Bristol	24431	24431	W	0	22	25	84	0.53	55	0.95	0.93 +/- 0.03	4.50 +/- 0.69	14	45	10	33	(2,2)
Bristol	24431	24447	W	0	22	25	79	1.10	55	0.96	0.93 +/- 0.03	3.89 +/- 0.66	12	45	9	33	(2,2)
Bristol	24447	24431	W	0	22	25	79	1.00	55	0.96	0.93 +/- 0.03	3.89 +/- 0.66	12	45	9	33	(2,2)
Bristol	24447	24447	W	0	23	25	81	0.54	57	0.96	0.93 +/- 0.02	3.31 +/- 0.63	11	47	8	35	(2,2)
East Kilbride	25053	25053	S	0	9	12	49	0.27	36	0.86	1.26 +/- 0.08	1.43 +/- 0.75	59	3	57	0	(0,0)
East Kilbride	25053	04443	S	0	8	11	43	1.59	33	0.79	1.21 +/- 0.10	1.01 +/- 0.85	48	0	47	0	(0,0)
East Kilbride	04443	25053	S	0	8	11	43	1.26	33	0.79	1.21 +/- 0.10	1.01 +/- 0.85	48	0	47	0	(0,0)
East Kilbride	04443	04443	S	0	8	10	43	0.24	33	0.76	1.25 +/- 0.11	-0.07 +/- 0.93	50	0	50	0	(0,0)
East Kilbride	25053	25053	W	0	11	14	77	0.61	54	0.91	0.98 +/- 0.04	3.37 +/- 0.50	15	11	12	4	(0,0)
East Kilbride	25053	04443	W	0	11	13	77	1.97	54	0.93	0.97 +/- 0.04	2.55 +/- 0.44	9	11	7	4	(0,0)
East Kilbride	04443	25053	W	0	11	13	77	1.16	54	0.93	0.97 +/- 0.04	2.55 +/- 0.44	9	11	7	4	(0,0)
East Kilbride	04443	04443	W	0	11	12	77	0.61	54	0.93	0.97 +/- 0.04	1.62 +/- 0.44	7	11	5	4	(0,0)
Teddington	24431	24431	S	0	20	20	83	0.77	50	0.89	0.89 +/- 0.04	2.09 +/- 0.97	19	30	18	20	(2,0)
Teddington	24431	24447	S	0	21	20	80	1.03	49	0.90	0.87 +/- 0.04	2.21 +/- 0.94	21	31	21	20	(2,0)
Teddington	24447	24431	S	0	21	20	80	1.41	49	0.90	0.87 +/- 0.04	2.21 +/- 0.94	21	31	21	20	(2,0)
Teddington	24447	24447	S	0	20	20	82	0.88	50	0.89	0.84 +/- 0.04	2.49 +/- 0.94	25	30	25	20	(2,0)
Teddington	24431	24431	W	0	25	22	122	0.32	29	0.95	0.90 +/- 0.04	-0.33 +/- 1.01	25	55	24	45	(0,0)
Teddington	24431	24447	W	0	26	23	85	0.64	20	0.96	0.93 +/- 0.04	-1.05 +/- 1.21	22	60	20	50	(0,0)
Teddington	24447	24431	W	0	26	23	85	0.52	20	0.96	0.93 +/- 0.04	-1.05 +/- 1.21	22	60	20	50	(0,0)
Teddington	24447	24447	W	0	26	23	85	0.35	20	0.96	0.92 +/- 0.04	-1.05 +/- 1.26	23	60	21	50	(0,0)
All Data			-	0	18	19	1746	0.88	1362	0.92	0.93 +/- 0.01	2.33 +/- 1.15	13	29	11	19	-
Data <20 µg m ⁻³			-	0	13	14	1360	0.88	970	0.70	0.99 +/- 0.02	1.68 +/- 0.23	12	-	-	-	-
Data >=20 µg m ⁻³			-	0	32	31	623	0.93	392	0.85	0.95 +/- 0.02	1.34 +/- 0.62	18	-	-	-	-
Data <25 µg m ⁻³			-	0	14	15	1504	0.87	1101	0.77	1.01 +/- 0.01	1.36 +/- 0.21	-	-	12	-	-
Data >=25 µg m ⁻³			-	0	36	35	432	0.91	261	0.82	0.99 +/- 0.03	-0.60 +/- 0.99	-	-	16	-	-

Table 6: Summary of experiment 1, the comparison between the model (using the TEOM and FDMS purge measurements from the equivalence sites) and the PM₁₀ KFG reference method. Season is denoted as Summer (S) and Winter (W). Expanded uncertainties greater than 25% are highlighted in red. Datasets with less than the required 40 paired measurements are coloured grey.

3.2 Experiment 2

Experiment 2 used measurements from the collocated pairs of reference and TEOM instruments from the UK Equivalence Programme. The TEOM measurements were corrected using FDMS purge measurements from remote sites as described in section 2.6.2.

Summary statistics for the whole experiment are not applicable since these would have been skewed by sites with high W_{CM} .

The performance of the model in experiment 2 is summarised in Table 7; only datasets with an $n_{c,s}$ of 40 days or greater are included. The model performance in terms of the equivalence procedure as set out in section 0 is as follows:

1. The maximum 24-hour between sampler uncertainty ($0.89 \mu\text{g m}^{-3}$) was less than $3 \mu\text{g m}^{-3}$, and as such, the model in experiment 2 is suitable for consideration as a candidate method.
2. The slopes of the individual datasets are both greater and less than 1 (range: 0.67 to 1.29), and the intercepts are both greater and less than zero (range: -0.21 to 8.26). 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 10 combinations; the distance between the sites is shown in parentheses:

East Kilbride to Bristol FDMS 24431	Winter (490 km)
East Kilbride to Bristol FDMS 24447	Winter (490 km)
East Kilbride to Drax Hemingborough	Winter (302 km)
East Kilbride to Acton Town Hall FDMS	Winter (538 km)
East Kilbride to Marylebone Road FDMS	Winter (540 km)
East Kilbride to Westhorne Avenue	Winter (553 km)
Bristol to East Kilbride FDMS 04443	Winter (490 km)
Bristol to East Kilbride FDMS 25053	Winter (490 km)
Teddington to Westhorne Avenue	Summer (27 km)
Teddington to Drax Barlow	Summer (263 km)

The effect of distance on the W_{CM} is shown in Figure 16. It is clear that at distances of up to 200 km the expanded uncertainty of the modelled concentration remains below the 25% for both the annual and the daily limit values (with the exception of Westhorne Avenue).

The W_{CM} for Teddington to Westhorne Avenue during the summer was 28 % for both the annual and daily limit values. This is considered a marginal breach of the 25 % limit for W_{CM} . Given that the overwhelming majority of deployments with separation distances of less than 200 km meet the criteria (22/23), this single marginal failure was not deemed suitable justification for rejection.

The KCL Volatile Correction Model was therefore deemed to meet the criteria for the equivalence employed in the UK Equivalence Programme using FDMS purge measurements from remote sites up to approximately 200 km distant.

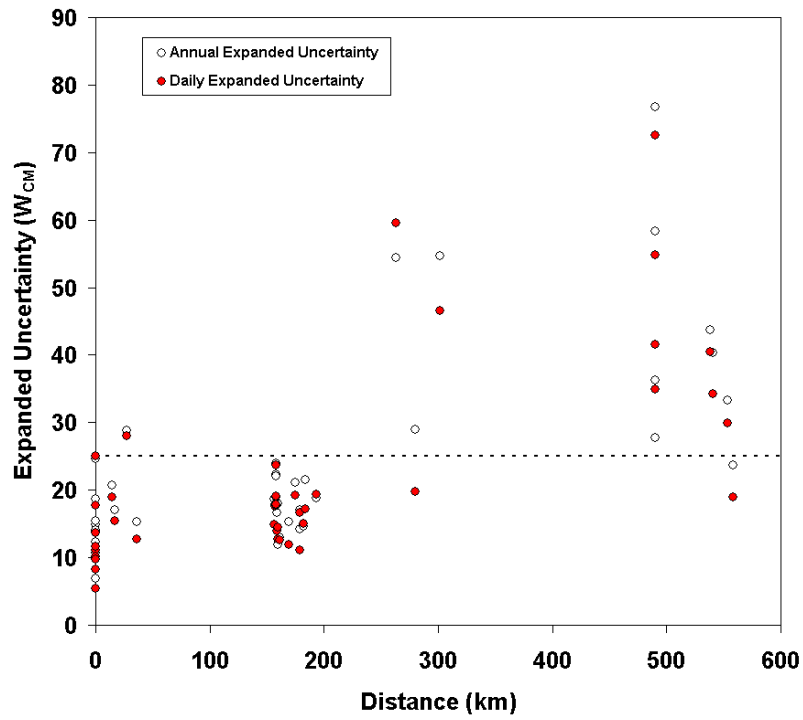


Figure 16: Scatter plot showing the results of experiment 2; the relationship between WCM for the daily and annual mean limit values with distance. The data quality objective of 25 % is shown as a dotted line.

Dataset			Distance Between Sites	Reference Mean	Modelled Mean	24 hour		Orthogonal Regression				Annual Limit Value (40 µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)		
Reference Site (KFG and TEOM)	FDMS (Serial # where applicable)	Season				n _{bs}	u _{bs}	n _{c,s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	W _{CM} (%)	%> 20 µg m ⁻³	W _{CM} (%)	%> 25 µg m ⁻³	(n _{ES} , n _{EC})
Birmingham	Belvedere	S	179	17	21	63	0.38	45	0.91	0.87 +/- 0.04	5.83 +/- 0.85	14	20	11	13	(1,1)
Birmingham	Belvedere	W	179	20	21	108	0.21	54	0.86	0.87 +/- 0.05	3.58 +/- 1.02	17	37	17	22	(1,0)
Birmingham	Thames Road	W	183	21	21	106	0.21	56	0.82	0.99 +/- 0.06	0.69 +/- 1.33	21	39	17	27	(1,1)
Birmingham	Drax Hemingborough	W	159	19	18	73	0.21	41	0.86	0.98 +/- 0.06	-1.01 +/- 1.21	17	34	14	22	(0,0)
Birmingham	Drax Hemingborough	W	156	20	19	102	0.21	54	0.83	1.02 +/- 0.06	-0.68 +/- 1.24	19	35	15	22	(1,0)
Birmingham	Westthorne Ave	W	175	19	17	87	0.21	40	0.84	0.92 +/- 0.06	0.25 +/- 1.24	21	33	19	15	(1,0)
Birmingham	North Kensington	S	157	18	21	68	0.40	42	0.86	0.83 +/- 0.05	5.94 +/- 1.06	18	21	18	14	(1,0)
Birmingham	Marylebone Road	S	160	17	20	72	0.38	42	0.93	0.85 +/- 0.04	5.39 +/- 0.74	12	19	13	14	(1,0)
Birmingham	Marylebone Road	W	160	20	22	113	0.21	56	0.83	0.95 +/- 0.05	2.31 +/- 1.19	18	39	14	25	(0,0)
Birmingham	Teddington 24431	W	158	20	20	110	0.21	55	0.83	0.90 +/- 0.05	2.02 +/- 1.11	19	36	18	24	(0,0)
Birmingham	Teddington 24447	W	158	21	20	84	0.18	43	0.88	0.83 +/- 0.05	3.02 +/- 1.03	22	42	24	26	(0,0)
Bristol	Thames Road	W	193	24	24	74	0.53	47	0.92	0.85 +/- 0.04	3.46 +/- 0.96	19	49	19	38	(2,2)
Bristol	Drax Hemingborough	W	280	23	30	79	0.51	56	0.83	0.86 +/- 0.05	9.57 +/- 1.27	29	48	20	36	(2,2)
Bristol	Acton Town Hall	W	161	23	23	79	0.52	54	0.95	0.9 +/- 0.03	2.8 +/- 0.74	13	46	13	35	(2,2)
Bristol	East Kilbride 25053	W	490	23	23	82	0.54	56	0.92	0.67 +/- 0.03	8.26 +/- 0.68	28	46	35	34	(2,0)
Bristol	East Kilbride 04443	W	490	23	21	82	0.54	56	0.93	0.68 +/- 0.02	6.02 +/- 0.64	36	46	42	34	(2,0)
Bristol	Westthorne Ave	W	182	24	24	82	0.54	53	0.95	0.88 +/- 0.03	3.26 +/- 0.76	15	51	15	38	(2,2)
Bristol	Marylebone Road	W	169	23	26	83	0.52	55	0.92	0.89 +/- 0.03	5.00 +/- 0.9	15	47	12	36	(2,2)
East Kilbride	Bristol 24431	W	490	11	17	74	0.61	51	0.66	1.29 +/- 0.1	3.01 +/- 1.26	77	12	72	4	(0,0)
East Kilbride	Bristol 24447	W	490	11	15	71	0.61	49	0.72	1.22 +/- 0.09	2.24 +/- 1.12	58	12	55	4	(0,0)
East Kilbride	Thames Road	W	558	11	13	66	0.60	44	0.62	1.00 +/- 0.09	2.57 +/- 1.17	24	11	19	5	(0,0)
East Kilbride	Drax Hemingborough	W	302	11	19	72	0.60	50	0.65	1.08 +/- 0.09	7.10 +/- 1.11	55	12	47	4	(0,0)
East Kilbride	Acton Town Hall	W	538	10	14	71	0.60	52	0.67	1.15 +/- 0.09	1.75 +/- 1.08	44	10	40	4	(0,0)
East Kilbride	Westthorne Ave	W	553	11	14	73	0.61	52	0.73	1.09 +/- 0.08	1.98 +/- 0.97	33	12	30	4	(0,0)
East Kilbride	Marylebone Road	W	540	11	16	74	0.62	51	0.61	1.06 +/- 0.09	4.52 +/- 1.17	40	12	34	4	(0,0)
Teddington	Birmingham 04443	S	158	21	21	61	0.44	46	0.84	0.96 +/- 0.06	0.90 +/- 1.37	22	28	18	20	(2,1)
Teddington	Birmingham 25053	S	158	21	22	74	0.83	47	0.83	0.99 +/- 0.06	1.78 +/- 1.44	24	30	19	21	(2,1)
Teddington	Belvedere	S	36	21	23	77	0.86	44	0.91	0.91 +/- 0.04	3.81 +/- 1.03	15	32	13	23	(2,2)
Teddington	Drax Barlow	S	263	21	19	70	0.92	46	0.66	0.58 +/- 0.06	6.87 +/- 1.34	54	33	60	22	(2,0)
Teddington	Westthorne Ave	S	27	20	18	58	0.35	44	0.91	0.86 +/- 0.04	0.55 +/- 0.93	29	25	28	16	(2,1)
Teddington	North Kensington	S	14	21	21	80	0.89	48	0.84	0.88 +/- 0.05	3.53 +/- 1.22	21	29	19	19	(2,1)
Teddington	Marylebone Road	S	17	20	21	84	0.88	52	0.88	0.89 +/- 0.04	3.42 +/- 1.02	17	29	15	19	(2,1)

Table 7: Summary of experiment 2, the comparison between the model (using the TEOM from the equivalence sites and a distant FDMS purge measurement) and the PM₁₀ KFG reference method from the equivalence sites. Season is denoted as Summer (S) and Winter (W). Expanded uncertainties greater than 25% are highlighted in red.

3.3 Experiment 3

Experiment 3 planned to use gravimetric and TEOM measurements from Defra's AURN network and correct these using FDMS purge measurements from remote sites. This experiment was divided into two sections. Experiment 3i quantified the differences in W_{CM} arising from the modification in the application of the equivalence test method due to the lack of paired measurements in the AURN sites and the use of a non-reference sampler. Experiment 3ii tested the equivalence of the model against AURN measurements using the modified test method.

3.3.1 Experiment 3i

Experiment 3i aimed to quantify the change to W_{CM} due to the modified equivalence test approach as summarised in Table 5.

Box plots are used to summarise the results of the equivalence tests, which can be grouped by sites or methodology. This allowed the results to be compared but should not be interpreted as a robust statistical analysis, especially where the number of individual equivalence tests is low.

Part 1 – KCL Volatile Correction Model

Difference in W_{CM} of the model due to the modified equivalence test was assessed by comparing the model firstly with two reference samplers (KFGs) and then with single Partisols. These results are reported in full in Section 8.5. For completeness, datasets with an n_{c_s} of less than 40 days were reported in the tables but should be treated with caution. The expanded uncertainty at the annual mean limit value ($40 \mu\text{g m}^{-3}$) and daily mean limit value ($50 \mu\text{g m}^{-3}$) was summarised as a box plot in Figure 17, datasets with an n_{c_s} of less than 40 were not included in this analysis.

The number of possible tests increased in the second test as the instruments were unpaired and the KFG was replaced by the more reliable Partisol.

The mean expanded uncertainty was 15 % and 13 % for the two KFG dataset at $40 \mu\text{g m}^{-3}$ and $50 \mu\text{g m}^{-3}$ respectively. The mean expanded uncertainty was 22 % and 21 % for the single Partisol dataset at $40 \mu\text{g m}^{-3}$ and $50 \mu\text{g m}^{-3}$ respectively. The spread of data when compared with the KFG was increased by the inclusion of the unpaired Partisol measurements and also by those measurements excluded by Harrison (2006) on the basis of the Grubbs' test. Additionally, the improved reliability of the Partisol when compared with the KFG also meant that the Partisol dataset included many East Kilbride comparisons that were excluded from the KFG dataset due to a low n_{c_s} . The inclusion of these additional comparisons also increased the spread of the Partisol results when compared with the KFG. An additional 7 - 8 % in the mean expanded uncertainty was found to be associated with using a single Partisol rather than paired KFG instruments.

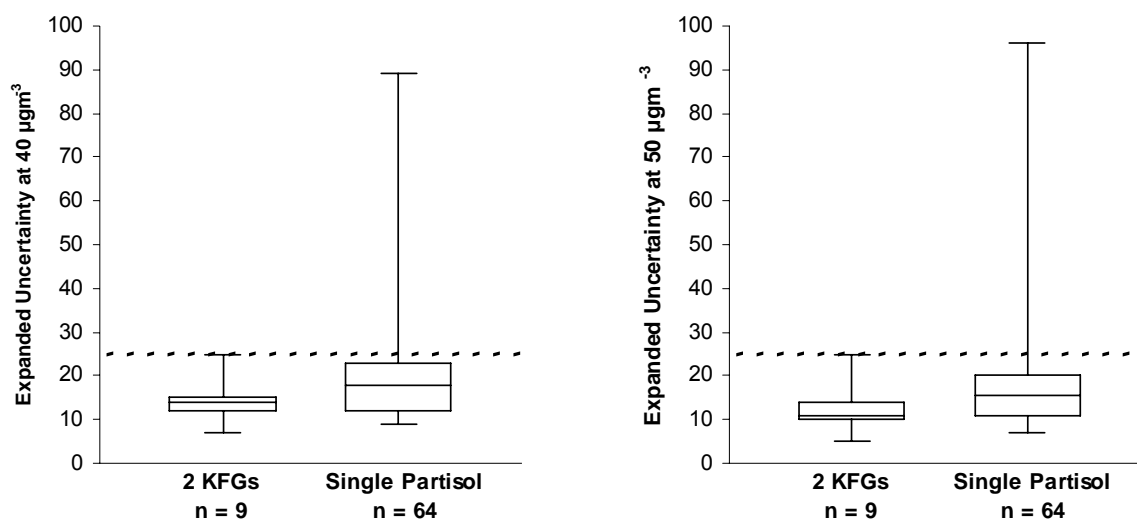


Figure 17: Parallel box plots showing the expanded uncertainty at the annual mean limit value (left) and daily mean limit value (right) of the model from a subset of experiment 1 (two KFGs) and the single Partisol instruments. The bar in the box plot represents the median, the box represents the interquartile range and the whiskers show the minimum and maximum values.

Part 2 – ‘Equivalence’ of FDMS PM₁₀ measurements at AURN sites.

Differences between the PM₁₀ concentrations measured by FDMS and by AURN Partisol were observed in a previous study (Green and Fuller, 2006). It was therefore necessary to quantify the difference between FDMS and by AURN Partisol, in terms of W_{CM} , before the KCL Volatile Correction Model could be tested at the AURN sites.

The modified equivalence test approach as summarised in Table 5; (single rather than paired measurements and a non-reference sampler) was applied to AURN sites with collocated FDMS instruments. The results are presented in Table 8. The FDMS failed to show equivalence with the AURN Partisol instruments at Marylebone Road and Belfast Centre and at North Kensington after the summer of 2005. The FDMS did show equivalence at North Kensington during the winter of 2003 and the whole of 2004 and at Harwell during the winter of 2004 (the only period it operated). W_{CM} increased between summer 2004 and winter 2005 at both North Kensington and Marylebone Road. This increase in W_{CM} was driven by an increase in the PM₁₀ mean from the Partisol, which was not apparent in the FDMS PM₁₀ concentration.

Dataset			Distance Between Sites	Reference Mean	FDMS Mean	24 hour			Orthogonal Regression			Annual Limit Value (40 µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)		
Reference Site	Year	Season				n _{bs}	U _{bs}	n _{c,s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	W _{CM} (%)	% > 20 µg m ⁻³	W _{CM} (%)	% > 25 µg m ⁻³	(n _{ES} , n _{EC})
Belfast Centre	2003	W	0	24	20	85	-	81	0.94	0.83 +/- 0.02	-0.45 +/- 0.6	39	56	38	41	(2,0)
Belfast Centre	2004	S	0	22	15	28	-	28	0.98	0.87 +/- 0.03	-4.19 +/- 0.66	48	43	44	29	(1,1)
Belfast Centre	2004	W	0	27	21	78	-	71	0.97	0.84 +/- 0.02	-1.45 +/- 0.51	40	58	38	41	(9,3)
Harwell	2004	W	0	20	17	88	-	82	0.95	0.95 +/- 0.02	-2.44 +/- 0.54	23	39	20	21	(1,0)
North Kensington	2003	W	0	19	23	59	-	46	0.86	0.92 /- 0.05	5.35 +/- 1.14	21	41	16	22	(0,1)
North Kensington	2004	S	0	20	18	76	-	60	0.92	1.05 +/- 0.04	-2.98 +/- 0.89	14	43	11	27	(1,1)
North Kensington	2004	W	0	19	23	83	-	66	0.93	0.90 +/- 0.03	6.43 +/- 0.67	17	33	11	21	(1,1)
North Kensington	2005	S	0	23	21	170	-	124	0.81	1.03 +/- 0.04	-2.64 +/- 1.06	28	52	22	31	(5,7)
North Kensington	2005	W	0	27	24	132	-	120	0.76	0.85 +/- 0.04	0.54 +/- 1.22	43	63	39	47	(11,8)
Marylebone Road Partisol	2004	S	0	33	29	175	-	146	0.78	0.97 +/- 0.04	-2.98 +/- 1.32	32	88	26	79	(8,6)
Marylebone Road Partisol	2004	W	0	42	35	154	-	140	0.88	0.69 +/- 0.02	6.38 +/- 0.95	38	91	41	79	(33,20)
Marylebone Road Partisol	2005	S	0	38	32	157	-	153	0.83	0.87 +/- 0.03	-1.62 +/- 1.21	43	95	39	85	(19,10)
Marylebone Road Partisol	2005	W	0	42	31	177	-	145	0.60	0.65 +/- 0.04	4.02 +/- 1.75	67	93	65	86	(42,17)

Table 8: Summary of the FDMS equivalence analysis when compared to a single Partisol instrument at AURN sites. U_{ref} was taken as 1.21. Season is denoted as Summer (S) and Winter (W). Expanded uncertainties greater than 25% are highlighted in red. Datasets with less than the required 40 paired measurements are coloured grey.

It is clear from Table 8 that the AURN Partisol comparisons with the FDMS instruments resulted in much larger expanded uncertainties at both the daily and annual means when compared with the measurements from the Equivalence Programme. The measurements from the UK Equivalence Programme resulted in mean expanded uncertainties of 15 % at 40 µg m⁻³ and 14 % at 50 µg m⁻³. The mean expanded uncertainty for the AURN Partisol comparisons with the FDMS instruments was 35 % at 40 µg m⁻³ and 32 % at 50 µg m⁻³. These increases in expanded uncertainty were therefore not entirely due to the modified equivalence test method and could therefore be isolated to:

- **The differences between the FDMS or TEOM measurements.** TEOM and FDMS measurements were reported at ambient temperature and pressure by the instruments used in the Equivalence Programme while the other TEOM and FDMS measurements were adjusted to ambient temperature and pressure using local meteorological measurements (Belfast Centre, Marylebone Road and North Kensington) or from best available meteorological measurements (Harwell) using the technique described by Green *et al* (2006). Green *et al* (2006) showed that the daily mean Marylebone Road TEOM PM₁₀ concentrations reported at standard temperature and pressure were -1 to +7 µg m⁻³ different to those reported at ambient temperature and pressure. The ambient temperature and pressure correction method duplicated the mathematical correction employed by the instruments in the Equivalence programme. The additional uncertainty due to the use of distant meteorological measurements was expected to be small and predominantly induced by differences in the temperature measurements at a rate of 0.18 µg m⁻³ for every 1 °C difference at an ambient PM₁₀ concentration of 50 µg m⁻³.

- **The differences between site locations.** The monitoring locations used in the Equivalence Programme (Birmingham, Bristol, East Kilbride and Teddington) and those available through the AURN (Belfast Centre, Harwell, Marylebone Road and North Kensington) may represent different conditions. Although the site types were similar, there were some pertinent differences. Marylebone Road is an extremely heavily trafficked location that was difficult to represent in the Equivalence Programme. Belfast also has local sources of domestic coal burning that was not reflected at the Equivalence Programme sites. The most useful comparison was between North Kensington and Teddington. These are both background sites in London that were operating at the same time during the winter of 2004 and summer of 2005. During the winter of 2004 the comparisons between a single Partisol from Teddington with an FDMS yielded W_{CM} between 16 % and 19 % at $40 \mu\text{g m}^{-3}$ and between 12 % and 14 % at $50 \mu\text{g m}^{-3}$. This was similar to the winter 2004 W_{CM} at North Kensington of 17 % at $40 \mu\text{g m}^{-3}$ and 11 % at $50 \mu\text{g m}^{-3}$. During the summer of 2005 the W_{CM} at North Kensington rose to 28 % at $40 \mu\text{g m}^{-3}$ and 22 % at $50 \mu\text{g m}^{-3}$. This rise W_{CM} at North Kensington was not reflected in at Teddington. This suggested that the differences in site locations alone could not explain the failure of the FDMS to meet the Equivalence Criteria at the AURN sites.
- **The differences between the gravimetric measurement methodologies** with respect to filter media, filter storage in sampler, weighing criteria, filter storage and transport and use of the Grubbs' test as summarised in Table 5. Brown *et al.* (2006) found that the choice of filter media could impact on the repeatability of measurement due to the loss of filter integrity, the loss of sampled material during storage and transport and the degree to which of temperature and humidity during conditioning affect the mass measurement. Consequently, the Equivalence Programme used Emfab filters, while the AURN used (and continues to use) quartz fibre filters, in accordance with EN12341. Stricter protocols for storage, transport, conditioning and weighing were also used in the Equivalence Programme as proposed in Brown *et al.* (2006) and in EN14907. These included chilled storage and transport, additional conditioning time pre and post exposure, tighter temperature and relative humidity controls and the reweighing of unloaded and loaded filters to ensure repeatability (leading to discarding of filters). Additionally, the Grubbs' test was used in the Equivalence Programme to eliminate paired data from the gravimetric measurements based on the difference between the paired measurements.

It is likely that the differences in gravimetric measurement methods would have been responsible for the majority of the differences identified in Table 8. However, it should be noted that the FDMS has passed an equivalence type test with quartz filters during a single deployment in France (Ampe *et al.*, 2005) where it exhibited a W_{CM} similar to that found in the UK Equivalence Programme.

3.3.2 Experiment 3ii

In this experiment the model was tested at the AURN sites (Belfast Centre, Birmingham Centre, Harwell, Manchester Piccadilly, Marylebone Road, Northampton, North Kensington and Port Talbot) by correcting the TEOM daily mean measurements with the FDMS purge daily mean measurements from a remote site and comparing them to the AURN Partisol measurements as described in section 2.6.3.2. This test was undertaken for FMDS to TEOM distances of less than 200 km in line with the results from Experiment 2. The results of this experiment for 2004 are summarised in Figure 18 and results for 2005 are summarised in Figure 19. All results from experiment 3ii are reported in Appendix 8.6.

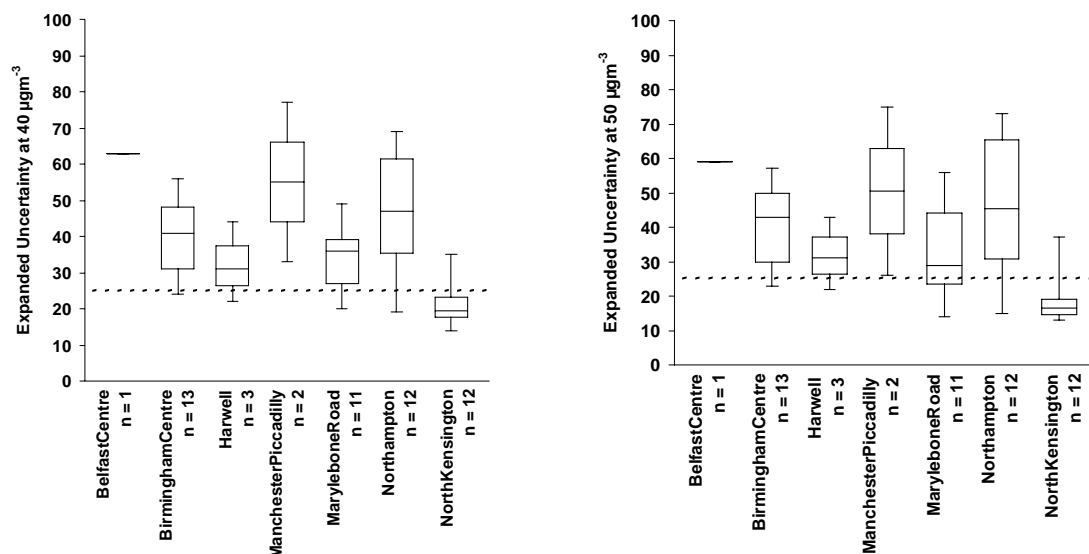


Figure 18: Parallel box plots showing the expanded uncertainty at the annual mean limit value (left) and daily mean limit value (right) of the model for 2004 where the distance between sites was less than 200 km. The bar in the box plot represents the median, the represents the interquartile range and the whiskers show the minimum and maximum values.

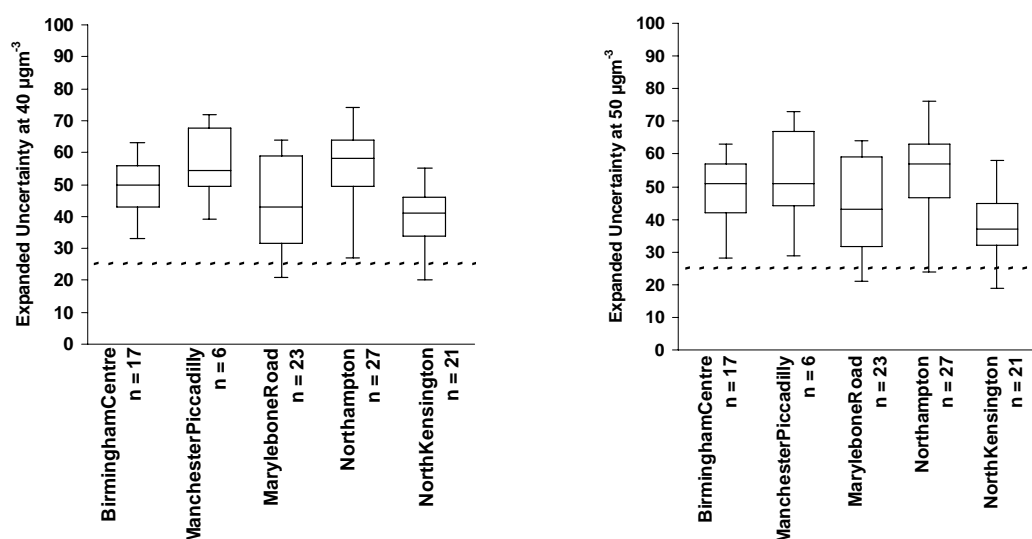


Figure 19: Parallel box plots showing the expanded uncertainty at the annual mean limit value (left) and daily mean limit value (right) of the model for 2005 where the distance between sites was less than 200 km. The bar in the box plot represents the median, the represents the interquartile range and the whiskers show the minimum and maximum values.

It was immediately clear that the KCL Volatile Correction Model failed to demonstrate equivalence to the AURN Partisols in the vast majority of tests. This was not surprising given that the model was derived from FDMS measurements and that the FDMS instruments at Belfast, Marylebone Road and (in some instances) North Kensington also failed to demonstrate equivalence.

There were some similarities between the results in Figure 18, Figure 19 and those in Table 8. The W_{CM} for both the FDMS and the model was lowest at North Kensington. The W_{CM} for the model (<200 km separations) and the FDMS were similar during 2004 and 2005; 14% to 55% for the model and 14 % to 43 % for the FDMS. On some occasions the model performed better than the collocated FDMS and Partisol instruments, specifically at Harwell using the FDMS measurement from North Kensington and on numerous occasions at Marylebone Road.

The divergence noted between the FDMS and the Partisol over time in section 3.3.1 was also apparent when examining the model performance. Table 9 shows a subset of the expanded uncertainties from experiment 3ii where four consecutive year and season combinations were available. The mean W_{CM} increased from 37 % in 2004 to 47 % in 2005. This was due to the increase in the seasonal mean of the Partisol measurements during 2005, which was not reflected in the TEOM measurements. The mean Partisol measurements at the five AURN sites increased between 2004 and 2005; from 26 $\mu\text{g m}^{-3}$ to 30 $\mu\text{g m}^{-3}$ while the TEOM mean was unchanged. Importantly, the FDMS did not fully reflect the increase in the mean PM₁₀ measured by the Partisol. The Partisol mean PM₁₀ at Marylebone Road increased from 33 $\mu\text{g m}^{-3}$ to 42 $\mu\text{g m}^{-3}$ (9 $\mu\text{g m}^{-3}$) between summer 2004 and winter 2005 but the FDMS only measured an increase in PM₁₀ from 30 $\mu\text{g m}^{-3}$ to 32 $\mu\text{g m}^{-3}$ (2 $\mu\text{g m}^{-3}$). At North Kensington the Partisol mean PM₁₀ increased from 27 $\mu\text{g m}^{-3}$ to 33 $\mu\text{g m}^{-3}$ (6 $\mu\text{g m}^{-3}$) and the FDMS measured an increase from 19 $\mu\text{g m}^{-3}$ to 23 $\mu\text{g m}^{-3}$ (4 $\mu\text{g m}^{-3}$).

AURN Site	Year	Season	Partisol Mean ($\mu\text{g m}^{-3}$)	FDMS Mean ($\mu\text{g m}^{-3}$)	TEOM Mean ($\mu\text{g m}^{-3}$)	FDMS Site Expanded Uncertainty at Annual Mean ($40 \mu\text{g m}^{-3}$)			
						Belvedere	Marylebone Road	North Kensington	Thames Road
Birmingham Centre	2004	S	21	-	14	24	31	39	37
	2004	W	26	-	13	53	41	26	48
	2005	S	27	-	16	40	38	33	43
	2005	W	31	-	15	50	51	56	60
Manchester Piccadilly	2004	S	21	-	15	31	35	36	33
	2004	W	21	-	15	98	68	33	69
	2005	S	23	-	15	47	48	45	57
	2005	W	27	-	16	-	61	70	71
Marylebone Road	2004	S	33	30	28	19	17	15	24
	2004	W	41	35	28	23	19	25	22
	2005	S	38	31	29	20	26	27	38
	2005	W	42	32	28	37	41	46	46
Kensington North	2004	S	27	19	15	36	30	23	34
	2004	W	31	24	15	39	36	20	40
	2005	S	28	22	15	29	32	33	40
	2005	W	33	23	16	52	58	61	62
Northampton	2004	S	20	-	12	21	38	-	41
	2004	W	21	-	11	67	43	51	60
	2005	S	24	-	11	49	49	44	50
	2005	W	26	-	11	54	58	60	64

Table 9: Subset of results from experiment 3ii, the comparison between the AURN Partisol and the model using collocated TEOM and a distant FDMS purge measurement, where four consecutive year and season combinations are available. Season is denoted as Summer (S) and Winter (W). Seasons are from any single year, therefore winter 2005 was made up of 1st January - 31st March 2005 and 1st October - 31st December 2005, while summer was 1st April – 31st September 2005). TEOM mean concentrations are expressed without the internal correction factor and at atmospheric temperature and pressure.

These changes can also be seen clearly in Figure 20, which show that the Partisol measurements at both sites increased relative to the TEOM and FDMS measurements at the start of 2004. No change is evident in the FDMS purge measurement, which would respond to a change in the volatile particulate matter concentration and may have had a greater impact on the Partisol measurement than the TEOM (due to the 50 °C sample temperature). The reason for this change in concentration therefore requires further investigation.

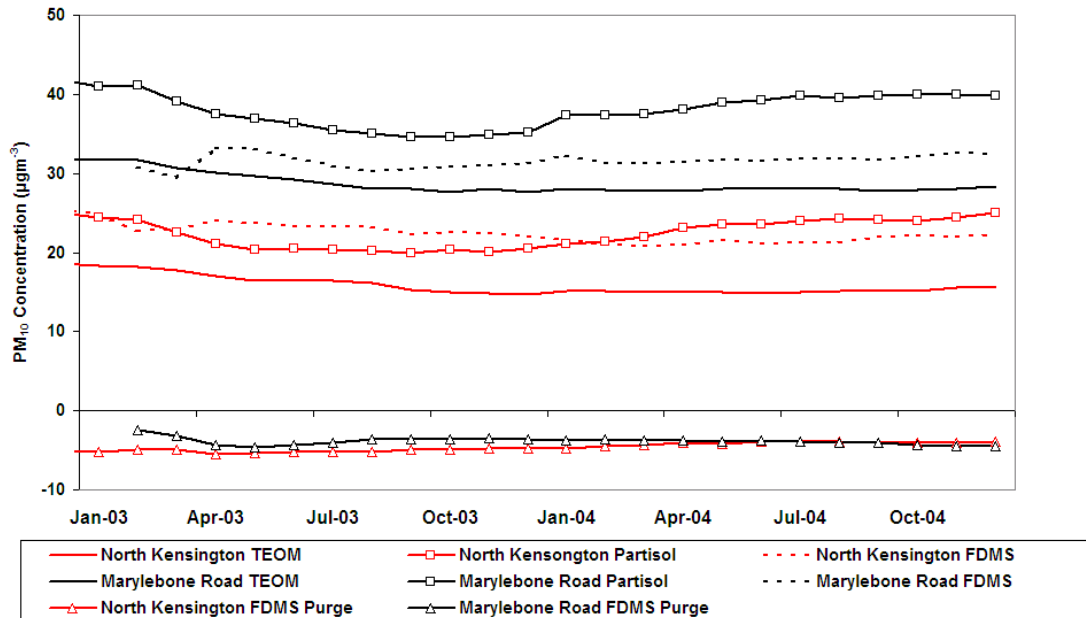


Figure 20: Annual mean calculated on a monthly basis and labelled start month between January 2003 and December 2004 for TEOM, FDMS and Partisol measurements from North Kensington and Marylebone Road

3.4 Developing an FDMS Monitoring Strategy for the UK

The results of experiment 2 and the relationship summarised in Figure 16 show that the KCL Volatile Correction Model can utilise FDMS purge measurements from sites up to 200 km distant to correct TEOM measurements to reference equivalent PM₁₀ concentrations. A small national network of FDMS instruments could therefore be used to correct the existing network of TEOM instruments in the UK. This part of the report aimed to determine if Defra's planned 2007 FDMS deployment would be sufficient to allow the KCL Volatile Correction Model to be applied to all current AURN TEOM instruments.

The current AURN network of is shown in green in Figure 25. The planned first phase role out of FDMS instruments and those already installed are marked in red. The analysis in experiment 2 (section 3.2) demonstrated that the model could employ FDMS purge measurements to correct a TEOM measurement with a separation of up to approximately 200 km. However, a degree of redundancy is required in this type of network as the failure of an individual FDMS instrument would impact on a large number of TEOM measurements. The distance between each AURN site and each of the FDMS sites (currently operational or planned) was calculated. Table 10 shows each of the AURN monitoring sites alongside the nearest three (primary, secondary and tertiary) FDMS instruments and the distances between them. This analysis demonstrates that FDMS instruments from the current and first phase deployment would provide adequate coverage, with a degree of redundancy, for all of the AURN monitoring sites in the UK except Northern Ireland and Scotland. Three additional instruments would be required to provide adequate coverage for each of these areas. In England, further coverage would be advantageous the northeast and northwest where separation distances are high. Further coverage in East Anglia, Kent and the south coast would provide important information regarding the transport of volatile particulate matter from the continent. The London Marylebone Road FDMS used in Table 10 is not part of the AURN but is instead jointly funded by Westminster City Council and KCL. Given the prominence of this site and its geographical significance, this FDMS should be funded as part of the AURN.

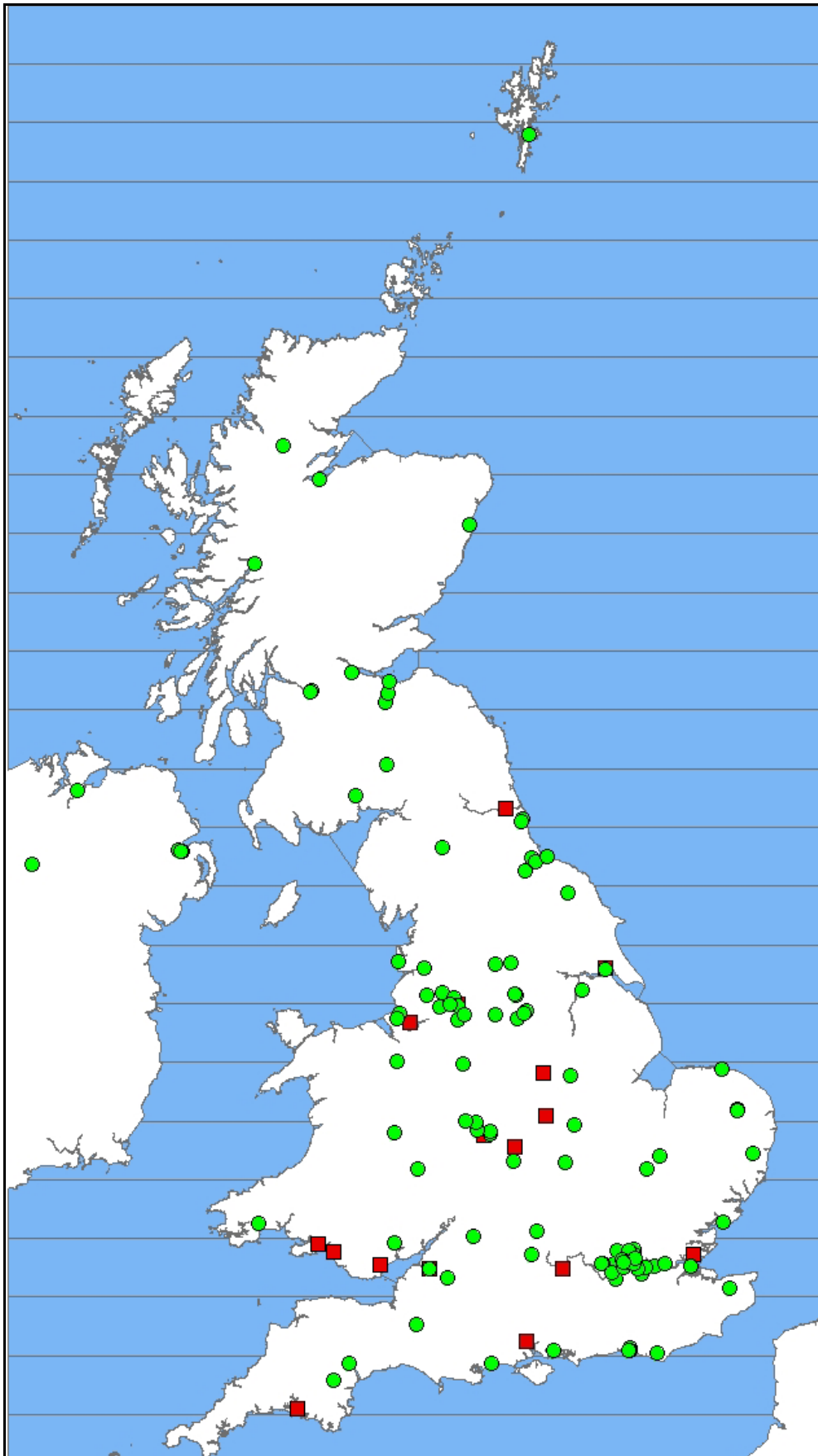


Figure 21: All monitoring sites in the AURN (not just PM₁₀). FDMS sites (currently operational or planned) are marked in red squares other monitoring sites are in green circles.

AURN Site	FDMS Site					
	Primary		Secondary		Tertiary	
	Site	Distance (km)	Site	Distance (km)	Site	
Lerwick	Newcastle Centre	575	Hull Freetown	713	Manchester Piccadilly	744
Strath Vaich	Newcastle Centre	364	Manchester Piccadilly	499	Liverpool Speke	503
Inverness	Newcastle Centre	323	Manchester Piccadilly	463	Liverpool Speke	469
Fort William	Newcastle Centre	300	Liverpool Speke	413	Manchester Piccadilly	414
Aberdeen	Newcastle Centre	244	Hull Freetown	395	Manchester Piccadilly	409
Lough Navar	Liverpool Speke	350	Manchester Piccadilly	383	Swansea Roadside	406
Derry	Liverpool Speke	346	Newcastle Centre	366	Manchester Piccadilly	373
Grangemouth	Newcastle Centre	175	Manchester Piccadilly	297	Liverpool Speke	302
Glasgow Kerbside	Newcastle Centre	194	Liverpool Speke	294	Manchester Piccadilly	295
Glasgow Centre	Newcastle Centre	194	Liverpool Speke	294	Manchester Piccadilly	295
Glasgow City Chambers	Newcastle Centre	194	Liverpool Speke	294	Manchester Piccadilly	295
Edinburgh Centre	Newcastle Centre	148	Manchester Piccadilly	282	Liverpool Speke	291
Edinburgh St Leonards	Newcastle Centre	146	Manchester Piccadilly	281	Liverpool Speke	290
Belfast Centre	Liverpool Speke	246	Manchester Piccadilly	272	Newcastle Centre	281
Bush Estate	Newcastle Centre	141	Manchester Piccadilly	272	Liverpool Speke	281
Belfast East	Liverpool Speke	244	Manchester Piccadilly	270	Newcastle Centre	279
Belfast Clara St	Liverpool Speke	243	Manchester Piccadilly	269	Newcastle Centre	278
Auchencorth Moss	Newcastle Centre	137	Manchester Piccadilly	265	Liverpool Speke	273
Eskdalemuir	Newcastle Centre	108	Manchester Piccadilly	214	Liverpool Speke	220
Dumfries	Newcastle Centre	129	Manchester Piccadilly	198	Liverpool Speke	198
Sibton	Southend-on-Sea	100	London Marylebone Road	141	Leicester Centre	180
Newcastle Centre	Newcastle Centre	0	Hull Freetown	160	Manchester Piccadilly	172
Sunderland	Newcastle Centre	17	Hull Freetown	145	Manchester Piccadilly	168
Sunderland Silksworth	Newcastle Centre	17	Hull Freetown	144	Manchester Piccadilly	165
Norwich Centre	Southend-on-Sea	128	London Marylebone Road	159	Leicester Centre	164
Norwich Roadside (new)	Southend-on-Sea	128	London Marylebone Road	158	Leicester Centre	164
Weybourne	Hull Freetown	132	Nottingham Centre	152	Leicester Centre	156
Blackpool Marton	Liverpool Speke	52	Manchester Piccadilly	62	Nottingham Centre	156
Great Dun Fell	Newcastle Centre	63	Manchester Piccadilly	135	Liverpool Speke	151
Redcar	Newcastle Centre	53	Hull Freetown	107	Manchester Piccadilly	147
Canterbury	Southend-on-Sea	42	London Marylebone Road	91	Reading New Town	144
St Osyth	Southend-on-Sea	37	London Marylebone Road	88	Reading New Town	143
Plymouth Centre	Plymouth Centre	0	Port Talbot	137	Cardiff Centre	141
Billingham	Newcastle Centre	47	Hull Freetown	113	Manchester Piccadilly	140
Middlesbrough	Newcastle Centre	52	Hull Freetown	108	Manchester Piccadilly	138
Preston	Manchester Piccadilly	43	Liverpool Speke	48	Nottingham Centre	136
High Muffles	Hull Freetown	72	Newcastle Centre	88	Manchester Piccadilly	133
Hull Centre	Hull Freetown	0	Nottingham Centre	103	Manchester Piccadilly	129
Hull Freetown	Hull Freetown	0	Nottingham Centre	103	Manchester Piccadilly	129
Stockton-on-Tees Yarm	Newcastle Centre	55	Hull Freetown	107	Manchester Piccadilly	128
Liverpool Centre	Liverpool Speke	11	Manchester Piccadilly	50	Birmingham Centre	126
Wirral Tranmere	Liverpool Speke	12	Manchester Piccadilly	54	Birmingham Centre	124
Wigan Centre	Liverpool Speke	26	Manchester Piccadilly	28	Nottingham Centre	119
Liverpool Speke	Liverpool Speke	0	Manchester Piccadilly	43	Birmingham Centre	115
Southend-on-Sea	Southend-on-Sea	0	London Marylebone Road	58	Reading New Town	113
Bolton	Manchester Piccadilly	17	Liverpool Speke	37	Nottingham Centre	110
Narberth	Swansea Roadside	54	Port Talbot	68	Cardiff Centre	110
Rochester	Southend-on-Sea	10	London Marylebone Road	55	Reading New Town	110
Yarner Wood	Plymouth Centre	39	Cardiff Centre	105	Port Talbot	109
Lullington Heath	London Marylebone Road	84	Southend-on-Sea	90	Reading New Town	108
Scunthorpe	Hull Freetown	27	Nottingham Centre	78	Manchester Piccadilly	107
Scunthorpe Town	Hull Freetown	27	Nottingham Centre	78	Manchester Piccadilly	107
Glazebury	Manchester Piccadilly	16	Liverpool Speke	28	Nottingham Centre	105
Aston Hill	Birmingham Centre	77	Liverpool Speke	95	Coventry Memorial Park	104
Wicken Fen	Southend-on-Sea	88	London Marylebone Road	92	Leicester Centre	104
Southampton Centre	Southampton Centre	0	Reading New Town	68	Bristol Centre	103
Portsmouth	Southampton Centre	25	Reading New Town	70	London Marylebone Road	100
Bury Roadside	Manchester Piccadilly	7	Liverpool Speke	43	Nottingham Centre	100
Bournemouth	Southampton Centre	35	Bristol Centre	96	Reading New Town	100
Salford Eccles	Manchester Piccadilly	6	Liverpool Speke	37	Nottingham Centre	99
Leeds Centre	Manchester Piccadilly	58	Hull Freetown	80	Nottingham Centre	98
Cambridge Roadside	London Marylebone Road	78	Southend-on-Sea	83	Leicester Centre	98
Wrexham	Liverpool Speke	35	Manchester Piccadilly	71	Birmingham Centre	97
Exeter Roadside	Plymouth Centre	58	Cardiff Centre	88	Port Talbot	96
Somerton	Bristol Centre	48	Cardiff Centre	58	Port Talbot	94
Manchester South	Manchester Piccadilly	1	Liverpool Speke	43	Nottingham Centre	94
Market Harborough	Manchester Piccadilly	0	Liverpool Speke	43	Nottingham Centre	93
Bradford Centre	Manchester Piccadilly	47	Liverpool Speke	88	Hull Freetown	93
Brighton Roadside PM10	London Marylebone Road	78	Southampton Centre	89	Reading New Town	90
Brighton Roadside	London Marylebone Road	78	Southampton Centre	89	Reading New Town	90
Hove Roadside	London Marylebone Road	78	Southampton Centre	88	Reading New Town	89
Brighton Preston Park	London Marylebone Road	76	Reading New Town	88	Southampton Centre	88
Thurrock	Southend-on-Sea	26	London Marylebone Road	33	Reading New Town	88
Manchester Piccadilly	Manchester Piccadilly	13	Liverpool Speke	40	Nottingham Centre	87
Bath Roadside (new)	Bristol Centre	18	Cardiff Centre	58	Southampton Centre	86
Leominster	Birmingham Centre	63	Coventry Memorial Park	85	Bristol Centre	86
Sheffield Centre	Nottingham Centre	52	Manchester Piccadilly	52	Hull Freetown	86
Stockport Shaw Heath	Manchester Piccadilly	10	Liverpool Speke	46	Nottingham Centre	84
Walsall Willenhall	Bristol Centre	47	Reading New Town	81	Cardiff Centre	83

AURN Site	FDMS Site					
	Primary		Secondary		Tertiary	
	Site	Distance (km)	Site	Distance (km)	Site	Distance (km)
Bristol Old Market	Bristol Centre	0	Cardiff Centre	41	Port Talbot	83
Bristol Centre	Bristol Centre	0	Cardiff Centre	41	Port Talbot	83
Bristol St Paul's	Bristol Centre	1	Cardiff Centre	41	Port Talbot	83
Harwell	Reading New Town	30	Southampton Centre	74	London Marylebone Road	81
Oxford Centre	Reading New Town	40	Coventry Memorial Park	74	London Marylebone Road	80
Barnsley Gawber	Manchester Piccadilly	49	Nottingham Centre	72	Hull Freetown	80
Sheffield Tinsley	Nottingham Centre	53	Manchester Piccadilly	56	Hull Freetown	79
London Hillingdon	London Marylebone Road	21	Reading New Town	34	Southend-on-Sea	79
Barnsley 12	Manchester Piccadilly	51	Nottingham Centre	70	Hull Freetown	79
London Bexley	London Marylebone Road	24	Southend-on-Sea	35	Reading New Town	78
London Harlington	London Marylebone Road	20	Reading New Town	35	Southend-on-Sea	78
Bottesford	Nottingham Centre	22	Leicester Centre	40	Coventry Memorial Park	76
Rotherham Centre	Nottingham Centre	55	Manchester Piccadilly	59	Hull Freetown	76
Northampton	Leicester Centre	43	Coventry Memorial Park	45	Birmingham Centre	73
Ladybower	Manchester Piccadilly	33	Nottingham Centre	64	Liverpool Speke	73
London Teddington	London Marylebone Road	17	Reading New Town	42	Southend-on-Sea	72
London Eltham	London Marylebone Road	17	Southend-on-Sea	43	Reading New Town	71
London A3 Roadside	London Marylebone Road	19	Reading New Town	46	Southend-on-Sea	70
Brentford Roadside	London Marylebone Road	11	Reading New Town	44	Southend-on-Sea	69
Reading New Town	Reading New Town	0	London Marylebone Road	55	Southampton Centre	68
Wolverhampton Centre	Birmingham Centre	19	Coventry Memorial Park	47	Leicester Centre	68
Nottingham Centre	Nottingham Centre	0	Leicester Centre	36	Coventry Memorial Park	67
London Bromley	London Marylebone Road	18	Southend-on-Sea	48	Reading New Town	67
London Brent	London Marylebone Road	11	Reading New Town	49	Southend-on-Sea	66
London Lewisham	London Marylebone Road	13	Southend-on-Sea	49	Reading New Town	64
Stoke-on-Trent Centre	Manchester Piccadilly	51	Liverpool Speke	57	Birmingham Centre	64
Tower Hamlets Roadside	London Marylebone Road	8	Southend-on-Sea	50	Reading New Town	63
Haringey Roadside	London Marylebone Road	10	Southend-on-Sea	52	Reading New Town	63
London Hackney	London Marylebone Road	8	Southend-on-Sea	51	Reading New Town	63
London N. Kensington	London Marylebone Road	4	Reading New Town	51	Southend-on-Sea	62
Southwark Roadside	London Marylebone Road	8	Southend-on-Sea	52	Reading New Town	61
West London	London Marylebone Road	4	Reading New Town	52	Southend-on-Sea	61
London Wandsworth	London Marylebone Road	8	Reading New Town	52	Southend-on-Sea	61
Sandwell West Bromwich	Birmingham Centre	8	Coventry Memorial Park	35	Leicester Centre	60
Walsall Alumwell	Birmingham Centre	13	Coventry Memorial Park	39	Leicester Centre	60
London Cromwell Road 2	London Marylebone Road	3	Reading New Town	53	Southend-on-Sea	59
London Southwark	London Marylebone Road	5	Southend-on-Sea	54	Reading New Town	59
Camden Kerbside	London Marylebone Road	3	Reading New Town	54	Southend-on-Sea	59
London Haringey	London Marylebone Road	7	Southend-on-Sea	56	Reading New Town	59
London Marylebone Road	London Marylebone Road	0	Reading New Town	55	Southend-on-Sea	58
London Bloomsbury	London Marylebone Road	2	Southend-on-Sea	56	Reading New Town	57
London Westminster	London Marylebone Road	3	Southend-on-Sea	56	Reading New Town	57
Swansea Roadside	Swansea Roadside	0	Port Talbot	14	Cardiff Centre	56
Birmingham Centre	Birmingham Centre	0	Coventry Memorial Park	28	Leicester Centre	55
Manchester Town Hall	Leicester Centre	26	Nottingham Centre	51	Coventry Memorial Park	54
Cwmbran	Cardiff Centre	22	Bristol Centre	36	Port Talbot	53
Birmingham East	Birmingham Centre	6	Coventry Memorial Park	24	Leicester Centre	50
Birmingham Tyburn	Birmingham Centre	6	Coventry Memorial Park	25	Leicester Centre	49
Leamington Spa	Coventry Memorial Park	12	Birmingham Centre	33	Leicester Centre	47
Cardiff Centre	Cardiff Centre	0	Bristol Centre	41	Port Talbot	42
Port Talbot	Port Talbot	0	Swansea Roadside	14	Cardiff Centre	42
Coventry Memorial Park	Coventry Memorial Park	0	Birmingham Centre	28	Leicester Centre	37

Table 10: AURN PM₁₀ monitoring sites alongside the nearest three (primary, secondary and tertiary) FDMS instruments and the distance between them. Sites with a separation of more than 200 km distance, identified as falling outside the 25 % data quality threshold, are coloured red.

3.5 FDMS Coverage in the UK

Once installed, it is important to test whether the FDMS instruments provide (and continue to provide) the required geographical coverage. The analysis so far was concerned with demonstrating that the model produced daily and annual mean concentrations that had an expanded uncertainty (W_{CM}) of less than 25% when compared to the UK Equivalence Programme measurements. However, it is not intended that the Equivalence Programme will operate on an on-going basis. An alternative method was therefore required to demonstrate that the FDMS network would continue to maintain sufficient coverage to allow the KCL Volatile Correction Model to operate at all AURN sites.

To quantify the changes in FDMS purge concentrations with distance, the concept of between sampler uncertainty was applied to the FDMS purge concentrations. The between purge uncertainty (u_{purge}) was calculated using the FDMS purge measurements from the local and distant sites by modifying the between sampler uncertainty calculation (Harrison, 2006).

The results of this analysis are shown in Figure 22 and demonstrated that there was a relationship between the expanded uncertainty (W_{CM}) and the between purge uncertainty (u_{purge}). It can be seen from Figure 22 that a between purge uncertainty of greater than $1.5 \mu\text{g m}^{-3}$ yielded an expanded uncertainty greater than 25%. The exception to this is the combination of Teddington and Westhorne Avenue (also identified as an outlier in experiment 2) with an expanded uncertainty of 29% at the annual mean Limit Value from a between purge uncertainty of $0.72 \mu\text{g m}^{-3}$.

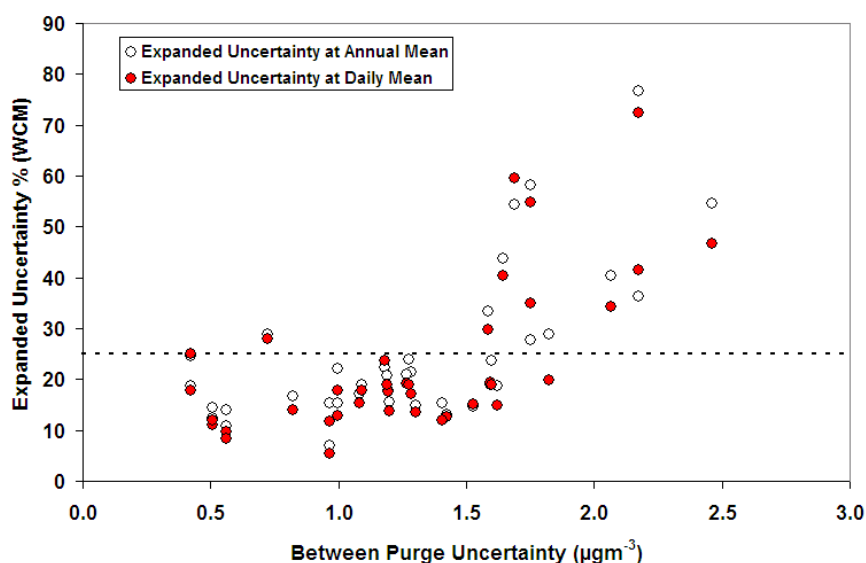


Figure 22: Scatter plot showing the between purge uncertainty and the W_{CM} for the daily and annual mean limit values. The data quality objective of 25 % is shown as a dotted line.

The between purge uncertainty was also compared to the distance between sites; the results of this analysis are shown in Figure 23. This analysis demonstrated that at a distance of 200 km, (the maximum distance over which the model could be applied from in experiment 2) the between purge uncertainty between the sites was less than $2 \mu\text{g m}^{-3}$. This is higher than the value of $1.5 \mu\text{g m}^{-3}$ derived from Figure 22. A precautionary between purge uncertainty value of $1.5 \mu\text{g m}^{-3}$ is therefore recommended as a requirement to determine the validity of the KCL Volatile Correction Model between two FDMS instruments.

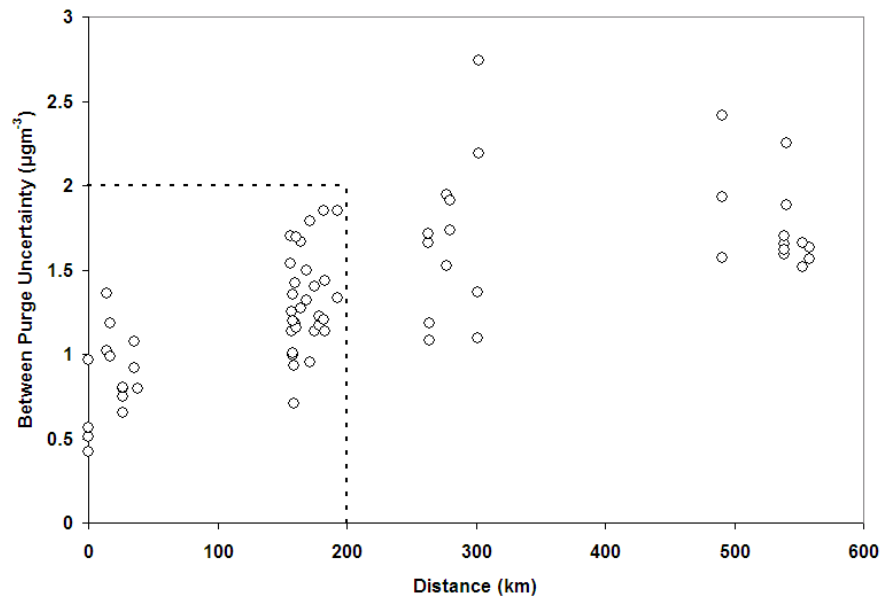


Figure 23: Scatter plot showing the relationship between distance between sites and the between purge uncertainty. The maximum between purge uncertainty required to yield the data quality objective of 25 % is shown as a dotted line, as is the 200 km maximum distance between sites required to yield the data quality objective calculated in experiment 2.

4 CONCLUSIONS

The KCL Volatile Correction Model allows the correction of TEOM measurements to enable them to meet the equivalence criteria for the measurement of PM₁₀. The model equation is:

$$\text{Reference Equivalent PM}_{10} = \text{TEOM} - 1.87 \text{ FDMS purge}$$

Where the FDMS purge concentration may be measured at a remote site.

The KCL Volatile Correction Model passed the Guidance equivalence criteria at the sites used in the UK Equivalence Programme and can therefore be considered an equivalent method.

Further, the model passed the equivalence criteria using remote FDMS purge measurements over a maximum distance of approximately 200 km. Twenty two out of twenty three tests at less than 200 km passed the equivalence criteria, the single failure was marginal. This proved that the model is a viable tool for correcting measurements from TEOM instruments on the national and local government networks using FDMS purge measurements from a more limited network of sites.

The model was also tested against measurements at AURN sites. The AURN sites were outside the UK Equivalence Programme, they employed different measurement methodologies and due to equipment constraints a modified equivalence test had to be applied. The FDMS failed the equivalence criteria when tested against the majority of AURN measurements. The model was derived from FDMS measurements and unsurprisingly it also failed in the majority of circumstances.

The reason for the failure of both the FDMS and the model to achieve equivalence when tested against AURN measurements was examined. A modified test was required at the AURN sites due to the operation of an equivalent, rather than reference, gravimetric sampler and single rather than paired instruments. It was found that the modified equivalence test at these sites was up to 8 % more stringent in terms of expanded uncertainty when compared to the procedure in the Guidance but this did not account for the failure of the FDMS and the model to demonstrate equivalence at AURN sites. It was therefore concluded that the failure of the FDMS and the model to pass the equivalence criteria at these sites was predominantly due to the differences in the AURN measurement methodology (which conforms to EN12341) from that employed in the UK Equivalence Programme.

Accepting that the model has a range of 200 km, the current and planned network of FDMS instruments was assessed. It was found to provide adequate coverage (with redundancy) for the whole of the UK, except Scotland and Northern Ireland. Three FDMS additional instrument would be required to cover each of these areas. Additional sites in the northwest and northeast would be advantageous to improve regional coverage. Additional sites in East Anglia, Kent and the south coast would provide important information regarding the transport of volatile particulate matter from the continent.

To determine the on-going spatial validity of the KCL Volatile Correction Model a test based on uncertainty between two distant FDMS purge measurements was derived. This between purge uncertainty was related to the expanded uncertainty derived in experiment 2 to produce an estimate of between purge uncertainty ($1.5 \mu\text{g m}^{-3}$) at which the 25 % data quality objective would be exceeded. When the between purge uncertainty was examined alongside the distance between the FDMS sites this value of $1.5 \mu\text{g m}^{-3}$ was found to be consistent with a distance of 200 km (the distance identified as the geographical limit of the model).

Between 2004 and 2005 the PM₁₀ concentration measured by the AURN Partisol instruments increased by 2004 and 2005; from $26 \mu\text{g m}^{-3}$ to $30 \mu\text{g m}^{-3}$ while the TEOM mean was unchanged. Increases in the annual mean PM₁₀ measured by AURN Partisol at Marylebone Road and North Kensington were not fully reflected in FDMS measurements. These instrument dependent changes in PM₁₀ concentration suggest the need for an on-going co-located measurement programme to confirm the continued equivalence of both the FDMS and the KCL Volatile Correction Model.

5 RECOMMENDATIONS FOR FURTHER WORK

The measurements of particulate matter using the FDMS, especially its assessment of the volatile component, is a new and very important topic. There are still many questions that remain to be answered with respect to the FDMS and in relation to the KCL Volatile Correction Model.

Investigation of the Physical / Chemical Basis of the KCL Volatile Correction Model

The physical / chemical mechanisms require further investigation to understand how the model will react to future changes in volatile particulate.

Review of the FDMS Purge Measurements from the First phase AURN deployment

The measurements from the first phase FDMS instruments will need to be reviewed with reference to the analysis in section 3.5. This would test for temporal changes in the model applicability and needs to be carried out on the ratified measurements after at least 6 months.

Extension of the KCL Volatile Correction Model to PM_{2.5}

FDMS measurements of PM₁₀ and PM_{2.5} in London indicate that the FDMS purge measurement does not differ in magnitude between PM₁₀ and PM_{2.5} and offers the opportunity to extend the model to PM_{2.5} measurements. It may be prudent to build TEOM PM_{2.5} measurements into the FDMS trials in Teddington.

Applicability of the KCL Volatile Correction Model to Hourly Measurements

For data dissemination requirements and short-term changes in particulate matter concentrations it is necessary to assess the applicability of the model on an hourly basis.

Use of the KCL Volatile Correction Model by Local Authorities

The model would allow local authorities to correct their own TEOM PM₁₀ measurements using the FDMS purge measurements from the AURN. KCL would develop a web portal to generate the daily (or hourly) correction factor for the any given any UK location.

On-Going Equivalence of the FDMS and the KCL Volatile Correction Model

An on-going co-located measurement programme is recommended to confirm the continued equivalence of both the FDMS and the KCL Volatile Correction Model. From a cost perspective it would clearly be desirable to use only single rather than paired instruments.

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8 APPENDIX

8.1 Alternative Model Parameterisation

As part of the model optimisation process, experiment 1 was repeated with three model parameterisations. The optimised linear model performed the best in terms of providing the lowest W_{CM} using the approach in experiment 1. The results from the optimised linear model are presented in section 3.1. The results from experiment 1 for the alternative model parameterisations are reported here, as is the derivation of the orthogonal regression model parameterisation.

1. The original model parameterisation inferred from Green and Fuller (2006):

$$\text{Reference Equivalent PM}_{10} = \text{TEOM} - 2 \text{ FDMS purge}$$

2. The optimised linear model parameterisation (used in the analysis):

$$\text{Reference Equivalent PM}_{10} = \text{TEOM} - 1.87 \text{ FDMS purge}$$

3. The orthogonal regression model parameterisation:

$$\text{Reference Equivalent PM}_{10} = \text{TEOM} - 2.39 \text{ FDMS purge} + 2.13 \mu\text{g m}^{-3}$$

Dataset				Distance Between Sites Reference Mean	Modelled Mean	24 hour		Orthogonal Regression				Annual Limit Value (40 µg m-3)		Daily Limit Value (50 µg m-3)			
Reference Site	FDMS Serial #1	FDMS Serial #2	Season			nbs	ubs	nc_s	r2	Slope (b) +/- Ub	Intercept (a) +/- Ua	WCM (%)	%> 20 µg m-3	WCM (%)	%> 25 µg m-3	(nES,nEC)	
Birmingham	04443	04443	S	0	18	19	60	0.38	39	0.96	0.98 +/- 0.03	1.76 +/- 0.67	11	18	9	15	(1,1)
Birmingham	04443	25053	S	0	18	20	60	1.11	39	0.96	0.99 +/- 0.03	2.51 +/- 0.69	14	18	11	15	(1,2)
Birmingham	25053	04443	S	0	18	20	60	1.41	39	0.96	0.99 +/- 0.03	2.51 +/- 0.69	14	18	11	15	(1,2)
Birmingham	25053	25053	S	0	18	21	69	0.38	41	0.95	0.99 +/- 0.04	3.45 +/- 0.77	20	20	16	15	(1,2)
Birmingham	04443	04443	W	0	19	18	84	0.15	47	0.90	1.00 +/- 0.05	-0.16 +/- 0.93	11	32	9	15	(1,1)
Birmingham	04443	25053	W	0	19	18	84	0.86	47	0.91	1.00 +/- 0.04	-0.49 +/- 0.91	11	32	9	15	(1,1)
Birmingham	25053	04443	W	0	19	18	84	0.88	47	0.91	1.00 +/- 0.04	-0.49 +/- 0.91	11	32	9	15	(1,1)
Birmingham	25053	25053	W	0	21	20	106	0.17	59	0.94	0.98 +/- 0.03	-0.54 +/- 0.71	12	39	10	25	(1,1)
Bristol	24431	24431	S	0	22	25	44	0.38	36	0.95	1.08 +/- 0.04	1.90 +/- 0.94	27	39	25	25	(0,1)
Bristol	24431	24447	S	0	22	24	44	1.19	36	0.96	1.09 +/- 0.04	0.91 +/- 0.92	24	39	23	25	(0,1)
Bristol	24447	24431	S	0	22	24	44	1.32	36	0.96	1.09 +/- 0.04	0.91 +/- 0.92	24	39	23	25	(0,1)
Bristol	24447	24447	S	0	22	24	44	0.38	36	0.96	1.10 +/- 0.04	-0.11 +/- 0.92	22	39	21	25	(0,1)
Bristol	24431	24431	W	0	22	26	84	0.53	55	0.95	0.96 +/- 0.03	4.36 +/- 0.74	18	45	13	33	(2,2)
Bristol	24431	24447	W	0	22	25	79	1.15	55	0.96	0.96 +/- 0.03	3.72 +/- 0.71	16	45	12	33	(2,2)
Bristol	24447	24431	W	0	22	25	79	1.06	55	0.96	0.96 +/- 0.03	3.72 +/- 0.71	16	45	12	33	(2,2)
Bristol	24447	24447	W	0	23	25	81	0.54	57	0.96	0.96 +/- 0.03	3.11 +/- 0.68	14	47	10	35	(2,2)
East Kilbride	25053	25053	S	0	9	13	49	0.27	36	0.85	1.30 +/- 0.08	1.44 +/- 0.79	68	3	66	0	(0,0)
East Kilbride	25053	04443	S	0	8	11	43	1.69	33	0.78	1.25 +/- 0.10	1.01 +/- 0.91	56	0	55	0	(0,0)
East Kilbride	04443	25053	S	0	8	11	43	1.36	33	0.78	1.25 +/- 0.10	1.01 +/- 0.91	56	0	55	0	(0,0)
East Kilbride	04443	04443	S	0	8	11	43	0.24	33	0.75	1.3 +/- 0.11	-0.18 +/- 1.00	59	0	59	0	(0,0)
East Kilbride	25053	25053	W	0	11	14	77	0.61	54	0.90	1.01 +/- 0.04	3.45 +/- 0.53	21	11	17	4	(0,0)
East Kilbride	25053	04443	W	0	11	13	77	2.07	54	0.92	1.00 +/- 0.04	2.58 +/- 0.46	14	11	11	4	(0,0)
East Kilbride	04443	25053	W	0	11	13	77	1.25	54	0.92	1.00 +/- 0.04	2.58 +/- 0.46	14	11	11	4	(0,0)
East Kilbride	04443	04443	W	0	11	12	77	0.61	54	0.92	0.99 +/- 0.04	1.58 +/- 0.47	10	11	8	4	(0,0)
Teddington	24431	24431	S	0	20	21	83	0.77	50	0.90	0.93 +/- 0.04	1.91 +/- 0.97	16	30	14	20	(2,0)
Teddington	24431	24447	S	0	21	20	80	1.08	49	0.91	0.90 +/- 0.04	2.03 +/- 0.94	18	31	17	20	(2,0)
Teddington	24447	24431	S	0	21	20	80	1.47	49	0.91	0.90 +/- 0.04	2.03 +/- 0.94	18	31	17	20	(2,0)
Teddington	24447	24447	S	0	20	20	82	0.88	50	0.90	0.87 +/- 0.04	2.32 +/- 0.94	21	30	21	20	(2,0)
Teddington	24431	24431	W	0	25	23	122	0.32	29	0.96	0.92 +/- 0.04	-0.47 +/- 1.02	21	55	19	45	(0,0)
Teddington	24431	24447	W	0	26	24	85	0.67	20	0.96	0.96 +/- 0.04	-1.25 +/- 1.21	18	60	16	50	(0,0)
Teddington	24447	24431	W	0	26	24	85	0.54	20	0.96	0.96 +/- 0.04	-1.25 +/- 1.21	18	60	16	50	(0,0)
Teddington	24447	24447	W	0	26	24	85	0.35	20	0.96	0.95 +/- 0.05	-1.26 +/- 1.27	19	60	17	50	(0,0)
All Data	-	-		0	18	20	1746	0.93	1362	0.92	0.96 +/- 0.01	2.24 +/- 0.15	14	29	11	19	-
Data <20 µg m-3	-	-		0	13	14	1360	0.93	970	0.69	1.01 +/- 0.02	1.68 +/- 0.24	16	-	-	-	-
Data >20 µg m-3	-	-		0	32	32	623	0.98	392	0.86	1 +/- 0.02	0.79 +/- 0.64	19	-	-	-	-
Data <25 µg m-3	-	-		0	14	16	1504	0.92	1101	0.76	1.03 +/- 0.02	1.36 +/- 0.22	-	-	16	-	-
Data >25 µg m-3	-	-		0	36	36	432	0.96	261	0.82	1.04 +/- 0.03	-1.31 +/- 1.02	-	-	16	-	-

Table 11: Summary of experiment 1 for the original model parameterisation (TEOM – 2 FDMS Purge), the comparison between the model (using the TEOM and FDMS purge measurements from the equivalence sites) and the PM₁₀ KFG reference method. Season is denoted as Summer (S) and Winter (W).

8.1.1 The orthogonal regression model parameterisation

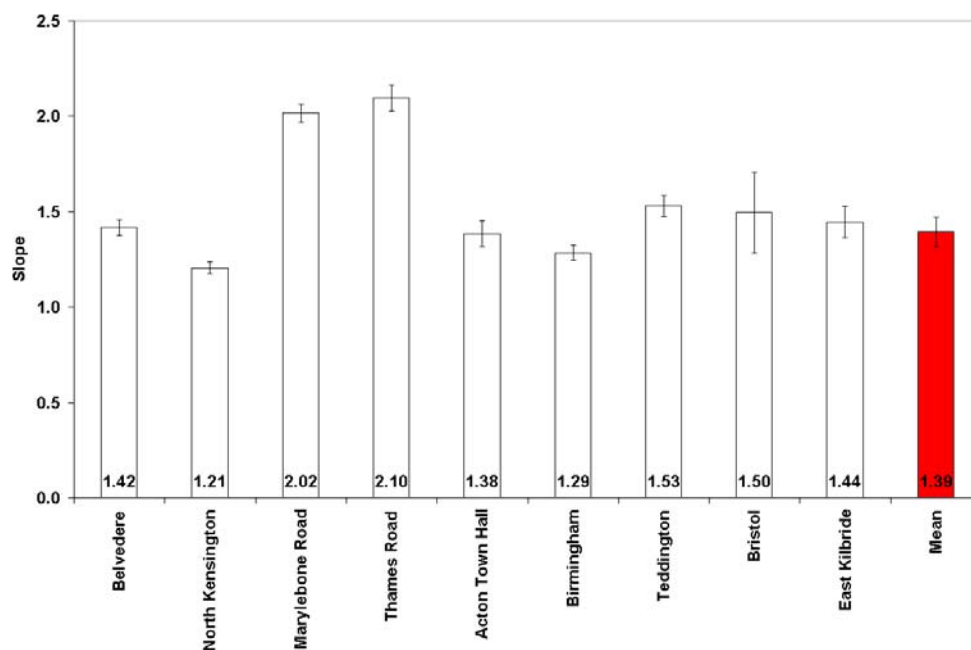


Figure 24: Slope of the orthogonal regression analysis between the FDMS purge measurements (x) and (TEOM-FDMS Base) measurements (y) from each of the sites in London and those in the UK Equivalence Programme. Error bars are the calculated uncertainty in the intercept. The UK Equivalence Programme sites are shown as the mean of the potential combinations of the paired instruments. The mean excludes Marylebone Road and Thames Road.

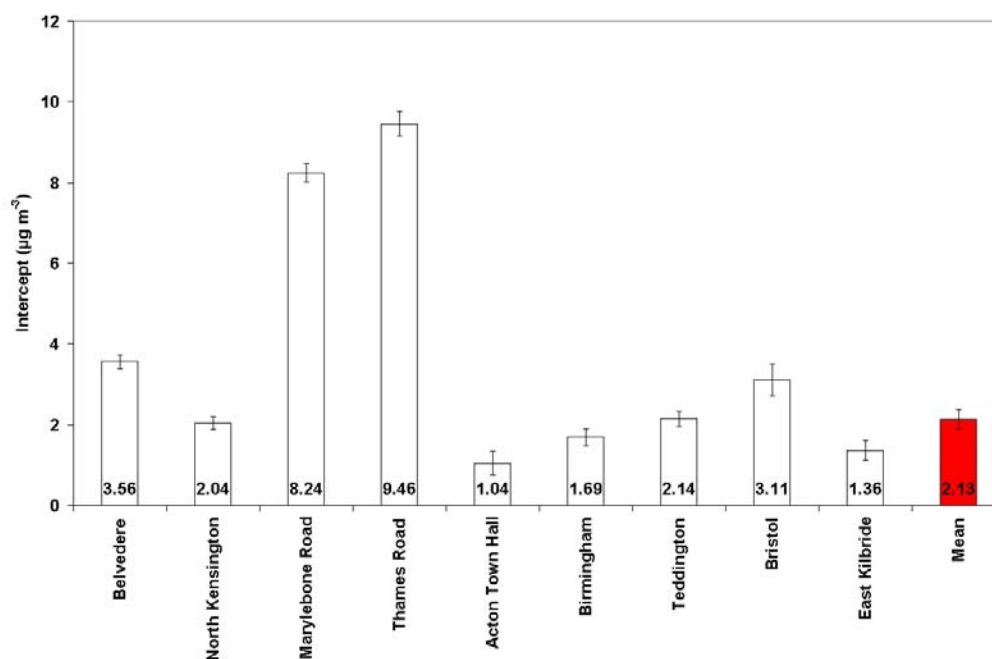


Figure 25: Intercept of the orthogonal regression analysis between the FDMS purge measurements (x) and (TEOM-FDMS Base) measurements (y) from each of the sites in London and those in the UK Equivalence Programme. Error bars are the calculated uncertainty in the intercept. The UK Equivalence Programme sites are shown as the mean of the potential combinations of the paired instruments. The mean excludes Marylebone Road and Thames Road.

Dataset				Distance Between Sites	Reference Mean	Modelled Mean	24 hour		Orthogonal Regression			Annual Limit Value (40 µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)			
Reference Site	FDMS 1 Serial #	FDMS 2 Serial #	Season				n _{bs}	u _{bs}	n _{c,s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	W _{CM} (%)	%> 20 µg m ⁻³	W _{CM} (%)	%> 25 µg m ⁻³	(n _{ES} , n _{EC})
Birmingham	04443	04443	S	0	18	18	60	0.38	39	0.96	1.11 +/- 0.04	-1.10 +/- 0.77	19	18	19	15	(1,1)
Birmingham	04443	25053	S	0	18	19	60	1.33	39	0.96	1.11 +/- 0.04	-0.21 +/- 0.8	24	18	23	15	(1,2)
Birmingham	25053	04443	S	0	18	19	60	1.63	39	0.96	1.11 +/- 0.04	-0.21 +/- 0.8	24	18	23	15	(1,2)
Birmingham	25053	25053	S	0	18	20	69	0.38	41	0.94	1.12 +/- 0.04	0.89 +/- 0.88	31	20	29	15	(1,2)
Birmingham	04443	04443	W	0	19	17	84	0.15	47	0.89	1.12 +/- 0.06	-3.43 +/- 1.13	16	32	16	15	(1,1)
Birmingham	04443	25053	W	0	19	17	84	1.03	47	0.89	1.12 +/- 0.05	-3.81 +/- 1.11	15	32	15	15	(1,1)
Birmingham	25053	04443	W	0	19	17	84	1.04	47	0.89	1.12 +/- 0.05	-3.81 +/- 1.11	15	32	15	15	(1,1)
Birmingham	25053	25053	W	0	21	19	106	0.17	59	0.93	1.09 +/- 0.04	-3.70 +/- 0.86	13	39	11	25	(1,1)
Bristol	24431	24431	S	0	22	25	44	0.38	36	0.95	1.18 +/- 0.05	-0.56 +/- 1.08	35	39	35	25	(0,1)
Bristol	24431	24447	S	0	22	24	44	1.42	36	0.95	1.19 +/- 0.04	-1.76 +/- 1.06	31	39	32	25	(0,1)
Bristol	24447	24431	S	0	22	24	44	1.54	36	0.95	1.19 +/- 0.04	-1.76 +/- 1.06	31	39	32	25	(0,1)
Bristol	24447	24447	S	0	22	23	44	0.38	36	0.95	1.2 +/- 0.05	-2.98 +/- 1.07	28	39	30	25	(0,1)
Bristol	24431	24431	W	0	22	25	84	0.53	55	0.94	1.05 +/- 0.04	1.77 +/- 0.9	25	45	21	33	(2,2)
Bristol	24431	24447	W	0	22	25	79	1.32	55	0.94	1.06 +/- 0.03	1.01 +/- 0.86	22	45	19	33	(2,2)
Bristol	24447	24431	W	0	22	25	79	1.22	55	0.94	1.06 +/- 0.03	1.01 +/- 0.86	22	45	19	33	(2,2)
Bristol	24447	24447	W	0	23	25	81	0.54	57	0.95	1.05 +/- 0.03	0.33 +/- 0.84	18	47	16	35	(2,2)
East Kilbride	25053	25053	S	0	9	12	49	0.27	36	0.83	1.44 +/- 0.1	-0.72 +/- 0.94	85	3	86	0	(0,0)
East Kilbride	25053	04443	S	0	8	10	43	1.99	33	0.73	1.38 +/- 0.12	-1.19 +/- 1.07	70	0	71	0	(0,0)
East Kilbride	04443	25053	S	0	8	10	43	1.65	33	0.73	1.38 +/- 0.12	-1.19 +/- 1.07	70	0	71	0	(0,0)
East Kilbride	04443	04443	S	0	8	9	43	0.24	33	0.69	1.45 +/- 0.14	-2.78 +/- 1.2	77	0	79	0	(0,0)
East Kilbride	25053	25053	W	0	11	13	77	0.61	54	0.89	1.1 +/- 0.05	1.53 +/- 0.61	29	11	27	4	(0,0)
East Kilbride	25053	04443	W	0	11	12	77	2.37	54	0.91	1.08 +/- 0.04	0.49 +/- 0.54	20	11	19	4	(0,0)
East Kilbride	04443	25053	W	0	11	12	77	1.55	54	0.91	1.08 +/- 0.04	0.49 +/- 0.54	20	11	19	4	(0,0)
East Kilbride	04443	04443	W	0	11	11	77	0.61	54	0.91	1.08 +/- 0.05	-0.73 +/- 0.56	16	11	15	4	(0,0)
Teddington	24431	24431	S	0	20	20	83	0.77	50	0.92	1.03 +/- 0.04	-0.79 +/- 0.99	16	30	13	20	(2,0)
Teddington	24431	24447	S	0	21	20	80	1.23	49	0.92	0.99 +/- 0.04	-0.65 +/- 0.94	15	31	12	20	(2,0)
Teddington	24447	24431	S	0	21	20	80	1.65	49	0.92	0.99 +/- 0.04	-0.65 +/- 0.94	15	31	12	20	(2,0)
Teddington	24447	24447	S	0	20	19	82	0.88	50	0.91	0.96 +/- 0.04	-0.35 +/- 0.94	18	30	15	20	(2,0)
Teddington	24431	24431	W	0	25	22	122	0.32	29	0.96	1.00 +/- 0.04	-3.06 +/- 1.07	18	55	14	45	(0,0)
Teddington	24431	24447	W	0	26	23	85	0.76	20	0.97	1.04 +/- 0.04	-4.02 +/- 1.26	15	60	11	50	(0,0)
Teddington	24447	24431	W	0	26	23	85	0.62	20	0.97	1.04 +/- 0.04	-4.02 +/- 1.26	15	60	11	50	(0,0)
Teddington	24447	24447	W	0	26	23	85	0.35	20	0.96	1.04 +/- 0.05	-4.04 +/- 1.34	17	60	13	50	(0,0)
All Data	-	-	-	0	18	19	1746	1.07	1362	0.92	1.05 +/- 0.01	-0.19 +/- 0.17	18	29	16	19	-
Data <20 µg m ⁻³	-	-	-	0	13	13	1360	1.09	970	0.65	1.1 +/- 0.02	-0.58 +/- 0.27	21	-	-	-	-
Data >20 µg m ⁻³	-	-	-	0	32	32	623	1.13	392	0.86	1.13 +/- 0.02	-3.07 +/- 0.7	23	-	-	-	-
Data <25 µg m ⁻³	-	-	-	0	14	14	1504	1.07	1101	0.73	1.11 +/- 0.02	-0.86 +/- 0.25	-	-	22	-	-
Data >25 µg m ⁻³	-	-	-	0	36	37	432	1.11	261	0.83	1.18 +/- 0.03	-5.76 +/- 1.13	-	-	22	-	-

Table 12: Summary of experiment 1 for the orthogonal regression model parameterisation (TEOM-2.39 FDMS Purge + 2.13 µg m⁻³), the comparison between the model (using the TEOM and FDMS purge measurements from the equivalence sites) and the PM₁₀ KFG reference method. Season is denoted as Summer (S) and Winter (W).

8.2 Model Code

```

SET nocount on
Declare @RefSite1 varchar(4),@RefSite2 varchar(4),@CandSite1 varchar(4),@CandSite2 varchar(4),@PurgeSite1
varchar(4),@PurgeSite2 varchar(4)
Declare @RefSite varchar(6),@CandSite varchar(12),@FullSite varchar(18)
DEclare @DailyLV Real,@AnnualLV Real, @Coverage_k Real
Declare @Season varchar(6)
Declare @Factor real,@Offset real
--Select @Season='All'
--Select @Factor=2
--Select @Offset=0
Select @DailyLV=50
Select @AnnualLV=40
Select @Coverage_k=2
DECLARE @Ref_Ubs Real,@Cand_Ubs Real,@N_Ref INTEGER, @N_Cand INTEGER
DECLARE @RefMean_xbar Real,@CandMean_ybar Real,@Nc_s Real
Declare @Ref_Percent20 Real, @Ref_Percent25 Real
Declare @Ref_D_LV_Ex Integer, @Cand_D_LV_Ex Integer
Declare @Sxx Real,@Syy Real,@Sxy Real,@Slope Real,@Intercept Real, @U_Slope Real, @U_Intercept Real
DECLARE @R2 real
DECLARE @RSS real
DECLARE @Uc_s_Y_Daily Real,@Uc_s_Y_Annual Real
DECLARE @Wc_CM_Y_Daily Real,@Wc_CM_Y_Annual Real
DECLARE @W_CM_Y_Daily Real,@W_CM_Y_Annual Real
DECLARE @Distance Real
/*****
START OF TD & BI Section needed because of the varying Gravimetric Filter change times
*****/
Declare Matrix_Cursor_TDBI CURSOR for
Select GravimetricSite1,GravimetricSite2,TEOMSite1,TEOMSite2,PurgeSite1,PurgeSite2,Season,Factor,Offset
FROM FDMSEquivalence_10am
WHERE GravimetricSite1 IN ('TD1','TD2','BI1','BI2')
AND GravimetricSite2 IN ('TD1','TD2','BI1','BI2')
Open Matrix_Cursor_TDBI
FETCH NEXT FROM Matrix_Cursor_TDBI INTO
@RefSite1,@RefSite2,@CandSite1,@CandSite2,@PurgeSite1,@PurgeSite2,@Season,@Factor,@Offset
While (@@fetch_status<>-1)
Begin
SET @Ref_Ubs = NULL
SET @Cand_Ubs = NULL
SET @N_Ref = NULL
SET @N_Cand = NULL
SET @RefMean_xbar = NULL
SET @CandMean_ybar = NULL
SET @Nc_s = NULL
SET @Ref_Percent20 = NULL
SET @Ref_Percent25 = NULL
SET @Ref_D_LV_Ex = NULL
SET @Cand_D_LV_Ex = NULL
SET @Sxx = NULL
SET @Syy = NULL
SET @Sxy = NULL
SET @Slope = NULL
SET @Intercept = NULL
SET @U_Slope = NULL
SET @U_Intercept = NULL
SET @R2 = NULL
SET @RSS = NULL
SET @Uc_s_Y_Daily = NULL
SET @Uc_s_Y_Annual = NULL
SET @Wc_CM_Y_Daily = NULL
SET @Wc_CM_Y_Annual = NULL
SET @W_CM_Y_Daily = NULL
SET @W_CM_Y_Annual = NULL
SET @Distance = NULL
Select @RefSite1='TD1'
Select @RefSite2='TD2'
Select @CandSite1='TD3'
Select @CandSite2='TD4'
Select @PurgeSite1='TD5'
Select @PurgeSite2='TD6'
Select @RefSite='TD' ---Don't Need these if done one at a time
Select @CandSite='TD' ---Don't Need these if done one at a time
Select @FullSite='TD' ---Don't Need these if done one at a time

```

```

/****Build time adjusted tables*****/
/****DUST**/
SELECT SiteCode, dbo.StartOf('day',
CASE
WHEN @RefSite1 Like 'TD%' AND DateTime<'21-nov-2005 15:00' THEN DATEADD(hh,-DATEPART(hh,'21-nov-2005
15:00'),DateTime)
WHEN @RefSite1 Like 'TD%' AND DateTime>='22-nov-2005 10:00' THEN DATEADD(hh,-DATEPART(hh,'22-nov-2005
10:00'),DateTime)
WHEN @RefSite1 Like 'TD%' AND DateTime>='21-nov-2005 15:00' AND DateTime<'22-nov-2005 10:00' THEN
dbo.StartOf('day','21-nov-2005 15:00')
WHEN @RefSite1 Like 'BI%' AND DateTime<'10-feb-2005 10:00' THEN DATEADD(hh,-DATEPART(hh,'10-feb-2005
10:00'),DateTime)
WHEN @RefSite1 Like 'BI%' AND DateTime>='11-feb-2005 11:00' THEN DATEADD(hh,-DATEPART(hh,'11-feb-2005
11:00'),DateTime)
WHEN @RefSite1 Like 'BI%' AND DateTime>='10-feb-2005 10:00' AND DateTime<'11-feb-2005 11:00' THEN
dbo.StartOf('day','10-feb-2005 10:00')
END
) AS DateTime, Mean, 'V' AS Status, Conversion,
MeanScaled
INTO #DUSTatp_hourly_TDBI_adjusted
FROM dbo.DUSTatp_hourly
WHERE Status IN ('V','v','')
AND SiteCode IN (@RefSite1,@RefSite2,@CandSite1,@CandSite2)
AND DateTime >='1-jan-2004'
AND DateTime<'1-jan-2006'
Order By SiteCode,DateTime
SELECT SiteCode, dbo.StartOf('day', MIN(DateTime)) AS DateTime, AVG(MeanScaled) AS MeanScaled
INTO #DUSTatp_daily_TDBI_adjusted
FROM #DUSTatp_hourly_TDBI_adjusted
WHERE (Status = '') OR (Status = 'V') OR (Status = 'v')
GROUP BY SiteCode, DATEPART(dd, DateTime), DATEPART(mm, DateTime), DATEPART(yy, DateTime)
HAVING (COUNT(*) >21) --90% data capture
Order By SiteCode,DateTime
/****Purge****/
SELECT SiteCode, dbo.StartOf('day',
CASE
WHEN @RefSite1 Like 'TD%' AND DateTime<'21-nov-2005 15:00' THEN DATEADD(hh,-DATEPART(hh,'21-nov-2005
15:00'),DateTime)
WHEN @RefSite1 Like 'TD%' AND DateTime>='22-nov-2005 10:00' THEN DATEADD(hh,-DATEPART(hh,'22-nov-2005
10:00'),DateTime)
WHEN @RefSite1 Like 'TD%' AND DateTime>='21-nov-2005 15:00' AND DateTime<'22-nov-2005 10:00' THEN
dbo.StartOf('day','21-nov-2005 15:00')
WHEN @RefSite1 Like 'BI%' AND DateTime<'10-feb-2005 10:00' THEN DATEADD(hh,-DATEPART(hh,'10-feb-2005
10:00'),DateTime)
WHEN @RefSite1 Like 'BI%' AND DateTime>='11-feb-2005 11:00' THEN DATEADD(hh,-DATEPART(hh,'11-feb-2005
11:00'),DateTime)
WHEN @RefSite1 Like 'BI%' AND DateTime>='10-feb-2005 10:00' AND DateTime<'11-feb-2005 11:00' THEN
dbo.StartOf('day','10-feb-2005 10:00')
END
) AS DateTime, Mean, 'V' AS Status, Conversion,
MeanScaled
INTO #PMFRatp_hourly_TDBI_adjusted
FROM dbo.PMFRatp_hourly
WHERE Status IN ('V','v','')
AND SiteCode IN (@PurgeSite1,@PurgeSite2)
AND DateTime >='1-jan-2004'
AND DateTime<'1-jan-2006'
Order By SiteCode,DateTime
SELECT SiteCode, dbo.StartOf('day', MIN(DateTime)) AS DateTime, AVG(MeanScaled) AS MeanScaled
INTO #PMFRatp_daily_TDBI_adjusted
FROM #PMFRatp_hourly_TDBI_adjusted
WHERE (Status = '') OR (Status = 'V') OR (Status = 'v')
GROUP BY SiteCode, DATEPART(dd, DateTime), DATEPART(mm, DateTime), DATEPART(yy, DateTime)
HAVING (COUNT(*) >21) --90% data capture
Order By SiteCode,DateTime
SELECT SiteCode, dbo.StartOf('day',
CASE
WHEN @RefSite1 Like 'TD%' AND DateTime<'21-nov-2005 15:00' THEN DATEADD(hh,-DATEPART(hh,'21-nov-2005
15:00'),DateTime)
WHEN @RefSite1 Like 'TD%' AND DateTime>='22-nov-2005 10:00' THEN DATEADD(hh,-DATEPART(hh,'22-nov-2005
10:00'),DateTime)
WHEN @RefSite1 Like 'TD%' AND DateTime>='21-nov-2005 15:00' AND DateTime<'22-nov-2005 10:00' THEN
dbo.StartOf('day','21-nov-2005 15:00')
WHEN @RefSite1 Like 'BI%' AND DateTime<'10-feb-2005 10:00' THEN DATEADD(hh,-DATEPART(hh,'10-feb-2005
10:00'),DateTime)

```

```

WHEN @RefSite1 Like 'BI%' AND DateTime>='11-feb-2005 11:00' THEN DATEADD(hh,-DATEPART(hh,'11-feb-2005
11:00'),DateTime)
WHEN @RefSite1 Like 'BI%' AND DateTime>='10-feb-2005 10:00' AND DateTime<'11-feb-2005 11:00' THEN
dbo.StartOf('day','10-feb-2005 10:00')
END
) AS DateTime, Mean, 'V' AS Status, Conversion, MeanScaled
INTO #NO3atp_hourly_TDBI_adjusted
FROM dbo.NO3atp_hourly
WHERE Status IN ('V','v',' ')
AND SiteCode IN (@PurgeSite1, @PurgeSite1)
AND DateTime >='1-jan-2004'
AND DateTime<'1-jan-2006'
Order By SiteCode,DateTime
SELECT SiteCode, dbo.StartOf('day', MIN(DateTime)) AS DateTime, AVG(MeanScaled) AS MeanScaled
INTO #NO3atp_daily_TDBI_adjusted
FROM #NO3atp_hourly_TDBI_adjusted
WHERE (Status = '') OR (Status = 'V') OR (Status = 'v')
GROUP BY SiteCode, DATEPART(dd, DateTime), DATEPART(mm, DateTime), DATEPART(yy, DateTime)
HAVING (COUNT(*) >21) --90% data capture
Order By SiteCode,DateTime

/*****End of time adjusted table building*****/
/*****Build Purge Adjustment table*****/
---There is no check here if there was both FDMS and NO3 at the same site, but should never occur
Create Table #TDBI_Purge (SiteCode VARCHAR(4), DateTime SMALLDATETIME, MeanScaled Real)
Insert into #TDBI_Purge
SELECT SiteCode,DateTime,-MeanScaled---Since we are using purge to increase TEOM value it needs to be +ve
FROM #PMFRatp_daily_TDBI_adjusted
WHERE (SiteCode = @PurgeSite1 OR SiteCode = @PurgeSite2)
AND DateTime>='1-jan-2004' AND DateTime<'1-jan-2006'
AND ((UPPER(@Season)='WINTER' AND DATEPART(Quarter,DateTime) IN (1,4)) OR
(UPPER(@Season)='SUMMER' AND DATEPART(Quarter,DateTime) IN (2,3)) OR
UPPER(@Season)='ALL')
Order BY DateTime
Insert into #TDBI_Purge
SELECT SiteCode,DateTime,MeanScaled
FROM #NO3atp_daily_TDBI_adjusted
WHERE (SiteCode = @PurgeSite1 OR SiteCode = @PurgeSite2)
AND DateTime>='1-jan-2004' AND DateTime<'1-jan-2006'
AND ((UPPER(@Season)='WINTER' AND DATEPART(Quarter,DateTime) IN (1,4)) OR
(UPPER(@Season)='SUMMER' AND DATEPART(Quarter,DateTime) IN (2,3)) OR
UPPER(@Season)='ALL')
Order BY DateTime
/**Select Reference and Candidate data sets Candidate is adjusted with purge. This will only select the data where
there are readings from both samplers*****/
Select @RefSite 'SiteCode',d1.DateTime,
d1.MeanScaled 'Sampler1MeanScaled',
d2.MeanScaled 'Sampler2MeanScaled'
into #TDBI_Ref_Core_DataSet
From #DUSTatp_daily_TDBI_adjusted d1 join #DUSTatp_daily_TDBI_adjusted d2 on d1.DateTime=d2.DateTime
WHERE d1.SiteCode=@RefSite1
AND d2.SiteCode=@RefSite2
AND d1.DateTime>='1-jan-2004' AND d2.DateTime<'1-jan-2006'
AND ((UPPER(@Season)='WINTER' AND DATEPART(Quarter,d1.DateTime) IN (1,4)) OR
(UPPER(@Season)='SUMMER' AND DATEPART(Quarter,d1.DateTime) IN (2,3)) OR
UPPER(@Season)='ALL')
Order By d1.DateTime
Select @CandSite 'SiteCode',d1.DateTime,
d1.MeanScaled+(@Factor*p1.MeanScaled)-@Offset 'Sampler1MeanScaled', ---
Dust1+(Factor*Purge1)-Offset
d2.MeanScaled+(@Factor*p2.MeanScaled)-@Offset 'Sampler2MeanScaled' ---
Dust2+(Factor*Purge2)-Offset
into #TDBI_Cand_Core_DataSet
From #DUSTatp_daily_TDBI_adjusted d1 join #DUSTatp_daily_TDBI_adjusted d2 on d1.DateTime=d2.DateTime
join #TDBI_Purge p1 on d1.DateTime=p1.DateTime
join #TDBI_Purge p2 on d2.DateTime=p2.DateTime
WHERE d1.SiteCode=@CandSite1
AND d2.SiteCode=@CandSite2
AND p1.SiteCode=@PurgeSite1
AND p2.SiteCode=@PurgeSite2
AND d1.DateTime>='1-jan-2004' AND d1.DateTime<'1-jan-2006'
AND ((UPPER(@Season)='WINTER' AND DATEPART(Quarter,d1.DateTime) IN (1,4)) OR
(UPPER(@Season)='SUMMER' AND DATEPART(Quarter,d1.DateTime) IN (2,3)) OR
UPPER(@Season)='ALL')
Order By d1.DateTime
/*****TEST OUTPUT dataset*****/

```

```

Select      r.Sampler1MeanScaled      'RM1',r.Sampler2MeanScaled      'RM2',c.Sampler1MeanScaled
'CM1',c.Sampler2MeanScaled 'CM2'
FROM #Ref_Core_DataSet r join #Cand_Core_DataSet c
on r.DateTime=c.DateTime
**/
/*****Intersampler results*****/
Select SiteCode,DateTime,
SQUARE(Sampler1MeanScaled-Sampler2MeanScaled) 'SquareofSamplerDiff',
(Sampler1MeanScaled+Sampler2MeanScaled)/2 'SamplerMean'
into #TDBI_Ref_InterSampler_DataSet
From #TDBI_Ref_Core_DataSet
Select SiteCode,DateTime,
SQUARE(Sampler1MeanScaled-Sampler2MeanScaled) 'SquareofSamplerDiff',
(Sampler1MeanScaled+Sampler2MeanScaled)/2 'SamplerMean'
into #TDBI_Cand_InterSampler_DataSet
From #TDBI_Cand_Core_DataSet
/*****Between Sampler Uncertainty*****/
SELECT @N_Ref= COUNT(*) FROM #TDBI_Ref_InterSampler_DataSet
SELECT @N_Cand= COUNT(*) FROM #TDBI_Cand_InterSampler_DataSet
IF @RefSite1<> @RefSite2 ---If 2 samplers calculate
BEGIN
Select @Ref_Ubs=
SQRT(SUM(SquareofSamplerDiff)/(2*@N_Ref))
FROM #TDBI_Ref_InterSampler_DataSet
END
ELSE ---If 1 sampler then load given value
BEGIN
Select @Ref_Ubs=ReferenceUncertainty FROM FDMSEquivalence_10am
WHERE @RefSite1=GravimetricSite1 AND
@RefSite2=GravimetricSite2 AND
@CandSite1=TEOMSite1 AND
@CandSite2=TEOMSite2 AND
@PurgeSite1=PurgeSite1 AND
@PurgeSite2=PurgeSite2
END
--Select '@Ref_Ubs',@Ref_Ubs
Select @Cand_Ubs=
SQRT(SUM(SquareofSamplerDiff)/(2*@N_Cand))
FROM #TDBI_Cand_InterSampler_DataSet
--Select '@Cand_Ubs',@Cand_Ubs
/*****Join Reference and Candidate results into one data set so only matching results*****/
Select R.SiteCode,R.DateTime,'Ref_x'=R.SamplerMean, 'Cand_y'=C.SamplerMean
into #TDBI_BothSampler_DataSet
From #TDBI_Ref_InterSampler_DataSet R join #TDBI_Cand_InterSampler_DataSet C
on R.DateTime=C.DateTime
IF (SELECT COUNT(*) FROM #TDBI_BothSampler_DataSet)=0 GOTO NextRowTDBI
/*****Data Set Averages xbar ybar Nc-s*****/
Select @RefMean_xbar=AVG(Ref_x)
From #TDBI_BothSampler_DataSet
--Select '@RefMean_xbar',@RefMean_xbar
Select @CandMean_ybar=AVG(Cand_y)
From #TDBI_BothSampler_DataSet
--Select '@CandMean_ybar',@CandMean_ybar
Select @Nc_s= count(*)
From #TDBI_BothSampler_DataSet
--Select '@Nc_s',@Nc_s
/*****Counts for output*****/
SELECT @Ref_D_LV_Ex=COUNT(*) FROM #TDBI_BothSampler_DataSet WHERE Ref_x>=@DailyLV
SELECT @Cand_D_LV_Ex=COUNT(*) FROM #TDBI_BothSampler_DataSet WHERE Cand_y>=@DailyLV
SELECT @Ref_Percent20=(COUNT(*)*100)/@Nc_s FROM #TDBI_BothSampler_DataSet WHERE Ref_x>=20
SELECT @Ref_Percent25=(COUNT(*)*100)/@Nc_s FROM #TDBI_BothSampler_DataSet WHERE Ref_x>=25
/*****Stats for Slope and Intercept*****/
Select
@Sxx= SUM(SQUARE(Ref_x-@RefMean_xbar)),
@Syy= SUM(SQUARE(Cand_y-@CandMean_ybar)),
@Sxy= SUM((Ref_x-@RefMean_xbar)*(Cand_y-@CandMean_ybar))
FROM #TDBI_BothSampler_DataSet
Select @Slope=(@Syy-@Sxx+SQRT(SQUARE(@Syy-@Sxx)+(4*SQUARE(@Sxy))))/(2*@Sxy)
--Select 'Slope',@Slope
Select @Intercept=@CandMean_ybar-(@Slope*@RefMean_xbar)
--Select 'Intercept',@Intercept
--SELECT @Sxx,@Syy,@Sxy,@Nc_s
SELECT @U_Slope=SQRT((@Syy-(SQUARE(@Sxy)/@Sxx))/((@Nc_s-2)*@Sxx))
--Select 'Slope Uncertainty',@U_Slope
Select @U_Intercept=SQRT(SQUARE(@U_Slope)*(SUM(SQUARE(Ref_x))/@Nc_s))
FROM #TDBI_BothSampler_DataSet

```

```

--Select 'Intercept Uncertainty', @U_Intercept
/******
r2 *****/
Select @R2=SQUARE(
( (@Nc_s*SUM(Ref_x*Cand_y))-(SUM(Ref_x)*SUM(Cand_y)) )/
SQRT( (@Nc_s*SUM(SQUARE(Ref_x))-SQUARE(SUM(Ref_x))) *((@Nc_s*SUM(SQUARE(Cand_y)))-
SQUARE(SUM(Cand_y))) )
)FROM #TDBI_BothSampler_DataSet
--Select '@R2',@R2
/******
RSS *****/
SELECT @RSS= SUM( SQUARE(Cand_y-@Intercept-(@Slope*Ref_x)) )
FROM #TDBI_BothSampler_DataSet
--SELECT '@RSS',@RSS
/******
Uc_s(Y) E.C.13 *****/
SELECT @Uc_s_Y_Daily=SQRT((@RSS/(@Nc_s-2))+SQUARE(@Intercept+((@Slope-1)*@DailyLV))-
SQUARE(@Ref_Ubs))
SELECT @Uc_s_Y_Annual=SQRT(
(@RSS/(@Nc_s-2))+SQUARE(@Intercept+((@Slope-1)*@AnnualLV))-SQUARE(@Ref_Ubs))
--SELECT '@Uc_s_Y_Daily',@Uc_s_Y_Daily
--SELECT '@Uc_s_Y_Annual',@Uc_s_Y_Annual
/******
Wc_CM_Y E.C. 16 Combined uncertainty *****/
SELECT @Wc_CM_Y_Daily= 100*(@Uc_s_Y_Daily/@DailyLV)
SELECT @Wc_CM_Y_Annual= 100*(@Uc_s_Y_Annual/@AnnualLV)
--SELECT '@Wc_CM_Y_Daily',@Wc_CM_Y_Daily
--SELECT '@Wc_CM_Y_Annual',@Wc_CM_Y_Annual
/******W_CM_YE.C. 17 Expanded Uncertainty *****/
SELECT @W_CM_Y_Daily=@Coverage_k*@Wc_CM_Y_Daily
SELECT @W_CM_Y_Annual=@Coverage_k*@Wc_CM_Y_Annual
--SELECT '@W_CM_Y_Daily',@W_CM_Y_Daily
--SELECT '@W_CM_Y_Annual',@W_CM_Y_Annual
NextRowTDBI:
SELECT @Distance=
ROUND((SQRT(SQUARE(s1.os_grid_x-s2.os_grid_x)+SQUARE(s1.os_grid_y-s2.os_grid_y)))/1000,1) --'Distance In
km'
FROM site_info s1, site_info s2
WHERE s1.code=@RefSite1AND s2.code=@PurgeSite1 UPDATE FDMSEquivalence_10am
SET
GravimetricMean =@RefMean_xbar,
ModelledMean =@CandMean_ybar,
ReferenceCount=@N_Ref,
ReferenceUncertainty=@Ref_Ubs,
CandidateCount=@N_Cand,
CandidateUncertainty=@Cand_Ubs,
AllMeanCount=@Nc_s,
CorrelationCoefficient=@R2,
Slope=@Slope,
SlopeUncertainty=@U_Slope,
Intercept=@Intercept,
InterceptUncertainty=@U_Intercept,
AnnualExpandedUncertainty=@W_CM_Y_Annual,
PercentGreater20=@Ref_Percent20,
DailyExpandedUncertainty=@W_CM_Y_Daily,
PercentGreater25=@Ref_Percent25,
CandidateDailyLV=@Cand_D_LV_Ex,
ReferenceDailyLV=@Ref_D_LV_Ex,
Factor=@Factor,
Offset=@Offset,
Distance_G1P1=@Distance
WHERE GravimetricSite1=@RefSite1 AND
GravimetricSite2=@RefSite2 AND
TEOMSite1=@CandSite1 AND
TEOMSite2=@CandSite2 AND
PurgeSite1=@PurgeSite1 AND
PurgeSite2=@PurgeSite2 AND
Season=@Season
FETCH NEXT FROM Matrix_Cursor_TDBI INTO
@RefSite1,@RefSite2,@CandSite1,@CandSite2,@PurgeSite1,@PurgeSite2,@Season,@Factor,@Offset
DROP TABLE
#NO3atp_hourly_TDBI_adjusted,#NO3atp_daily_TDBI_adjusted,#PMFRatp_hourly_TDBI_adjusted,#PMFRatp_daily_T
DBI_adjusted,#DUSTatp_hourly_TDBI_adjusted,#DUSTatp_daily_TDBI_adjusted,#TDBI_Purge,#TDBI_Ref_Core_Data
Set,#TDBI_Cand_Core_DataSet,#TDBI_Ref_InterSampler_DataSet,#TDBI_Cand_InterSampler_DataSet,#TDBI_BothS
ampler_DataSet
END
CLOSE Matrix_Cursor_TDBI
DEALLOCATE Matrix_Cursor_TDBI

```

8.3 Database Testing

Daily means concentrations (starting at the time of the filter change) were extracted from the KCL database and compared to the daily mean concentrations published in the National Air Quality Archive:

http://www.airquality.co.uk/archive/reports/cat05/0607131442_UK_Equivalence_Trials_Data.xls

The results of this comparison are detailed in Table 13 and show that the KCL database agrees with the published database except for a single daily measurement which was not present in the archive dataset. On 12th April only 21 hourly measurements were available from Birmingham TEOM 25023, however 22 hours are required to reach the 90% data capture target and therefore make up a daily mean; this measurement was therefore included in the KCL database.

Site	Instrument	Serial #	Count		Mean		r ²
			Equivalence Programme (µg m ⁻³)	KCL (µg m ⁻³)	Equivalence Programme (µg m ⁻³)	KCL (µg m ⁻³)	
Birmingham	KFG	1	118	118	18.63	18.63	1.00
Birmingham	KFG	2	118	118	18.79	18.79	1.00
Bristol	KFG	1	103	103	22.51	22.51	1.00
Bristol	KFG	2	103	103	22.91	22.91	1.00
East Kilbride	KFG	1	96	96	9.65	9.65	1.00
East Kilbride	KFG	2	97	97	10.28	10.28	1.00
Teddington	KFG	1	106	106	21.68	21.68	1.00
Teddington	KFG	2	106	106	13.31	13.31	1.00
Birmingham	TEOM	25019	192	192	13.02	13.02	1.00
Birmingham	TEOM	25023	215	214	18.77	18.77	1.00
Bristol	TEOM	25018	147	147	18.42	18.42	1.00
Bristol	TEOM	25025	145	145	8.29	8.29	1.00
East Kilbride	TEOM	25019	133	133	7.80	7.80	1.00
East Kilbride	TEOM	25023	132	132	14.24	14.24	1.00
Teddington	TEOM	25018	201	201	14.54	14.54	1.00
Teddington	TEOM	25025	219	219	13.31	13.31	1.00
Birmingham	FDMS purge	04443	158	158	-3.60	-3.60	1.00
Birmingham	FDMS purge	25053	199	199	-3.78	-3.78	1.00
Bristol	FDMS purge	24431	153	153	-4.69	-4.69	1.00
Bristol	FDMS purge	24447	150	150	-4.02	-4.02	1.00
East Kilbride	FDMS purge	04443	143	143	-3.09	-3.09	1.00
East Kilbride	FDMS purge	25053	137	137	-1.99	-1.99	1.00
Teddington	FDMS purge	24431	213	213	-3.61	-3.61	1.00
Teddington	FDMS purge	24447	178	178	-3.43	-3.43	1.00

Table 13: Comparison of KCL and published equivalence trial daily means

8.4 Equivalence Statistical Output Testing

To test the SQL code written for this project, data was analysed manually using the equivalence spreadsheet circulated by CEN (received from Paul Quincey (NPL) on 24/12/2004) and using the KCL database code. The test was undertaken for the Bristol and East Kilbride sites for the whole equivalence trial period. The outputs are shown in Table 14.

Statistic	Bristol		East Kilbride	
	Manual Analysis	KCL Analysis	Manual Analysis	KCL Analysis
Gravimetric Mean	22.11	22.11	9.77	9.77
Modelled Mean	24.95	24.95	12.51	12.51
Reference Count	103	103	94	94
Reference Uncertainty	0.83	0.83	1.06	1.06
Candidate Count	123	123	120	120
Candidate Uncertainty	1.17	1.17	1.94	1.94
All Mean Count	91	91	87	87
Correlation Coefficient	-	0.95	-	0.90
Slope	1.00	1.00	1.02	1.02
Slope Uncertainty	0.02	0.02	0.04	0.04
Intercept	2.74	2.74	2.59	2.59
Intercept Uncertainty	0.57	0.57	0.39	0.39
Expanded Uncertainty (40 µg m ⁻³)	18.46	18.45	17.46	17.45
Percent Greater 20 µg m ⁻³	43	43	7	7
Expanded Uncertainty (50 µg m ⁻³)	14.92	14.91	14.54	14.55
Percent Greater 25 µg m ⁻³	30	30	2	2
Candidate Exceedences of Daily LV	3	3	0	0
Reference Exceedences of Daily LV	2	2	0	0

Table 14: Results of testing the KCL database code against the manual analysis using CEN supplied spreadsheet

8.5 Experiment 3i Tables

Datasey			Distance Between Sites	Reference Mean n _{bs}	Modelled Mean U _{bs}	24 hour		Orthogonal Regression				Annual Limit Value		Daily Limit Value (50 µg m ⁻³)		
Site	FDMS Seial #	Season				n _{c_s}	r ²	n _{bs}	U _{bs}	n _{c_s}	r ²	n _{bs}	U _{bs}	n _{c_s}	%> 25 µg m ⁻³	(nES / nEC)
Birmingham	04443	S	0	18	19	60	0.38	39	0.96	0.94 +/- 0.03	2.00 +/- 0.64	9	18	8	15	(1,1)
Birmingham	04443	W	0	19	18	84	0.15	47	0.91	0.96 +/- 0.04	0.20 +/- 0.87	12	32	11	15	(1,1)
Birmingham	25053	S	0	18	20	69	0.38	41	0.95	0.95 +/- 0.04	3.58 +/- 0.73	14	20	10	15	(1,2)
Birmingham	25053	W	0	21	19	106	0.17	59	0.95	0.95 +/- 0.03	-0.21 +/- 0.67	15	39	14	25	(1,1)
Bristol	24431	S	0	22	25	44	0.38	36	0.96	1.04 +/- 0.04	2.01 +/- 0.9	21	39	19	25	(0,1)
Bristol	24431	W	0	22	25	84	0.53	55	0.95	0.93 +/- 0.03	4.50 +/- 0.69	14	45	10	33	(2,2)
Bristol	24447	S	0	22	23	44	0.38	36	0.96	1.06 +/- 0.04	0.12 +/- 0.88	16	39	15	25	(0,1)
Bristol	24447	W	0	23	25	81	0.54	57	0.96	0.93 +/- 0.02	3.31 +/- 0.63	11	47	8	35	(2,2)
East Kilbride	25053	S	0	9	12	49	0.27	36	0.86	1.26 +/- 0.08	1.43 +/- 0.75	59	3	57	0	(0,0)
East Kilbride	25053	W	0	11	14	77	0.61	54	0.91	0.98 +/- 0.04	3.37 +/- 0.5	15	11	12	4	(0,0)
East Kilbride	04443	S	0	8	10	43	0.24	33	0.76	1.25 +/- 0.11	-0.07 +/- 0.93	50	0	50	0	(0,0)
East Kilbride	04443	W	0	11	12	77	0.61	54	0.93	0.97 +/- 0.04	1.62 +/- 0.44	7	11	5	4	(0,0)
Teddington	24431	S	0	20	20	83	0.77	50	0.89	0.89 +/- 0.04	2.09 +/- 0.97	19	30	18	20	(2,0)
Teddington	24431	W	0	25	22	122	0.32	29	0.95	0.90 +/- 0.04	-0.33 +/- 1.01	25	55	24	45	(0,0)
Teddington	24447	S	0	20	20	82	0.88	50	0.89	0.84 +/- 0.04	2.49 +/- 0.94	25	30	25	20	(2,0)
Teddington	24447	W	0	26	23	85	0.35	20	0.96	0.92 +/- 0.04	-1.05 +/- 1.26	23	60	21	50	(0,0)

Table 15: Subset of results from experiment 1, which used a single FDMS purge measurement rather than individual FDMS.

Dataset				Distance Between Sites Reference Mean	Modell'd Mean	24 hour		Orthogonal Regression			Annual Limit Value (40µgm ⁻³)		Daily Limit Value (50 µgm ⁻³)				
Site and Partisol Serial #	TEOM Serial #	FDMS Serial #	Season			n _{bs}	U _{bs}	n _{c,s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	WCM (%)	%> 20 µg m ⁻³	WCM (%)	%> 25 µg m ⁻³	(n _{ES} / n _{EC})	
Birmingham 21215	25019	04430	S	0	22	19	61		50	0.28	0.31 +/- 0.06	12.58 +/- 1.88	89	32	96	18	(2,1)
Birmingham 21215	25019	04430	W	0	23	21	84		41	0.93	0.98 +/- 0.04	-1.02 +/- 1.04	18	46	15	32	(3,3)
Birmingham 21215	25019	25053	S	0	22	21	70		53	0.26	0.31 +/- 0.06	14.32 +/- 1.86	81	34	89	19	(2,3)
Birmingham 21215	25019	25053	W	0	23	21	106		60	0.94	0.98 +/- 0.03	-2.01 +/- 0.79	18	52	15	35	(3,2)
Birmingham 21215	25023	04430	S	0	21	19	72		62	0.28	0.31 +/- 0.05	12.03 +/- 1.55	88	31	96	15	(2,1)
Birmingham 21215	25023	04430	W	0	23	21	84		41	0.93	0.97 +/- 0.04	-1.05 +/- 1.04	18	46	15	32	(3,3)
Birmingham 21215	25023	25053	S	0	21	20	90		65	0.27	0.31 +/- 0.05	13.66 +/- 1.55	81	32	89	15	(2,2)
Birmingham 21215	25023	25053	W	0	23	21	106		60	0.94	0.98 +/- 0.03	-2.05 +/- 0.79	19	52	16	35	(3,1)
Birmingham 21017	25019	04430	S	0	19	19	61		49	0.96	0.92 +/- 0.03	1.79 +/- 0.63	12	27	12	16	(2,1)
Birmingham 21017	25019	04430	W	0	23	21	84		45	0.93	0.95 +/- 0.04	-0.75 +/- 1.03	21	51	18	31	(3,3)
Birmingham 21017	25019	25053	S	0	19	21	70		52	0.96	0.93 +/- 0.03	3.30 +/- 0.59	9	29	7	17	(2,3)
Birmingham 21017	25019	25053	W	0	24	21	106		66	0.78	0.86 +/- 0.05	0.11 +/- 1.39	39	53	35	38	(4,2)
Birmingham 21017	25023	04430	S	0	18	19	72		61	0.95	0.90 +/- 0.03	2.20 +/- 0.57	13	21	14	13	(2,1)
Birmingham 21017	25023	04430	W	0	23	21	84		45	0.92	0.94 +/- 0.04	-0.79 +/- 1.04	22	51	19	31	(3,3)
Birmingham 21017	25023	25053	S	0	19	20	90		64	0.95	0.91 +/- 0.03	3.61 +/- 0.55	9	23	9	14	(2,2)
Birmingham 21017	25023	25053	W	0	24	21	106		66	0.78	0.85 +/- 0.05	0.14 +/- 1.39	39	53	36	38	(4,1)
Bristol 21218	25018	24431	S	0	23	24	45		45	0.83	1.04 +/- 0.07	-0.08 +/- 1.66	22	58	18	24	(1,1)
Bristol 21218	25018	24431	W	0	27	29	85		67	0.97	0.87 +/- 0.02	5.67 +/- 0.6	11	57	10	40	(7,7)
Bristol 21218	25018	24447	S	0	23	23	45		45	0.83	1.06 +/- 0.07	-2.05 +/- 1.69	21	58	17	24	(1,1)
Bristol 21218	25018	24447	W	0	28	28	82		69	0.97	0.87 +/- 0.02	4.31 +/- 0.6	11	58	12	42	(7,6)
Bristol 21218	25025	24431	S	0	24	25	47		45	0.83	1.05 +/- 0.07	-0.26 +/- 1.69	22	60	19	27	(1,2)
Bristol 21218	25025	24431	W	0	27	29	84		66	0.96	0.85 +/- 0.02	5.73 +/- 0.62	11	56	11	39	(7,6)
Bristol 21218	25025	24447	S	0	24	23	47		45	0.83	1.07 +/- 0.07	-2.19 +/- 1.73	21	60	18	27	(1,1)
Bristol 21218	25025	24447	W	0	27	28	81		68	0.97	0.86 +/- 0.02	4.38 +/- 0.61	12	57	13	41	(7,5)
Bristol 21249	25018	24431	S	0	23	24	45		44	0.83	1.04 +/- 0.07	0.25 +/- 1.68	23	57	19	30	(1,1)
Bristol 21249	25018	24431	W	0	27	29	85		68	0.97	0.87 +/- 0.02	5.52 +/- 0.54	9	56	9	41	(7,7)
Bristol 21249	25018	24447	S	0	23	23	45		44	0.83	1.07 +/- 0.07	-1.75 +/- 1.7	21	57	18	30	(1,1)
Bristol 21249	25018	24447	W	0	28	28	82		70	0.97	0.87 +/- 0.02	4.18 +/- 0.53	10	57	11	43	(7,6)
Bristol 21249	25025	24431	S	0	24	25	47		44	0.82	1.05 +/- 0.07	0.08 +/- 1.73	24	59	20	32	(1,2)
Bristol 21249	25025	24431	W	0	27	29	84		67	0.97	0.86 +/- 0.02	5.54 +/- 0.58	10	55	11	40	(7,6)
Bristol 21249	25025	24447	S	0	24	23	47		44	0.82	1.07 +/- 0.07	-1.87 +/- 1.76	22	59	18	32	(1,1)
Bristol 21249	25025	24447	W	0	27	28	81		69	0.97	0.86 +/- 0.02	4.22 +/- 0.56	11	57	13	42	(7,5)

Table 16: Summary of experiment 3i for Birmingham and Bristol, the comparison between the model (using a single TEOM and an single FDMS purge measurement from the equivalence sites) and a single PM₁₀ Partisol instrument from the equivalence sites. Season is denoted as Summer (S) and Winter (W).

Dataset				Distance Between Sites	Reference Mean	Modelled Mean	24 hour				Orthogonal Regression		Annual Limit Value (40µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)		
Reference Site and Partisol Serial #	TEOM Serial #	FDMS Serial #	Season				n _{bs}	U _{bs}	n _{c,s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	WCM (%)	% > 20 µg m ⁻³	WCM (%)	% > 25 µg m ⁻³	(n _{ES} /n _{EC})
East Kilbride 21215	25019	25053	25053	S	11	13	49	49	0.88	1.12 +/- 0.06	1.00 +/- 0.69	30	6	29	2	(0,0)	
East Kilbride 21215	25019	25053	25053	W	11	15	77	74	0.88	0.95 +/- 0.04	3.71 +/- 0.52	13	14	9	5	(0,0)	
East Kilbride 21215	25019	04430	04430	S	10	11	43	43	0.73	1.03 +/- 0.08	0.14 +/- 0.91	12	2	10	0	(0,0)	
East Kilbride 21215	25019	04430	04430	W	11	13	77	74	0.88	0.96 +/- 0.04	1.8 0 +/- 0.51	9	14	7	5	(0,0)	
East Kilbride 21215	25023	25053	25053	S	11	13	49	49	0.87	1.09 +/- 0.06	1.09 +/- 0.69	25	6	23	2	(0,0)	
East Kilbride 21215	25023	25053	25053	W	11	14	77	74	0.86	0.89 +/- 0.04	3.68 +/- 0.52	10	14	10	5	(0,0)	
East Kilbride 21215	25023	04430	04430	S	10	10	43	43	0.71	1.01 +/- 0.08	0.13 +/- 0.93	10	2	8	0	(0,0)	
East Kilbride 21215	25023	04430	04430	W	11	12	77	74	0.86	0.90 +/- 0.04	1.75 +/- 0.52	14	14	15	5	(0,0)	
East Kilbride 21017	25019	25053	25053	S	11	13	49	48	0.88	1.15 +/- 0.06	0.53 +/- 0.72	34	6	33	4	(0,0)	
East Kilbride 21017	25019	25053	25053	W	12	15	77	66	0.87	0.97 +/- 0.04	3.45 +/- 0.59	15	14	11	5	(0,0)	
East Kilbride 21017	25019	04430	04430	S	10	11	43	42	0.75	1.12 +/- 0.09	-0.87 +/- 0.97	21	2	21	0	(0,0)	
East Kilbride 21017	25019	04430	04430	W	12	13	77	66	0.87	0.98 +/- 0.04	1.60 +/- 0.59	11	14	8	5	(0,0)	
East Kilbride 21017	25023	25053	25053	S	11	13	49	48	0.88	1.12 +/- 0.06	0.63 +/- 0.72	28	6	27	4	(0,0)	
East Kilbride 21017	25023	25053	25053	W	12	14	77	66	0.85	0.92 +/- 0.04	3.40 +/- 0.59	10	14	9	5	(0,0)	
East Kilbride 21017	25023	04430	04430	S	10	11	43	42	0.73	1.10 +/- 0.09	-0.90 +/- 0.98	17	2	17	0	(0,0)	
East Kilbride 21017	25023	04430	04430	W	12	12	77	66	0.85	0.92 +/- 0.04	1.54 +/- 0.59	13	14	13	5	(0,0)	
Teddington 21218	25018	24431	24431	S	19	20	84	59	0.90	0.97 +/- 0.04	1.68 +/- 0.85	13	31	11	15	(2,0)	
Teddington 21218	25018	24431	24431	W	25	22	122	80	0.91	0.97 +/- 0.03	-1.67 +/- 0.88	21	61	18	43	(2,1)	
Teddington 21218	25018	24447	24447	S	19	20	83	60	0.90	0.91 +/- 0.04	2.21 +/- 0.8	14	32	14	17	(2,0)	
Teddington 21218	25018	24447	24447	W	26	23	85	59	0.92	0.96 +/- 0.04	-1.36 +/- 1.00	21	66	18	46	(2,1)	
Teddington 21218	25025	24431	24431	S	19	20	87	59	0.91	0.99 +/- 0.04	1.20 +/- 0.85	14	31	11	15	(2,0)	
Teddington 21218	25025	24431	24431	W	25	22	132	80	0.91	0.95 +/- 0.03	-1.59 +/- 0.87	23	61	20	43	(2,1)	
Teddington 21218	25025	24447	24447	S	19	20	87	60	0.90	0.94 +/- 0.04	1.53 +/- 0.81	13	32	12	17	(2,0)	
Teddington 21218	25025	24447	24447	W	26	23	95	59	0.92	0.94 +/- 0.04	-1.29 +/- 0.99	23	66	20	46	(2,0)	
Teddington 21249	25018	24431	24431	S	19	20	84	58	0.85	0.95 +/- 0.05	1.86 +/- 1.04	17	28	14	14	(2,0)	
Teddington 21249	25018	24431	24431	W	26	22	122	81	0.85	0.99 +/- 0.04	-3.38 +/- 1.18	27	69	22	46	(2,1)	
Teddington 21249	25018	24447	24447	S	19	19	83	59	0.86	0.89 +/- 0.05	2.34 +/- 0.95	18	29	17	15	(2,0)	
Teddington 21249	25018	24447	24447	W	26	23	85	58	0.89	0.95 +/- 0.04	-1.82 +/- 1.18	25	71	22	50	(2,1)	
Teddington 21249	25025	24431	24431	S	19	20	87	58	0.85	0.97 +/- 0.05	1.40 +/- 1.05	17	28	14	14	(2,0)	
Teddington 21249	25025	24431	24431	W	26	22	132	81	0.85	0.98 +/- 0.04	-3.29 +/- 1.17	29	69	24	46	(2,1)	
Teddington 21249	25025	24447	24447	S	19	19	87	59	0.86	0.93 +/- 0.05	1.68 +/- 0.99	17	29	15	15	(2,0)	
Teddington 21249	25025	24447	24447	W	26	23	95	58	0.89	0.93 +/- 0.04	-1.72 +/- 1.16	27	71	24	50	(2,0)	

Table 17: Summary of experiment 3i for East Kilbride and Teddington, the comparison between the model (using a single TEOM and an single FDMS purge measurement from the equivalence sites) and a single PM₁₀ Partisol instrument from the equivalence sites. Season is denoted as Summer (S) and Winter (W).

8.6 Experiment 3ii Tables

Dataset			Distance Between Sites	Reference Mean	Modelled Mean	24 hour		Orthogonal Regression			Annual Limit Value (40 µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)			
AURN Partisol Site	FDMS(Serial # where applicable)	Season				n _{bs}	u _{bs}	n _{c,s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	W _{CM} (%)	%> 20 µg m ⁻³	W _{CM} (%)	%> 25 µg m ⁻³	(n _{ES} ,n _{EC})
Belfast Centre	Belfast Centre	W	0	27	17	75	-	68	0.97	0.77 +/- 0.02	-3.42 +/- 0.51	63	59	59	41	(9,1)
Belfast Centre	Harwell	W	457	27	20	76	-	69	0.90	0.79 +/- 0.03	-1.19 +/- 0.95	52	59	49	41	(9,2)
Belfast Centre	North Kensington	W	514	26	25	71	-	65	0.84	0.82 +/- 0.04	3.48 +/- 1.28	32	58	31	40	(8,3)
Belfast Centre	Marylebone Road	W	517	30	25	52	-	45	0.85	0.73 +/- 0.04	2.64 +/- 1.51	48	64	48	51	(8,2)

Table 18: Summary of experiment 3ii for Belfast Centre during 2004, the comparison between the AURN Partisol and the model using collocated TEOM and a distant FDMS purge measurement. Season is denoted as Summer (S) and Winter (W).

Dataset			Distance Between Sites	Reference Mean	Modelled Mean	24 hour		Orthogonal Regression			Annual Limit Value (40 µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)			
AURN Partisol Site	FDMS(Serial # where applicable)	Season				n _{bs}	u _{bs}	n _{c,s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	W _{CM} (%)	%> 20 µg m ⁻³	W _{CM} (%)	%> 25 µg m ⁻³	(n _{ES} ,n _{EC})
Birmingham Centre	Harwell	W	109	23	18	60	-	60	0.92	0.77 +/- 0.03	0.47 +/- 0.74	46	48	45	23	(5,2)
Birmingham Centre	Drax Barlow	W	153	27	23	50	-	49	0.85	0.74 +/- 0.04	2.98 +/- 1.29	41	67	43	49	(3,1)
Birmingham Centre	Drax Hemingborough	S	156	20	18	96	-	91	0.83	0.91 +/- 0.04	-0.14 +/- 0.9	27	34	25	21	(3,0)
Birmingham Centre	North Kensington	S	158	21	18	70	-	42	0.83	0.77 +/- 0.05	2.00 +/- 1.23	39	45	40	31	(1,0)
Birmingham Centre	North Kensington	W	158	23	24	56	-	56	0.84	0.81 +/- 0.04	5.39 +/- 1.19	26	50	25	25	(5,3)
Birmingham Centre	Teddington 24431	W	159	26	20	42	-	41	0.89	0.67 +/- 0.04	2.43 +/- 1.07	56	51	57	39	(3,0)
Birmingham Centre	Marylebone Road	S	161	21	19	154	-	118	0.87	0.84 +/- 0.03	0.93 +/- 0.68	31	39	30	25	(4,0)
Birmingham Centre	Marylebone Road	W	161	25	22	104	-	103	0.83	0.72 +/- 0.03	4.18 +/- 0.88	41	54	43	35	(8,3)
Birmingham Centre	Millennium Village	W	172	24	19	55	-	55	0.86	0.68 +/- 0.04	2.69 +/- 0.96	52	53	54	31	(2,0)
Birmingham Centre	Belvedere	S	180	20	18	131	-	104	0.87	0.90 +/- 0.03	0.39 +/- 0.72	24	33	23	20	(3,0)
Birmingham Centre	Belvedere	W	180	24	19	42	-	41	0.77	0.68 +/- 0.05	2.78 +/- 1.42	53	54	55	39	(1,0)
Birmingham Centre	Thames Road	S	184	22	19	109	-	93	0.85	0.82 +/- 0.03	0.84 +/- 0.85	37	42	36	30	(4,0)
Birmingham Centre	Thames Road	W	184	25	21	62	-	62	0.85	0.69 +/- 0.04	3.58 +/- 0.98	48	53	50	35	(3,0)
Birmingham Centre	Belfast Centre	W	356	23	15	51	-	51	0.88	0.62 +/- 0.03	0.80 +/- 0.84	73	49	73	22	(4,0)

Table 19: Summary of experiment 3ii for Birmingham Centre during 2004, the comparison between the AURN Partisol and the model using collocated TEOM and a distant FDMS purge measurement. Season is denoted as Summer (S) and Winter (W).

Dataset			Distance Between Sites	Reference Mean	Modelled Mean	24 hour			Orthogonal Regression			Annual Limit Value (40 µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)		
AURN Partisol Site	FDMS(Serial # where applicable)	Season				n _{bs}	u _{bs}	n _{c_s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	W _{CM} (%)	%> 20 µg m ⁻³	W _{CM} (%)	%> 25 µg m ⁻³	(n _{ES} ,n _{EC})
Birmingham Centre	Birmingham 25053	S	3	30	24	71	-	49	0.86	0.80 +/- 0.04	0.12 +/- 1.4	43	88	42	63	(1,1)
Birmingham Centre	Bristol 24431	W	124	29	24	59	-	58	0.87	0.76 +/- 0.04	2.27 +/- 1.24	42	67	42	53	(5,4)
Birmingham Centre	Bristol 24447	W	124	29	22	56	-	55	0.93	0.72 +/- 0.03	1.57 +/- 0.9	51	65	52	51	(5,2)
Birmingham Centre	Drax Barlow	S	153	26	20	124	-	88	0.78	0.69 +/- 0.04	1.51 +/- 1.02	56	70	57	48	(1,1)
Birmingham Centre	Drax Barlow	W	153	32	23	108	-	75	0.78	0.67 +/- 0.04	1.16 +/- 1.33	63	87	63	75	(6,1)
Birmingham Centre	Drax Hemingborough	S	156	27	22	119	-	95	0.79	0.80 +/- 0.04	0.24 +/- 1.14	43	73	42	52	(2,2)
Birmingham Centre	Drax Hemingborough	W	156	30	25	108	-	84	0.75	0.71 +/- 0.04	4.30 +/- 1.35	46	71	46	60	(8,3)
Birmingham Centre	Acton Town Hall	W	156	29	21	58	-	57	0.92	0.71 +/- 0.03	0.31 +/- 0.9	58	67	58	53	(5,2)
Birmingham Centre	North Kensington	S	158	28	23	132	-	98	0.84	0.96 +/- 0.04	-3.45 +/- 1.19	33	72	28	52	(3,4)
Birmingham Centre	North Kensington	W	158	31	23	95	-	71	0.84	0.71 +/- 0.03	0.78 +/- 1.17	56	83	56	70	(5,1)
Birmingham Centre	Marylebone Road	S	161	28	24	115	-	77	0.81	0.88 +/- 0.04	-1.26 +/- 1.37	38	77	35	57	(2,2)
Birmingham Centre	Marylebone Road	W	161	31	25	134	-	103	0.82	0.70 +/- 0.03	2.66 +/- 1.04	51	78	51	66	(10,4)
Birmingham Centre	Westthorne Ave	W	176	32	22	130	-	100	0.89	0.70 +/- 0.02	-0.10 +/- 0.84	63	78	62	67	(10,4)
Birmingham Centre	Belvedere	S	180	29	24	72	-	47	0.85	0.83 +/- 0.05	-0.33 +/- 1.49	40	87	38	60	(1,1)
Birmingham Centre	Belvedere	W	180	35	27	74	-	43	0.83	0.66 +/- 0.04	4.41 +/- 1.64	50	88	53	79	(6,2)
Birmingham Centre	Thames Road	S	184	29	23	70	-	47	0.86	0.97 +/- 0.05	-5.99 +/- 1.74	43	77	35	57	(2,2)
Birmingham Centre	Thames Road	W	184	32	23	124	-	91	0.84	0.70 +/- 0.03	0.85 +/- 1.06	60	78	60	66	(10,3)
Birmingham Centre	East Kilbride 25053	W	393	30	21	58	-	57	0.85	0.47 +/- 0.03	6.99 +/- 0.87	72	68	78	54	(5,0)
Birmingham Centre	East Kilbride 04443	W	393	30	19	58	-	57	0.84	0.48 +/- 0.03	4.48 +/- 0.90	84	68	88	54	(5,0)

Table 20: Summary of experiment 3ii for Birmingham Centre during 2005, the comparison between the AURN Partisol and the model using collocated TEOM and a distant FDMS purge measurement. Season is denoted as Summer (S) and Winter (W).

Dataset			Distance Between Sites	Reference Mean	Modelled Mean	24 hour		Orthogonal Regression			Annual Limit Value (40 µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)			
AURN Partisol Site	FDMS(Serial # where applicable)	Season				n _{bs}	u _{bs}	n _{c,s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	W _{CM} (%)	%> 20 µg m ⁻³	W _{CM} (%)	%> 25 µg m ⁻³	(n _{ES} ,n _{EC})
Harwell	Harwell	W	0	20	15	64	-	62	0.92	0.80 +/- 0.03	-0.71 +/- 0.67	44	39	43	19	(1,0)
Harwell	North Kensington	W	77	20	21	59	-	57	0.83	0.83 +/- 0.05	4.36 +/- 1.07	22	39	22	19	(1,0)
Harwell	Marylebone Road	W	81	21	19	119	-	43	0.86	0.83 +/- 0.05	1.65 +/- 1.18	31	44	31	23	(1,0)
Harwell	Belfast Centre	W	457	19	12	55	-	53	0.71	0.63 +/- 0.05	0.39 +/- 1.10	74	36	74	19	(0,0)

Table 21: Summary of experiment 3ii for Harwell during 2004, the comparison between the AURN Partisol and the model using collocated TEOM and a distant FDMS purge measurement. Season is denoted as Summer (S) and Winter (W).

Dataset			Distance Between Sites	Reference Mean	Modelled Mean	24 hour		Orthogonal Regression			Annual Limit Value (40 µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)			
AURN Partisol Site	FDMS(Serial # where applicable)	Season				n _{bs}	u _{bs}	n _{c,s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	W _{CM} (%)	%> 20 µg m ⁻³	W _{CM} (%)	%> 25 µg m ⁻³	(n _{ES} ,n _{EC})
Manchester Piccadilly	Drax Barlow	W	86	35	25	58	-	58	0.39	0.61 +/- 0.08	3.23 +/- 2.93	77	86	75	78	(7,2)
Manchester Piccadilly	Drax Hemingborough	S	89	26	21	96	-	96	0.81	1.01 +/- 0.05	-5.38 +/- 1.25	33	74	26	44	(4,0)
Manchester Piccadilly	Harwell	W	221	28	20	58	-	57	0.89	0.78 +/- 0.04	-1.61 +/- 1.10	55	70	52	46	(4,1)
Manchester Piccadilly	North Kensington	S	258	27	22	69	-	69	0.80	1.01 +/- 0.06	-5.54 +/- 1.62	36	83	28	52	(2,1)
Manchester Piccadilly	North Kensington	W	258	28	26	57	-	56	0.81	0.81 +/- 0.05	3.54 +/- 1.55	33	70	32	46	(4,3)
Manchester Piccadilly	Marylebone Road	S	260	27	22	155	-	155	0.82	0.95 +/- 0.03	-3.53 +/- 0.94	35	79	29	50	(6,3)
Manchester Piccadilly	Marylebone Road	W	260	33	24	112	-	110	0.54	0.64 +/- 0.05	3.22 +/- 1.68	68	82	67	65	(12,4)
Manchester Piccadilly	Teddington 24431	W	263	37	21	42	-	42	0.39	0.59 +/- 0.09	-0.50 +/- 3.55	97	86	92	76	(6,2)
Manchester Piccadilly	Millennium Village	W	269	32	22	64	-	63	0.62	0.66 +/- 0.06	0.45 +/- 1.98	72	86	70	68	(5,2)
Manchester Piccadilly	Belfast Centre	W	272	28	18	47	-	47	0.88	0.70 +/- 0.04	-1.64 +/- 1.19	71	68	69	47	(4,1)
Manchester Piccadilly	Belvedere	S	275	26	22	129	-	129	0.83	0.99 +/- 0.04	-4.63 +/- 1.03	31	75	25	48	(4,3)
Manchester Piccadilly	Belvedere	W	275	33	19	46	-	45	0.19	0.32 +/- 0.08	8.86 +/- 2.78	98	84	105	71	(5,0)
Manchester Piccadilly	Thames Road	S	279	28	23	108	-	108	0.84	0.97 +/- 0.04	-4.16 +/- 1.12	33	80	27	50	(5,3)
Manchester Piccadilly	Thames Road	W	279	33	23	71	-	70	0.59	0.67 +/- 0.06	1.04 +/- 2.03	69	84	67	70	(6,2)

Table 22: Summary of experiment 3ii for Manchester during 2004, the comparison between the AURN Partisol and the model using collocated TEOM and a distant FDMS purge measurement. Season is denoted as Summer (S) and Winter (W).

Dataset			Distance Between Sites	Reference Mean	Modelled Mean	24 hour		Orthogonal Regression				Annual Limit Value (40 µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)		
AURN Partisol Site	FDMS(Serial # where applicable)	Season				n _{bs}	u _{bs}	n _{c_s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	W _{CM} (%)	%> 20 µg m ⁻³	W _{CM} (%)	%> 25 µg m ⁻³	(n _{ES} ,n _{EC})
Manchester Piccadilly	Drax Barlow	S	86	28	19	135	-	129	0.58	0.59 +/- 0.04	2.99 +/- 1.13	71	83	73	57	(5,0)
Manchester Piccadilly	Drax Barlow	W	86	35	24	135	-	84	0.79	0.63 +/- 0.03	1.44 +/- 1.31	72	87	72	65	(12,2)
Manchester Piccadilly	Drax Hemingborough	S	89	27	21	123	-	120	0.43	1.19 +/- 0.08	-10.95 +/- 2.2	39	84	29	59	(1,3)
Manchester Piccadilly	Drax Hemingborough	W	89	33	27	134	-	95	0.79	0.67 +/- 0.03	4.63 +/- 1.24	51	85	52	57	(13,4)
Manchester Piccadilly	Birmingham 04443	S	116	32	22	64	-	59	0.85	0.91 +/- 0.05	-7.08 +/- 1.61	58	86	50	69	(5,4)
Manchester Piccadilly	Birmingham 25053	S	116	31	23	82	-	77	0.83	0.93 +/- 0.04	-6.07 +/- 1.48	49	88	42	71	(5,5)
Manchester Piccadilly	Bristol 24431	S	227	25	26	41	-	41	0.66	1.22 +/- 0.11	-5.18 +/- 2.95	37	71	35	39	(1,3)
Manchester Piccadilly	Bristol 24447	S	227	25	24	42	-	42	0.66	1.25 +/- 0.11	-7.49 +/- 2.97	36	69	34	38	(1,3)
Manchester Piccadilly	Bristol 24431	W	227	34	26	85	-	83	0.88	0.75 +/- 0.03	0.62 +/- 1.1	51	87	50	58	(12,7)
Manchester Piccadilly	Bristol 24447	W	227	34	25	82	-	80	0.92	0.74 +/- 0.02	-0.54 +/- 0.94	58	86	56	56	(13,6)
Manchester Piccadilly	Acton Town Hall	W	257	33	23	80	-	78	0.90	0.75 +/- 0.03	-1.98 +/- 0.98	63	86	60	56	(10,2)
Manchester Piccadilly	North Kensington	S	258	29	23	141	-	136	0.56	1.02 +/- 0.06	-5.99 +/- 1.76	45	83	36	60	(6,6)
Manchester Piccadilly	North Kensington	W	258	35	23	120	-	75	0.86	0.69 +/- 0.03	-0.72 +/- 1.21	70	88	68	64	(11,3)
Manchester Piccadilly	Marylebone Road	S	260	29	23	126	-	120	0.53	0.92 +/- 0.06	-2.97 +/- 1.81	48	83	41	62	(5,6)
Manchester Piccadilly	Marylebone Road	W	260	34	25	161	-	112	0.82	0.69 +/- 0.03	1.09 +/- 1.11	61	86	60	61	(16,5)
Manchester Piccadilly	Teddington 24431	S	263	31	22	72	-	66	0.82	0.85 +/- 0.05	-4.30 +/- 1.54	56	91	50	76	(5,4)
Manchester Piccadilly	Teddington 24447	S	263	31	21	70	-	64	0.78	0.83 +/- 0.05	-4.65 +/- 1.71	62	91	56	77	(5,2)
Manchester Piccadilly	Westhorne Ave	S	273	32	20	62	-	56	0.81	0.84 +/- 0.05	-7.06 +/- 1.77	71	89	63	70	(5,3)
Manchester Piccadilly	Westhorne Ave	W	273	34	22	154	-	111	0.86	0.72 +/- 0.03	-2.15 +/- 1.01	70	85	67	60	(16,1)
Manchester Piccadilly	Belvedere	S	275	30	23	82	-	76	0.80	0.85 +/- 0.05	-2.41 +/- 1.46	47	88	43	67	(5,4)
Manchester Piccadilly	Thames Road	S	279	30	23	76	-	76	0.57	0.99 +/- 0.08	-6.83 +/- 2.49	57	80	45	62	(6,6)
Manchester Piccadilly	Thames Road	W	279	34	23	145	-	98	0.81	0.70 +/- 0.03	-0.98 +/- 1.21	71	84	68	61	(15,3)
Manchester Piccadilly	East Kilbride 25053	S	282	25	22	44	-	44	0.73	1.15 +/- 0.09	-6.17 +/- 2.36	26	68	21	36	(1,2)
Manchester Piccadilly	East Kilbride 25053	W	282	34	23	84	-	83	0.92	0.57 +/- 0.02	3.33 +/- 0.73	71	87	73	58	(13,1)
Manchester Piccadilly	East Kilbride 04443	W	282	34	21	84	-	83	0.91	0.59 +/- 0.02	0.53 +/- 0.77	80	87	80	58	(13,1)

Table 23: Summary of experiment 3ii for Manchester during 2005, the comparison between the AURN Partisol and the model using collocated TEOM and a distant FDMS purge measurement. Season is denoted as Summer (S) and Winter (W).

Dataset			Distance Between Sites	Reference Mean	Modelled Mean	24 hour		Orthogonal Regression				Annual Limit Value (40 µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)		
AURN Partisol Site	FDMS(Serial # where applicable)	Season				n _{bs}	u _{bs}	n _{c_s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	W _{CM} (%)	%> 20 µg m ⁻³	W _{CM} (%)	%> 25 µg m ⁻³	(n _{ES} ,n _{EC})
Marylebone Road	Marylebone Road	S	0	33	34	169	-	143	0.71	0.99 +/- 0.05	1.00 +/- 1.59	30	88	24	80	(8,12)
Marylebone Road	Marylebone Road	W	0	41	37	147	-	136	0.83	0.67 +/- 0.02	8.68 +/- 1.14	36	90	38	79	(31,22)
Marylebone Road	North Kensington	S	4	34	34	75	-	65	0.79	0.87 +/- 0.05	4.40 +/- 1.83	23	92	19	82	(5,3)
Marylebone Road	North Kensington	W	4	35	38	75	-	63	0.94	0.91 +/- 0.03	5.54 +/- 1.13	20	87	14	73	(12,13)
Marylebone Road	Millennium Village	W	12	41	34	75	-	69	0.86	0.72 +/- 0.03	4.42 +/- 1.49	39	94	41	86	(14,5)
Marylebone Road	Teddington 24431	W	17	52	38	45	-	40	0.90	0.54 +/- 0.03	9.89 +/- 1.63	49	93	56	83	(16,12)
Marylebone Road	Belvedere	S	22	32	34	137	-	118	0.60	1.05 +/- 0.06	0.15 +/- 2.04	36	87	29	78	(4,10)
Marylebone Road	Belvedere	W	22	43	35	57	-	51	0.87	0.53 +/- 0.03	12.25 +/- 1.42	39	96	48	82	(9,6)
Marylebone Road	Thames Road	S	25	35	35	118	-	100	0.60	0.92 +/- 0.06	1.99 +/- 2.21	34	94	28	88	(8,9)
Marylebone Road	Thames Road	W	25	46	37	84	-	76	0.85	0.57 +/- 0.03	11.09 +/- 1.36	40	95	47	86	(21,13)
Marylebone Road	Harwell	W	81	36	33	80	-	68	0.93	0.88 +/- 0.03	1.54 +/- 1.13	24	87	23	78	(12,6)
Marylebone Road	Drax Barlow	W	255	45	38	58	-	54	0.74	0.60 +/- 0.04	11.06 +/- 2.23	44	93	46	83	(15,8)
Marylebone Road	Drax Hemingborough	S	256	32	35	94	-	81	0.53	1.32 +/- 0.09	-8.03 +/- 3.17	48	89	46	83	(3,9)
Marylebone Road	Belfast Centre	W	517	35	30	73	-	61	0.82	0.78 +/- 0.04	2.57 +/- 1.68	39	87	38	75	(9,3)

Table 24: Summary of experiment 3ii for Marylebone Road during 2004, the comparison between the AURN Partisol and the model using collocated TEOM and a distant FDMS purge measurement. Season is denoted as Summer (S) and Winter (W).

Dataset			Distance Between Sites	Reference Mean	Modelled Mean	24 hour		Orthogonal Regression				Annual Limit Value (40 µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)		
AURN Partisol Site	FDMS(Serial # where applicable)	Season				n _{bs}	u _{bs}	n _{c_s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	W _{CM} (%)	% > 20 µg m ⁻³	W _{CM} (%)	% > 25 µg m ⁻³	(n _{ES} , n _{EC})
Marylebone Road	Marylebone Road	S	0	38	37	154	-	150	0.79	0.91 +/- 0.03	2.34 +/- 1.42	32	95	26	85	(19,26)
Marylebone Road	Marylebone Road	W	0	42	35	173	-	142	0.61	0.73 +/- 0.04	4.50 +/- 1.92	58	93	53	85	(41,24)
Marylebone Road	North Kensington	S	4	38	37	154	-	150	0.79	0.93 +/- 0.04	1.52 +/- 1.44	33	94	27	85	(21,25)
Marylebone Road	North Kensington	W	4	44	34	128	-	106	0.63	0.68 +/- 0.04	4.43 +/- 2.10	61	93	59	89	(33,14)
Marylebone Road	Acton Town Hall	W	8	42	37	81	-	79	0.72	0.76 +/- 0.05	4.33 +/- 2.2	49	95	45	86	(22,15)
Marylebone Road	Westhorne Ave	S	15	41	33	74	-	73	0.88	0.79 +/- 0.03	0.73 +/- 1.44	45	99	43	90	(11,7)
Marylebone Road	Westhorne Ave	W	15	43	33	165	-	133	0.62	0.71 +/- 0.04	2.96 +/- 1.93	64	94	60	86	(40,18)
Marylebone Road	Teddington 24431	S	17	40	37	88	-	87	0.77	0.74 +/- 0.04	6.75 +/- 1.74	34	97	34	89	(13,11)
Marylebone Road	Teddington 24447	S	17	40	36	86	-	86	0.75	0.72 +/- 0.04	6.67 +/- 1.77	37	97	37	88	(13,11)
Marylebone Road	Teddington 24431	W	17	40	30	81	-	57	0.79	0.62 +/- 0.04	5.00 +/- 1.75	58	89	60	82	(15,4)
Marylebone Road	Teddington 24447	W	17	44	31	52	-	43	0.76	0.65 +/- 0.05	2.55 +/- 2.48	64	100	64	95	(14,3)
Marylebone Road	Belvedere	S	22	40	38	97	-	95	0.81	0.81 +/- 0.04	5.81 +/- 1.56	29	97	27	88	(13,15)
Marylebone Road	Belvedere	W	22	40	31	84	-	57	0.81	0.66 +/- 0.04	4.93 +/- 1.8	52	89	53	82	(15,6)
Marylebone Road	Thames Road	S	25	39	35	85	-	83	0.77	0.96 +/- 0.05	-2.35 +/- 2.14	40	96	33	89	(13,15)
Marylebone Road	Thames Road	W	25	42	33	156	-	129	0.60	0.69 +/- 0.04	4.08 +/- 1.92	62	92	59	84	(35,17)
Marylebone Road	Birmingham 04443	S	160	41	35	72	-	72	0.86	0.80 +/- 0.04	2.19 +/- 1.62	38	99	36	92	(11,9)
Marylebone Road	Birmingham 25053	S	160	39	36	91	-	91	0.80	0.79 +/- 0.04	5.41 +/- 1.63	32	97	30	88	(12,13)
Marylebone Road	Birmingham 04443	W	160	40	29	72	-	53	0.80	0.63 +/- 0.04	4.04 +/- 1.86	60	89	62	83	(14,4)
Marylebone Road	Birmingham 25053	W	160	40	29	73	-	54	0.78	0.66 +/- 0.05	2.44 +/- 2.02	63	89	63	83	(15,5)
Marylebone Road	Bristol 24431	S	169	39	41	41	-	41	0.84	0.89 +/- 0.06	6.72 +/- 2.38	30	90	22	80	(8,12)
Marylebone Road	Bristol 24447	S	169	39	40	42	-	42	0.86	0.89 +/- 0.05	5.05 +/- 2.2	26	90	21	81	(8,10)
Marylebone Road	Bristol 24431	W	169	43	40	86	-	84	0.64	0.71 +/- 0.05	8.76 +/- 2.39	48	95	43	87	(25,20)
Marylebone Road	Bristol 24447	W	169	43	39	84	-	82	0.72	0.78 +/- 0.05	5.56 +/- 2.23	44	96	40	88	(22,19)
Marylebone Road	Drax Barlow	S	255	38	34	127	-	124	0.67	0.80 +/- 0.04	3.87 +/- 1.77	42	95	38	85	(14,10)
Marylebone Road	Drax Barlow	W	255	43	32	137	-	109	0.59	0.68 +/- 0.05	2.80 +/- 2.16	70	91	66	87	(34,12)
Marylebone Road	Drax Hemingborough	S	256	36	36	116	-	113	0.73	1.08 +/- 0.05	-3.10 +/- 2.01	34	96	27	84	(12,16)
Marylebone Road	Drax Hemingborough	W	256	40	36	134	-	119	0.52	0.86 +/- 0.06	1.92 +/- 2.53	63	92	52	84	(29,21)
Marylebone Road	East Kilbride 25053	S	540	37	38	43	-	42	0.79	0.87 +/- 0.06	5.57 +/- 2.53	29	90	24	79	(6,6)
Marylebone Road	East Kilbride 25053	W	540	42	35	84	-	82	0.43	0.56 +/- 0.06	11.83 +/- 2.58	56	95	56	87	(21,9)
Marylebone Road	East Kilbride 04443	W	540	42	33	84	-	82	0.44	0.56 +/- 0.06	9.65 +/- 2.57	62	95	63	87	(21,8)

Table 25: Summary of experiment 3ii for Marylebone Road during 2005, the comparison between the AURN Partisol and the model using collocated TEOM and a distant FDMS purge measurement. Season is denoted as Summer (S) and Winter (W).

Dataset			Distance Between Sites	Reference Mean	Modelled Mean	24 hour		Orthogonal Regression				Annual Limit Value (40 µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)		
AURN Partisol Site	FDMS(Serial # where applicable)	Season				n _{bs}	u _{bs}	n _{c_s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	W _{CM} (%)	%> 20 µg m ⁻³	W _{CM} (%)	%> 25 µg m ⁻³	(n _{ES} ,n _{EC})
Northampton	Harwell	W	84	19	17	61	-	52	0.74	1.11 +/- 0.08	-3.87 +/- 1.68	28	37	24	25	(0,0)
Northampton	North Kensington	W	96	19	23	57	-	49	0.71	1.20 +/- 0.09	-0.19 +/- 1.98	51	37	47	27	(0,0)
Northampton	Marylebone Road	S	98	21	18	123	-	83	0.58	0.89 +/- 0.07	-0.54 +/- 1.52	38	46	33	23	(2,0)
Northampton	Marylebone Road	W	98	22	20	119	-	107	0.71	0.73 +/- 0.04	3.84 +/- 1.01	43	50	44	33	(3,0)
Northampton	Teddington 24431	W	102	24	17	42	-	41	0.95	0.55 +/- 0.02	4.26 +/- 0.58	69	51	73	34	(3,0)
Northampton	Millennium Village	W	107	21	16	66	-	64	0.85	0.57 +/- 0.03	4.07 +/- 0.69	66	52	69	30	(1,0)
Northampton	Belvedere	S	113	21	17	107	-	78	0.81	1.05 +/- 0.05	-4.01 +/- 1.13	21	44	16	21	(1,0)
Northampton	Belvedere	W	113	20	16	47	-	47	0.89	0.56 +/- 0.03	4.22 +/- 0.69	67	43	71	23	(2,0)
Northampton	Thames Road	S	117	22	19	80	-	57	0.63	0.85 +/- 0.07	0.48 +/- 1.81	41	46	37	25	(3,0)
Northampton	Thames Road	W	117	23	18	73	-	71	0.89	0.59 +/- 0.02	4.55 +/- 0.63	60	52	64	35	(3,0)
Northampton	Drax Barlow	W	165	24	20	60	-	59	0.84	0.60 +/- 0.03	5.41 +/- 0.91	55	54	60	36	(3,0)
Northampton	Drax Hemingborough	S	166	21	17	74	-	68	0.83	1.16 +/- 0.06	-7.07 +/- 1.3	19	44	15	21	(1,0)
Northampton	Belfast Centre	W	423	19	14	50	-	44	0.64	0.86 +/- 0.08	-2.42 +/- 1.78	48	39	43	27	(0,0)

Table 26: Summary of experiment 3ii for Northampton during 2004, the comparison between the AURN Partisol and the model using collocated TEOM and a distant FDMS purge measurement. Season is denoted as Summer (S) and Winter (W).

Dataset			Distance Between Sites	Reference Mean	Modelled Mean	24 hour			Orthogonal Regression			Annual Limit Value (40 µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)		
AURN Partisol Site	FDMS(Serial # where applicable)	Season				n _{bs}	u _{bs}	n _{c,s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	W _{CM} (%)	%> 20 µg m ⁻³	W _{CM} (%)	%> 25 µg m ⁻³	(n _{ES} ,n _{EC})
Northampton	Birmingham 04443	S	74	27	18	65	-	63	0.84	0.83 +/- 0.04	-4.1 +/- 1.31	60	70	54	49	(5,1)
Northampton	Birmingham 25053	S	74	26	20	81	-	79	0.78	0.83 +/- 0.04	-2.04 +/- 1.3	51	71	47	49	(5,3)
Northampton	Birmingham 04443	W	74	26	19	69	-	69	0.94	0.69 +/- 0.02	0.91 +/- 0.62	59	59	60	46	(8,0)
Northampton	Birmingham 25053	W	74	27	19	70	-	70	0.96	0.69 +/- 0.02	0.17 +/- 0.52	62	60	62	47	(9,1)
Northampton	Acton Town Hall	W	95	27	17	80	-	65	0.86	0.73 +/- 0.04	-2.01 +/- 1.07	66	66	63	46	(8,0)
Northampton	North Kensington	S	96	25	20	142	-	139	0.66	0.90 +/- 0.05	-2.39 +/- 1.23	44	63	38	42	(6,4)
Northampton	North Kensington	W	96	26	19	120	-	104	0.83	0.72 +/- 0.03	-0.09 +/- 0.90	60	65	58	46	(9,0)
Northampton	Marylebone Road	S	98	25	20	129	-	126	0.66	0.79 +/- 0.04	0.44 +/- 1.16	49	61	46	44	(6,2)
Northampton	Marylebone Road	W	98	27	20	162	-	145	0.83	0.67 +/- 0.02	2.37 +/- 0.74	58	62	59	46	(16,0)
Northampton	Teddington 24431	S	102	27	19	75	-	73	0.82	0.76 +/- 0.04	-0.98 +/- 1.13	57	73	55	52	(5,1)
Northampton	Teddington 24447	S	102	27	18	73	-	71	0.78	0.74 +/- 0.04	-1.32 +/- 1.27	63	72	60	51	(5,1)
Northampton	Teddington 24431	W	102	25	18	73	-	73	0.89	0.61 +/- 0.02	2.93 +/- 0.71	64	53	66	40	(6,0)
Northampton	Teddington 24447	W	102	27	18	48	-	48	0.91	0.61 +/- 0.03	2.26 +/- 0.84	68	60	70	46	(4,0)
Northampton	Westhorne Ave	S	111	28	16	64	-	62	0.81	0.79 +/- 0.05	-5.73 +/- 1.41	74	71	67	52	(5,1)
Northampton	Westhorne Ave	W	111	27	18	155	-	142	0.87	0.67 +/- 0.02	-0.40 +/- 0.65	70	61	68	45	(17,0)
Northampton	Belvedere	S	113	26	20	85	-	83	0.79	0.78 +/- 0.04	-0.09 +/- 1.17	49	70	48	51	(5,2)
Northampton	Belvedere	W	113	26	21	77	-	77	0.90	0.64 +/- 0.02	4.21 +/- 0.73	54	56	57	43	(8,1)
Northampton	Thames Road	S	117	25	18	78	-	76	0.70	0.95 +/- 0.06	-5.83 +/- 1.67	50	63	42	42	(5,1)
Northampton	Thames Road	W	117	25	18	145	-	130	0.81	0.68 +/- 0.03	0.73 +/- 0.8	64	59	63	43	(13,1)
Northampton	Bristol 24431	S	149	21	21	43	-	42	0.75	0.89 +/- 0.07	1.74 +/- 1.67	27	43	24	24	(1,1)
Northampton	Bristol 24447	S	149	21	19	44	-	43	0.76	0.92 +/- 0.07	-0.25 +/- 1.66	29	42	26	23	(1,1)
Northampton	Bristol 24431	W	149	26	21	85	-	69	0.80	0.79 +/- 0.04	0.13 +/- 1.32	48	67	45	46	(7,2)
Northampton	Bristol 24447	W	149	27	19	82	-	65	0.85	0.76 +/- 0.04	-1.14 +/- 1.16	58	66	55	46	(8,2)
Northampton	Drax Barlow	S	165	24	17	133	-	130	0.62	0.57 +/- 0.03	3.14 +/- 0.91	74	60	76	40	(5,1)
Northampton	Drax Barlow	W	165	27	18	136	-	119	0.80	0.62 +/- 0.03	1.29 +/- 0.83	73	64	73	49	(12,0)
Northampton	Drax Hemingborough	S	166	23	18	125	-	123	0.52	0.90 +/- 0.06	-2.01 +/- 1.39	40	59	36	37	(1,1)
Northampton	Drax Hemingborough	W	166	24	20	133	-	117	0.73	0.74 +/- 0.04	1.59 +/- 1.03	51	58	50	39	(10,2)
Northampton	East Kilbride 25053	S	443	20	17	46	-	45	0.63	0.76 +/- 0.07	2.09 +/- 1.59	43	38	43	18	(0,0)
Northampton	East Kilbride 25053	W	443	27	17	84	-	68	0.78	0.50 +/- 0.03	3.81 +/- 0.93	83	66	86	46	(8,0)
Northampton	East Kilbride 04443	W	443	27	15	84	-	68	0.76	0.51 +/- 0.03	1.40 +/- 1.00	93	66	93	46	(8,0)

Table 27: Summary of experiment 3ii for Northampton during 2005, the comparison between the AURN Partisol and the model using collocated TEOM and a distant FDMS purge measurement. Season is denoted as Summer (S) and Winter (W).

Dataset			Distance Between Sites	Reference Mean	Modelled Mean	24 hour		Orthogonal Regression				Annual Limit Value (40 µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)		
AURN Partisol Site	FDMS(Serial # where applicable)	Season				n _{bs}	u _{bs}	n _{c_s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	W _{CM} (%)	%> 20 µg m ⁻³	W _{CM} (%)	%> 25 µg m ⁻³	(n _{ES} , n _{EC})
North Kensington	North Kensington	S	0	20	21	75	-	59	0.93	1.06 +/- 0.04	-0.67 +/- 0.82	15	44	13	27	(1,1)
North Kensington	North Kensington	W	0	19	25	68	-	53	0.92	0.90 +/- 0.03	8.12 +/- 0.79	25	36	17	23	(1,1)
North Kensington	Marylebone Road	S	4	21	21	173	-	141	0.87	0.99 +/- 0.03	-0.12 +/- 0.70	17	43	14	28	(3,3)
North Kensington	Marylebone Road	W	4	23	24	139	-	121	0.88	0.91 +/- 0.03	3.27 +/- 0.76	19	51	16	29	(3,3)
North Kensington	Teddington 24447	W	14	25	25	41	-	40	0.92	0.89 +/- 0.04	2.84 +/- 1.19	20	53	18	40	(1,2)
North Kensington	Teddington 24431	W	14	24	24	45	-	44	0.93	0.90 +/- 0.04	2.52 +/- 1.06	18	55	16	36	(1,2)
North Kensington	Millennium Village	W	16	22	20	76	-	71	0.83	0.75 +/- 0.04	3.61 +/- 0.93	35	55	37	24	(1,0)
North Kensington	Belvedere	S	26	21	20	144	-	119	0.82	0.99 +/- 0.04	0.00 +/- 0.87	19	40	15	24	(2,1)
North Kensington	Belvedere	W	26	21	21	56	-	53	0.82	0.97 +/- 0.06	0.65 +/- 1.37	23	51	19	25	(1,2)
North Kensington	Thames Road	S	29	22	21	125	-	108	0.86	0.91 +/- 0.03	0.78 +/- 0.85	24	45	21	31	(4,3)
North Kensington	Thames Road	W	29	24	23	83	-	79	0.86	0.92 +/- 0.04	1.39 +/- 1.05	22	59	19	32	(2,2)
North Kensington	Harwell	W	77	19	20	72	-	58	0.93	0.88 +/- 0.03	3.51 +/- 0.68	14	36	14	22	(1,1)
North Kensington	Drax Barlow	W	254	24	25	58	-	56	0.81	0.95 +/- 0.06	2.27 +/- 1.49	24	63	20	32	(1,3)
North Kensington	Drax Hemingborough	S	255	22	21	98	-	83	0.79	0.97 +/- 0.05	-0.06 +/- 1.19	23	42	19	30	(2,1)
North Kensington	Belfast Centre	W	514	19	18	62	-	58	0.80	0.75 +/- 0.05	3.79 +/- 1.02	37	36	39	22	(1,1)

Table 28: Summary of experiment 3ii for North Kensington during 2004, the comparison between the AURN Partisol and the model using collocated TEOM and a distant FDMS purge measurement. Season is denoted as Summer (S) and Winter (W).

Dataset			Distance Between Sites	Reference Mean	Modelled Mean	24 hour		Orthogonal Regression			Annual Limit Value (40 µg m ⁻³)		Daily Limit Value (50 µg m ⁻³)			
AURN Partisol Site	FDMS(Serial # where applicable)	Season				n _{bs}	u _{bs}	n _{c,s}	r ²	Slope (b) +/- U _b	Intercept (a) +/- U _a	W _{CM} (%)	%> 20 µg m ⁻³	W _{CM} (%)	%> 25 µg m ⁻³	(n _{ES} ,n _{EC})
North Kensington	North Kensington	S	0	23	22	165	-	119	0.79	0.98 +/- 0.04	-0.88 +/- 1.08	27	54	22	32	(4,5)
North Kensington	North Kensington	W	0	27	24	127	-	115	0.76	0.77 +/- 0.04	2.29 +/- 1.15	46	63	44	46	(11,7)
North Kensington	Marylebone Road	S	4	23	22	152	-	107	0.84	0.88 +/- 0.04	1.44 +/- 0.91	26	53	24	31	(4,3)
North Kensington	Acton Town Hall	W	4	26	23	81	-	72	0.69	0.85 +/- 0.06	0.57 +/- 1.74	46	58	41	39	(7,4)
North Kensington	Marylebone Road	W	4	27	24	170	-	155	0.77	0.77 +/- 0.03	3.53 +/- 0.96	41	60	39	45	(16,12)
North Kensington	Teddington 24431	S	14	26	22	88	-	64	0.85	0.85 +/- 0.04	0.54 +/- 1.21	34	61	32	38	(4,2)
North Kensington	Teddington 24447	S	14	26	22	86	-	63	0.81	0.84 +/- 0.05	0.11 +/- 1.37	39	62	37	38	(4,2)
North Kensington	Teddington 24431	W	14	25	21	80	-	75	0.88	0.67 +/- 0.03	4.23 +/- 0.83	49	57	52	45	(6,2)
North Kensington	Teddington 24447	W	14	28	22	51	-	48	0.83	0.64 +/- 0.04	4.14 +/- 1.25	55	69	58	54	(3,1)
North Kensington	Westhorne Ave	S	19	26	20	76	-	56	0.90	0.90 +/- 0.04	-3.14 +/- 1.14	41	59	36	39	(4,2)
North Kensington	Westhorne Ave	W	19	27	22	164	-	149	0.81	0.77 +/- 0.03	1.21 +/- 0.92	49	60	46	46	(16,8)
North Kensington	Belvedere	S	26	25	24	96	-	71	0.90	0.89 +/- 0.03	1.97 +/- 0.93	20	58	19	35	(4,4)
North Kensington	Belvedere	W	26	27	24	83	-	78	0.89	0.71 +/- 0.03	4.97 +/- 0.88	37	60	40	50	(8,4)
North Kensington	Thames Road	S	29	23	20	88	-	61	0.71	0.91 +/- 0.06	-1.12 +/- 1.66	38	51	33	34	(3,2)
North Kensington	Thames Road	W	29	26	23	153	-	140	0.78	0.76 +/- 0.03	2.55 +/- 0.97	46	57	45	41	(15,7)
North Kensington	Birmingham 04443	S	157	27	23	74	-	51	0.89	0.93 +/- 0.04	-2.21 +/- 1.34	33	63	28	43	(4,3)
North Kensington	Birmingham 25053	S	157	25	23	92	-	66	0.87	0.93 +/- 0.04	-0.18 +/- 1.2	27	61	23	36	(4,3)
North Kensington	Birmingham 04443	W	157	29	23	70	-	67	0.87	0.73 +/- 0.03	2.34 +/- 1.10	47	66	48	55	(9,4)
North Kensington	Birmingham 25053	W	157	29	23	71	-	68	0.85	0.75 +/- 0.04	1.37 +/- 1.22	49	66	48	56	(9,5)
North Kensington	Bristol 24431	W	165	27	26	86	-	77	0.73	0.83 +/- 0.05	3.67 +/- 1.61	40	57	35	39	(8,5)
North Kensington	Bristol 24447	W	165	27	25	83	-	77	0.72	0.84 +/- 0.05	2.31 +/- 1.63	43	57	37	39	(7,5)
North Kensington	Drax Barlow	S	254	23	19	134	-	96	0.71	0.68 +/- 0.04	3.94 +/- 1.01	49	50	51	29	(4,2)
North Kensington	Drax Barlow	W	254	28	23	136	-	124	0.69	0.71 +/- 0.04	2.64 +/- 1.22	55	66	54	49	(12,5)
North Kensington	Drax Hemingborough	S	255	21	20	126	-	84	0.54	0.99 +/- 0.07	-0.63 +/- 1.68	27	50	22	29	(0,2)
North Kensington	Drax Hemingborough	W	255	25	24	133	-	121	0.72	0.80 +/- 0.04	4.00 +/- 1.19	40	55	37	39	(12,8)
North Kensington	East Kilbride 25053	W	539	27	23	85	-	76	0.73	0.61 +/- 0.04	6.38 +/- 1.25	54	58	57	41	(8,2)
North Kensington	East Kilbride 04443	W	539	27	21	85	-	76	0.73	0.62 +/- 0.04	4.00 +/- 1.27	62	58	64	41	(8,2)

Table 29: Summary of experiment 3ii for North Kensington during 2005, the comparison between the AURN Partisol and the model using collocated TEOM and a distant FDMS purge measurement. Season is denoted as Summer (S) and Winter (W).

8.7 FDMS Purge Measurements

