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Volatile Correction Model (VCM) for PM_{10}

Application to hourly time resolution and

AURN FDMS purge measurements

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

May 2008

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King's College London

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Table of Contents

GLOSSARY

AURN	Automatic Urban and Rural Network
d_{max}	The maximum distance between the home site and any of the three away sites where away sites are less than 200 km away
d_{mean}	The mean distance between the home site and any of the three away sites where away sites are less than 200 km away
d_{min}	The minimum distance between the home site and any of the three away sites where away sites are less than 200 km away
DEFRA	Department for Environment Food and Rural Affairs.
EU	European Union.
FDMS	Filter Dynamics Measurement System.
FDMS purge	Mass concentration obtained from the FDMS at 30^{o}C with sample having passed through dryer and 4^{o}C chilled filter. Confusingly, termed FDMS Reference by the manufacturer.
$TEOM_{VCM}$	TEOM measurements corrected by the Volatile Correction Model.
LAQN	London Air Quality Network
$TEOM_{VCM(nh)}$	TEOM measurements corrected by the where the FDMS purge measurement input to the model is averaged over *n* hours.
King's	King's College London
u_{purge}	Between FDMS purge uncertainty.
VCM	Volatile Correction Model.
W_{CM}	Combined relative expanded uncertainty at the limit value.

SUMMARY

This report investigates whether the Volatile Correction Model (VCM) can be used to correct TEOM measurements for their loss of volatile particulate matter at an hourly time resolution in the UK. It also reports an assessment of the AURN (Automatic Urban and Rural Network) FDMS measurements from instruments deployed during 2007 and whether these measurements are suitable for use in the VCM on a national scale.

The VCM works by correcting TEOM measurements from a ('home') site using the model equation and FDMS purge measurements from distant ('away') sites to produce a $TEOM_{VCM}$ measurement. To assess whether the VCM is applicable at an hourly time resolution, the combined relative expanded uncertainty at the Limit Value (W_{CM}) of the $TEOM_{VCM}$ was calculated using hourly mean TEOM and FDMS purge measurements and compared to the hourly mean FDMS measurements.

The configuration of the model was optimised to use the mean of the purge measurements from three away sites. This ensured that the model was representative of the regional volatile particulate matter concentration and that the data capture was not adversely impacted by instrument malfunctions. **This analysis demonstrated that the VCM was applicable on an hourly time resolution; it also demonstrated that W_{CM} increased with separation distances between sites.**

The analysis of the AURN FDMS measurements found that, overwhelmingly, the FDMS purge measurements behaved as expected and are suitable for use in the VCM on a national scale.

A review of the spatial limits of the model domain was considered necessary following the results of the analysis of the hourly measurements and AURN FDMS measurements. Both these suggested that the maximum model domain was smaller than the 200 km concluded from the initial study. The methods used for assessing this distance in this study were less accurate than those used in the first study and a definitive model domain could not be concluded. However, reducing the model domain from 200 km did not adversely affect the use of the model in the UK as the distribution of sites in the AURN and London Air Quality Network (LAQN) is such that only a small number of additional areas were not covered by the optimum three away sites. All of these will be covered by at least one FDMS instrument and this was shown to be adequate for the VCM to function efficiently. **A reduction in the model domain to 133 km was therefore recommended until further measurements become available.**

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 objectives with respect to 'accuracy' and data capture.

The First Daughter Directive (1999/30/EC) included Limit Values for PM_{10} and also stipulated that PM_{10} should be measured gravimetrically as laid out in EN12341 (CEN, 1998). There is however a conflict between the requirement to measure PM_{10} 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 PM_{10}.

In the UK the majority of PM_{10} 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 *et al.*, 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 PM_{10} measurements with the EU Directive (DETR, 2000).

During 2004 Defra embarked upon a UK Equivalence Programme to determine the equivalence of several automated and non-automated PM_{10} and $PM_{2.5}$ measurement techniques (Harrison, 2006). Several instruments proved equivalent to the European PM_{10} reference method, importantly, the TEOM did not and is therefore not suitable for reporting PM_{10} 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 2007 King's College London (King's) used the measurements from the UK Equivalence Programme and those undertaken in the LAQN to develop the Volatile Correction Model (VCM) (Green *et al.*, 2007). The VCM used measurements of volatile particulate matter from FDMS instruments to correct TEOM measurements for this loss of volatiles using the equation below:

$$TEOM_{VCM}\ PM_{10} = TEOM\ PM_{10} - (1.87 \times \text{Regional FDMS } PM_{10}\text{ purge})$$

The geographical homogeneity of the volatile particulate matter meant that the FDMS measurements could be made up to 200 km away. The resulting corrected TEOM measurements ($TEOM_{VCM}$) proved equivalent to the European PM_{10} reference method for PM_{10}.

This study builds on the previous analysis to explore the possibility of using the VCM to correct TEOM measurements at an hourly time resolution so that $TEOM_{VCM}$ measurements can be

disseminated in real time. This is achieved by calculating the combined relative expanded uncertainty at the Limit Value (W_{CM}) between the $TEOM_{VCM}$ measurements with the FDMS measurements made during the UK Equivalence programme. It should also be noted that the VCM equation was optimised in the first report to produce $TEOM_{VCM}$ measurements that were equivalent to the gravimetric reference method, not the FDMS (Green *et al.*, 2007).

The FDMS measurements made on the AURN during 2007 are also analysed with respect to their application in the VCM on a national scale. One of the limitations of the first study was that the geographical coverage was limited to the London Air Quality Network (LAQN) and the four sites used in the UK Equivalence programme. There were 25 FDMS sites installed in the AURN during 2007, these provided an opportunity to assess the geographical homogeneity of the volatile particulate matter on a national scale.

The practical application of VCM in the UK was assessed in terms of FDMS instrument coverage from the AURN to the AURN and local authority TEOMs.

2 METHOD

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

2.1 Measurement methods

This study is uses measurements of PM_{10} made using the TEOM and FDMS methods.

2.1.1 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. The filter and the air stream passing through it were heated to 50 ºC to reduce the interferences from particle bound water and to minimise thermal expansion of the tapered element, which may affect the oscillating frequency. This heating has the widely acknowledged disadvantage of driving off semi-volatile material such as ammonium nitrate and organic aerosols (Ruppecht E. *et al.*, 1992; Allen *et al.*, 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 PM_{10} 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 (Ruppecht E. *et al.*, 1992). The second corrected for the reporting conditions of the TEOM, which default to 25 ºC, and 1 atmosphere pressure, which was the US EPA requirement prior to 1997.

2.1.2 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 PM_{10} inlet, and then used a dryer to remove water from the sample; this allowed the mass to be measured at 30 ºC rather than 50 ºC. After passing through the dryer, measurement was alternated between two cycles (base and purge), switching between them every six minutes. 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:

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

2.1.2.1 Base Measurement

The change in sample mass on the filter was measured by the microbalance after sample size selection and drying. This provided a mass concentration of PM_{10} analogous to that measured by the TEOM; the difference being the dryer and the reduced sampling temperature.

2.1.2.2 Purge measurement (referred to as 'reference' in manufacturer's literature)

During the purge cycle a filter, chilled to 4 ºC, 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). However, positive measurements were also made, indicating that adsorption was occurring during certain conditions.

2.2 Measurement programmes

Measurements were obtained from three measurement programmes.

2.2.1 UK Equivalence Programme

The 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 PM_{10} 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, further details can be found in Table 4. Measurements from the four locations were divided into separate summer and winter deployments to provide eight field campaigns from late 2004 to early 2006. Only the PM_{10} measurements made by TEOM and FDMS instruments were used in this study.

The TEOM and FDMS microbalance K_0 factors were subject to UKAS accredited audit by AEA Energy and Environment, UKAS accredited flow checks were undertaken by the National Physical Laboratory; Bureau Veritas ratified the measurements. All measurements from the UK Equivalence Programme have been made available online at:

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

These were obtained and entered into the KCL air quality database.

2.2.2 The UK Automatic Urban and Rural Network (AURN)

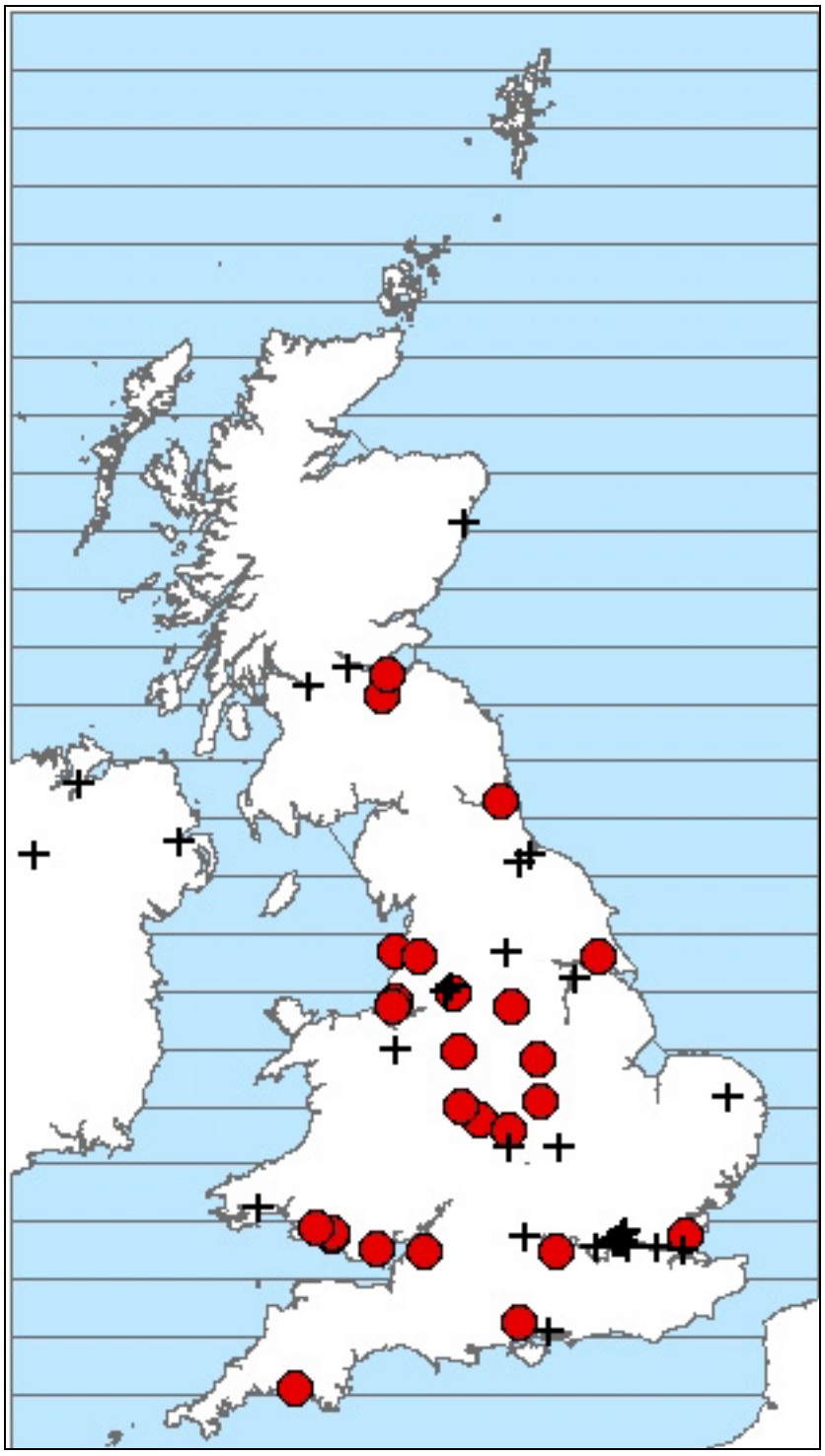

Figure 1: Map of the UK showing the location of the FDMS instruments in the AURN as of 1st January 2008

There were 25 PM_{10} and 2 $PM_{2.5}$ FDMS instruments in the AURN during 2007, further details can be found in Table 1. The FDMS flow and microbalance K_0 factors were subject to UKAS accredited audit and AEA Energy and Environment ratified the measurements. The measurements were ratified from the instrument installation dates until 30th September 2007. These were subjected to an additional sensibility check based on the ratification techniques developed for the LAQN FDMS instruments since 2003.

2.2.3 The London Air Quality Network

The 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 King's College London (King's). By the end of 2007 London Boroughs had supported the installation of FDMS instruments at eight sites as shown in Figure 2; further details can be found in Table 1. The FDMS sites are managed by KCL. FDMS sample flow rates and K_0 factors were subject UKAS accredited audits by the National Physical Laboratory and measurements were ratified by King's. Further details of the LAQN FDMS programme can be found in (Green and Fuller, 2004; Green and Fuller, 2006).

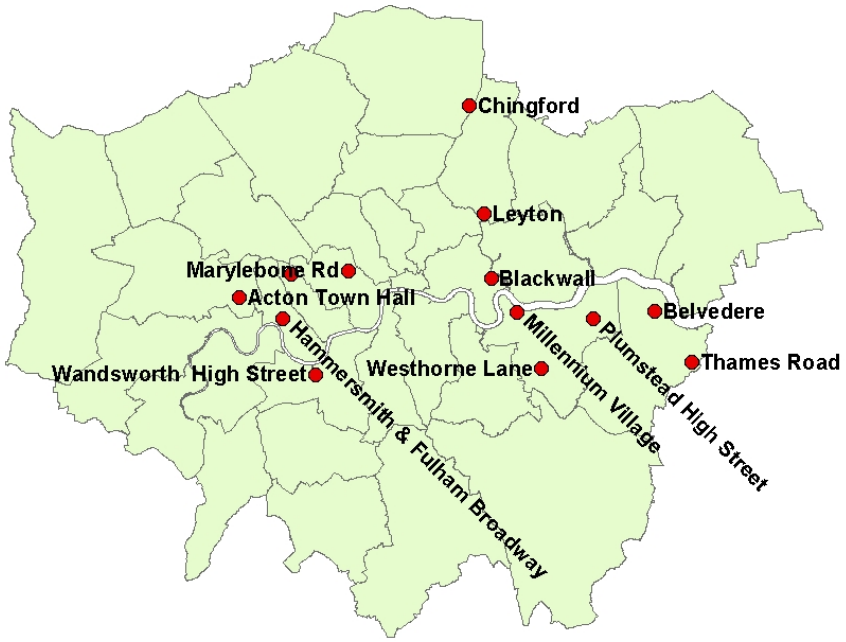

Figure 2: FDMS monitoring sites in the LAQN

Site	Network	Gravimetric Reference	TEOM	FDMS	OS Grid	Lat Long (Datum: WGS84)
Aberdeen	AURN		●		394416 807408	Lat: 57.157505N Long: 2.093945W
Acton Town Hall	LAQN		●	●	520300 180050	Lat: 51.506586N Long: 0.268023W
Auchencorth Moss	AURN			●	322227 656143	Lat: 55.792304N Long: 3.241930W
Belfast Centre	AURN		●		146231 529911	Lat: 54.600443N Long: 5.930566W
Belvedere	LAQN		●	●	550000 179070	Lat: 51.490685N Long: 0.159205E
Birmingham University	UKEP	●	●	●	404927 284168	Lat: 52.455443N Long: 1.928922W
Birmingham Centre	AURN			●	406342 286862	Lat: 52.479648N Long: 1.908049W
Blackpool Marton	AURN			●	333856 434738	Lat: 53.804713N Long: 3.005841W
Blackwall	LAQN			●	538299 181449	Lat: 51.515044N Long: 0.008290W
Bristol Roadside	UKEP	●	●	●	359469 172424	Lat: 51.449341N Long: 2.584642W
Bristol St Paul's	AURN			●	359501 173935	Lat: 51.462929N Long: 2.584355W
Bury Roadside	AURN		●		380922 404772	Lat: 53.539244N Long: 2.289340W
Camden Kerbside	LAQN		●		526640 184433	Lat: 51.544592N Long: 0.175146W
Cardiff Centre	AURN			●	318417 176505	Lat: 51.481594N Long: 3.176234W
Chingford	LAQN			●	536750 193750	Lat: 51.625957N Long: 0.025816W
Coventry Memorial Park	AURN			●	432801 277340	Lat: 52.393105N Long: 1.519408W
Derry	AURN		●		059578 580591	Lat: 55.081126N Long: 1.065634E
East Kilbride	UKEP	●	●	●	263975 653470	Lat: 55.755416N Long: 4.169038W
Edinburgh St Leonards	AURN			●	326250 673132	Lat: 55.945547N Long: 3.182414W
Glasgow Kerbside	AURN		●		258708 665200	Lat: 55.859218N Long: 4.258986W
Grangemouth	AURN		●		293840 681032	Lat: 56.010424N Long: 3.704241W
Hammersmith & Fulham	LAQN			●	523420 178590	Lat: 51.492793N Long: 0.223601W
Haringey Roadside	LAQN		●		533885 190669	Lat: 51.598959N Long: 0.068355W
Harwell	AURN		●		446772 186020	Lat: 51.571117N Long: 1.326536W
Hull Freetown	AURN			●	509478 429329	Lat: 53.748843N Long: 0.341279W
Leamington Spa	AURN		●		431932 265743	Lat: 52.288900N Long: 1.533276W
Leeds Centre	AURN		●		429976 434268	Lat: 53.803852N Long: 1.546328W
Leicester Centre	AURN			●	458767 304083	Lat: 52.631329N Long: 1.133153W
Leyton	LAQN			●	537804 186025	Lat: 51.556284N Long: 0.013629W
Liverpool Speke	AURN			●	343860 383598	Lat: 53.346281N Long: 2.844741W
London Bloomsbury	AURN		●		530107 182041	Lat: 51.522308N Long: 0.126061W
London Haringey	LAQN		●		529914 189132	Lat: 51.586076N Long: 0.126224W
London Harlington	AURN		●		508299 177809	Lat: 51.488869N Long: 0.441557W
London Marylebone Rd	LAQN		●	●	528120 182000	Lat: 51.522393N Long: 0.154700W
London N. Kensington	LAQN		●	●	524040 181740	Lat: 51.520967N Long: 0.213568W
Lough Navar	AURN		●		020780 518305	Lat: 54.523469N Long: 4.971371W
Manchester Piccadilly	AURN			●	384310 398325	Lat: 53.481409N Long: 2.237894W
Middlesbrough	AURN		●		450480 519632	Lat: 54.569399N Long: 1.220731W
Millennium Village	LAQN			●	540175 179000	Lat: 51.492575N Long: 0.017756E

Site	Network	Gravimetric Reference	TEOM	FDMS	OS Grid	Lat Long (Datum: WGS84)
Narberth	AURN		●		214640 212700	Lat: 51.782180N Long: 4.688584W
Newcastle Centre	AURN			●	425016 564940	Lat: 54.978444N Long: 1.610685W
Northampton	AURN	●	●		476111 264524	Lat: 52.273610N Long: 0.885950W
Norwich Centre	AURN		●		623078 308910	Lat: 52.632067N Long: 1.295041E
Nottingham Centre	AURN			●	457420 340050	Lat: 52.954761N Long: 1.146751W
Plumstead High Street	LAQN			●	545557 178533	Lat: 51.487020N Long: 0.095034E
Plymouth Centre	AURN			●	247742 546100	Lat: 54.786625N Long: 4.369333W
Port Talbot	AURN			●	278745 187410	Lat: 51.572479N Long: 3.751051W
Portsmouth	AURN		●		465686 103607	Lat: 50.828283N Long: 1.068722W
Preston	AURN			●	355248 430143	Lat: 53.765701N Long: 2.680378W
Reading New Town	AURN			●	473441 173198	Lat: 51.453011N Long: 0.944461W
Rochester	AURN		●		583133 176220	Lat: 51.455336N Long: 0.634483E
Salford Eccles	AURN		●		377932 398713	Lat: 53.484666N Long: 2.334027W
Scunthorpe Town	AURN		●		490421 410812	Lat: 53.586107N Long: 0.635558W
Sheffield Centre	AURN			●	435134 386885	Lat: 53.377657N Long: 1.473332W
Southampton Centre	AURN			●	442565 112255	Lat: 50.908202N Long: 1.395978W
Southend-on-Sea	AURN			●	585566 186130	Lat: 51.543553N Long: 0.674669E
Southwark Roadside	LAQN		●		534621 177680	Lat: 51.482062N Long: 0.062699W
Stockton-on-Tees Yarm	AURN		●		441908 512886	Lat: 54.509558N Long: 1.354263W
Stoke-on-Trent Centre	AURN			●	388348 347894	Lat: 53.028204N Long: 2.175183W
Swansea Roadside	AURN			●	265341 194458	Lat: 51.632768N Long: 3.947059W
Teddington	UKEP	●	●	●	515115 170778	Lat: 51.424331N Long: 0.345714W
Teddington	AURN		●		515115 170778	Lat: 51.424331N Long: 0.345714W
Thames Road	LAQN		●	●	552616 175415	Lat: 51.457146N Long: 0.195279E
Thurrock	AURN		●		561018 177894	Lat: 51.477093N Long: 0.317238E
Wandsworth High Street	LAQN			●	525760 174570	Lat: 51.456150N Long: 0.191342W
Westhorne Avenue	LAQN			●	541883 175016	Lat: 51.456350N Long: 0.040744E
Wirral Tranmere	AURN			●	332096 386644	Lat: 53.372274N Long: 3.022075W
Wolverhampton Centre	AURN			●	391368 298942	Lat: 52.588211N Long: 2.128844W

Table 1: Measurement sites, network, PM_{10} instrumentation used and location. UKEP = UK Equivalence Programme.

2.3 The Volatile Correction Model (VCM)

The correction of TEOM measurements to produce $TEOM_{VCM}$ can be summarised in three steps. The FDMS measurement equation (FDMS = FDMS base - FDMS purge) formed the basis for this and Figure 3 shows how each of the terms was substituted to derive a gravimetric reference equivalent PM_{10} measurement.

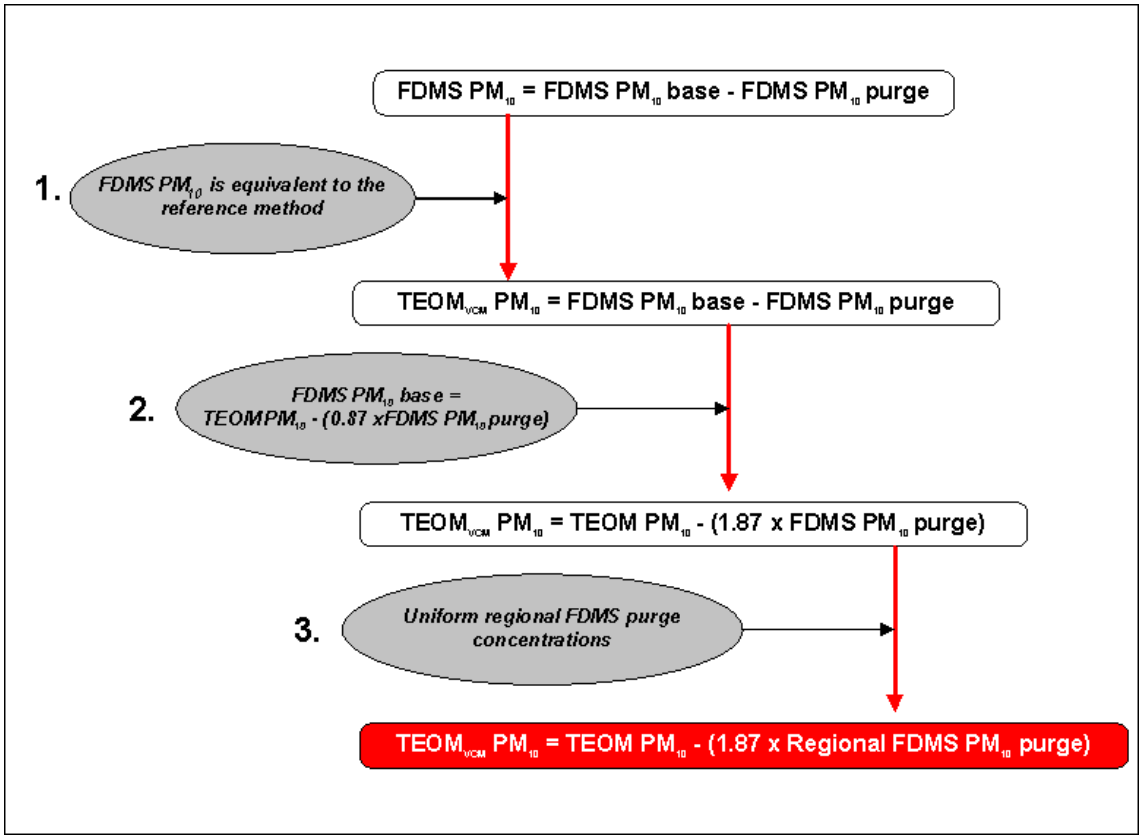

Figure 3: Stepwise derivation of the $TEOM_{VCM}$

1. The FDMS met the equivalence criteria and could therefore be considered equivalent to the method (EC, 2005; Harrison, 2006).

2. The difference between the TEOM and FDMS base measurement reflects the increased volatilisation at the higher sampling temperature of the TEOM (50 ºC) compared to the FDMS (30 ºC) and is consequently related to the FDMS purge measurement. Mignacca and Stubbs (1999) showed a clear relationship between TEOM sampling temperature (at 30 ºC, 40 ºC and 50ºC) and mass loss. The difference between the mass at 30ºC and 50ºC was 2.5 µg m^{-3}; similar to the differences experienced in the UK (Green *et al.*, 2007). 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 was undertaken for all nine sites operated between 2004 and 2006 and is shown in Table 2.

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 and Marylebone Road is a heavily trafficked environment. It was felt that including the results from Marylebone Road and Thames Road would confound the wider geographical application of the model and they were therefore excluded from the model derivation. The mean linear regression slope shown in Table 2 was therefore calculated excluding the results from Marylebone Road and Thames Road to provide a value of 0.87 (including these sites it would have been 0.71). The FDMS base concentration was therefore represented as TEOM – 0.87 FDMS purge. An alternative model parameterisation using the slope and intercept from orthogonal regression analysis was also tested but was found to perform less well than the model using the linear regression parameterisation.

Site	Slope	R^2
Acton Town Hall	1.12	0.81
Belvedere	0.63	0.5
Birmingham	0.98 (1.26 - 1.31)	0.79 (0.79 - 0.84)
Bristol	0.78 (1.34 - 1.66)	0.52 (0.42 - 0.71)
East Kilbride	0.83 (1.32 - 1.62)	0.38 (0.15 - 0.73)
Marylebone Road	0.31	0.44
North Kensington	0.8	0.65
Teddington	1.00 (1.48 - 1.57)	0.66 (0.56 - 0.77)
Thames Road	-0.06	-0.28
Mean (excluding Marylebone Road and Thames Road)	0.87	0.61

Table 2: Slope of the linear regression analysis between the FDMS purge measurements (independent variable) and (TEOM-FDMS Base) measurements (dependent variable) from each of the sites. 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); the range is shown in brackets. The mean excluded Marylebone Road and Thames Road.

3. The volatile particulate matter concentrations were found to be similar on a regional scale. This uniformity is demonstrated in Table 3, which shows mean purge concentrations from the FDMS instruments in London, these were separated by distances of up to 34 km. The mean purge concentrations differed by only 1.5 μg m^{-3} (between -4.2 μg m^{-3} and -2.8 μg m^{-3}). The large standard deviations of the daily means for the time series demonstrated the large variation in the daily mean purge concentrations. However, despite this the linear regression correlation coefficients (r^2) between the daily means at each site were very high; between 0.74 and 0.98 with an

average of 0.92 as shown in Table 3. It was therefore reasonable to assume that a single FDMS purge daily mean measurement was representative of a regional area. The size of this regional area was determined in the model tests.

	Acton Town Hall	Belvedere	Millennium Village	North Kensington	Marylebone Road	Teddington (#24431)	Teddington (#24447)	Thames Road	Westhorne Ave
n (daily means)	106	389	118	461	663	224	186	461	256
Mean µg m^{-3} ±SD	-2.9 ±2.7	-3.8 ±2.7	-2.9 ±1.8	-4.2 ±3.1	-4.0 ±2.8	-3.6 ±2.8	-3.4 ±2.8	-3.4 ±2.8	-2.8 ±3.1
Correlation Coefficients (daily means)									
Acton Town Hall	1.00								
Belvedere		1.00							
Millennium Village		0.91	1.00						
North Kensington	0.92	0.92	0.74	1.00					
Marylebone Road	0.87	0.95	0.93	0.91	1.00				
Teddington (#24431)		0.96	0.95	0.90	0.92	1.00			
Teddington (#24447)		0.96	0.97	0.85	0.91	0.98	1.00		
Thames Road	0.90	0.92	0.91	0.89	0.90	0.92	0.93	1.00	
Westhorne Ave	0.96	0.98	0.84	0.96	0.95	0.96	0.97	0.92	1.00

Table 3: Mean FDMS purge concentrations (upper) and correlation matrix of daily mean FDMS purge concentrations (lower) between 1st January 2004 and 31st December 2005. The two Teddington FDMS instruments are differentiated by the instrument serial number.

Therefore, the VCM equation is:

$$TEOM_{VCM}\ PM_{10} = TEOM\ PM_{10} - (1.87 \times Regional\ FDMS\ PM_{10}\ purge)$$

2.3.1 Model Testing

The $TEOM_{VCM}$ was treated as a candidate method and tested using the field test procedure for the demonstration of equivalence was determined by the EC Working Group on Guidance for the Demonstration of Equivalence (EC, 2005) to determine equivalence to the gravimetric reference method. The $TEOM_{VCM}$ proved equivalent to the reference method with the small deviations from this guidance recommended by Harrison (2006) for the UK Equivalence Programme. The performance of the VCM with respect to the W_{CM} and distance is shown in Figure 4. It is clear that at separation distances of up to 200 km the W_{CM} of the $TEOM_{VCM}$ remained below the 25% for both the annual and the daily limit values with the sole exception of Teddington TEOM corrected with the Westhorne Avenue FDMS purge (during the summer).

The W_{CM} for this was 28 % for both the annual and daily limit values. This was considered a marginal breach of the 25 % limit for W_{CM} given that the overwhelming majority of deployments (22 out of 23) with separation distances of less than 200 km met the criteria. This single marginal failure was not deemed suitable justification for rejection and the $TEOM_{VCM}$ was therefore deemed to meet the criteria for the reference equivalence using FDMS purge measurements from remote sites up to approximately 200 km away.

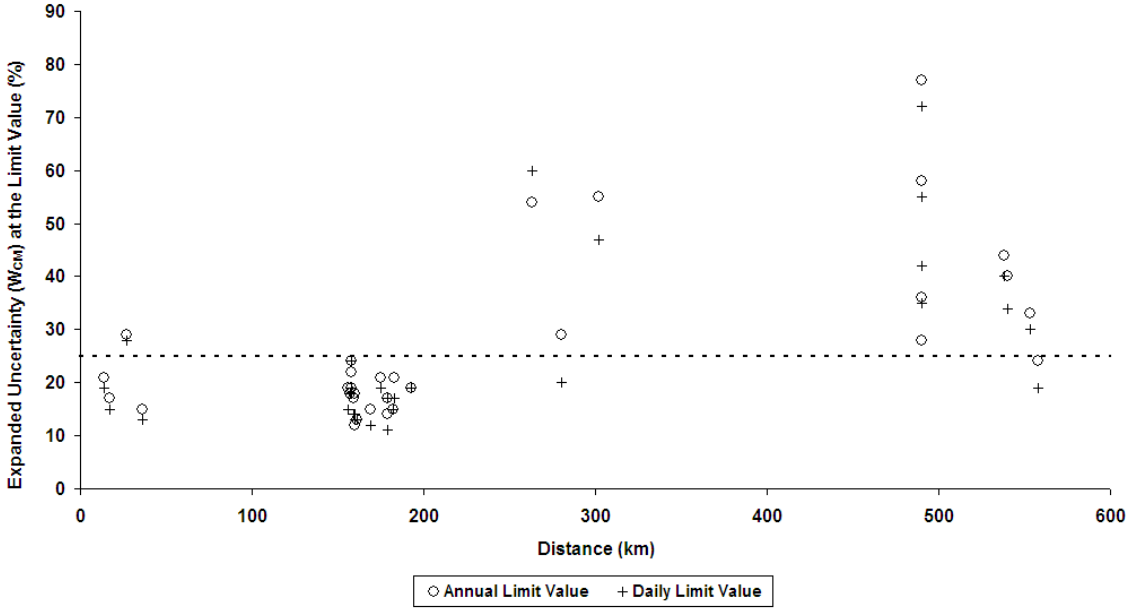

Figure 4: The relationship between W_{CM} of the $TEOM_{VCM}$ for the daily and the annual mean limit values with distance between the TEOM and FDMS sites. The data quality objective of 25 % is shown as a dotted line.

2.3.2 Chemical and physical basis for the model

The VCM used measurements of semi volatile particulate matter, made during the purge measurement cycle, from regionally deployed FDMS instruments as well as relationships derived between collocated TEOM and FDMS instruments to correct TEOM measurements to $TEOM_{VCM}$. These two areas describe loss of semi volatile particulate matter from the FDMS and TEOM filters respectively; these processes are fundamental to understanding the model.

During the purge measurement cycle, the mass lost due to the evaporation of semi volatile particulate matter tended to exceed the mass gained due to any condensation of gaseous material onto the filter; this resulted in a negative measurement in most cases. However, positive measurements were also made, indicating that adsorption was occurring during certain conditions. Nevertheless, the dominant process during this cycle was evaporation due to the semi volatile nature of many of the components of particulate matter (such as ammonium nitrate and some organic compounds). 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 completely for the vaporisation from the filter measured during the purge

cycle; a similar relationship has been found at Marylebone Road in London (Green, 2004). The evaporation of ammonium nitrate from the filter accounted completely for the purge cycle measurements in both these studies, nevertheless, influences from semi volatile organic material, cannot be discounted.

Unfortunately, measurements of semi volatile organic material were not available, however, it was possible to estimate the source strength of the semi volatile organic material by examining the concentration of secondary organic aerosol (SOA). SOA is formed through the gas phase oxidation of anthropogenic (e.g. aromatics, alkenes, alkanes and cycoalkanes) and biogenic sources (e.g. terpenes), the products then form aerosol through heterogeneous or homogeneous nucleation (Turpin *et al.*, 2000). The anthropogenic sources (e.g.diesel combustion) and many of the gas-phase oxidants involved in the reactions (e.g. OH) are the same as those responsible for the formation of ammonium nitrate. When correlating the nitrate and SOA measurements from Birmingham Harrison and Yin (2008) concluded that the main factors influencing secondary organic carbon concentrations (regional transport and semi-volatile loss) are broadly similar to those which determine fine particulate nitrate.

During a short period at the end of 2006, collocated measurements of PM_{10} using the FDMS (and hence purge measurements), elemental and organic carbon in PM_{10} using a Sunset Laboratories Carbon Aerosol Analysis Lab Instrument and nitrate in $PM_{2.5}$ using a Thermo 8400N were made at Marylebone Road; as described by Butterfield *et al.* (2007) and Green (2004) respectively. The SOA concentrations were calculated using the method described by Turpin and Huntzicker (1990) using the following equation:

$$SOA = OC - \left(\frac{OC}{EC}\right)_{prim} \times EC$$

Where $(OC/EC)_{prim}$ was the minimum OC:EC ratio for the measurement period; in this case 0.34 (close to the Birmingham roadside OC:EC ratio of 0.4 from Harrison and Yin (2008)). To account for associated oxygen and hydrogen atoms in the organic compounds, the measured organic carbon the mass of SOA was multiplied by 2.1, this is the value recommended for rural aerosol by Turpin and Lim (2001). The $PM_{2.5}$ nitrate was assumed present as NH_4NO_3 and therefore multiplied by 1.29 to give a mass of NH_4NO_3. The resulting concentrations of SOA, ammonium nitrate and PM_{10} FDMS purge measurements are shown in Figure 5. This demonstrates that the concentrations of ammonium nitrate and SOA are well correlated with the FDMS purge measurements (RMA correlation coefficients (R) of 0.66 and 0.74 respectively). However, it is clear that the SOA concentration is greater than the concentration of semi-volatile organic material that is likely to be influencing the FDMS purge concentrations. This is due to the gas-particle partitioning of semi-volatile organic material and is influenced by ambient and sampling temperature, pressure drop across the filter, aerosol water concentration, particle concentration, particle surface area, particle organic matter concentration and gas concentration

(Turpin *et al.*, 2000). It is worth noting that the largest peak in SOA occurs on 5th November (Guy Fawkes night), there nevertheless appear to be high concentrations of ammonium nitrate and SOA.

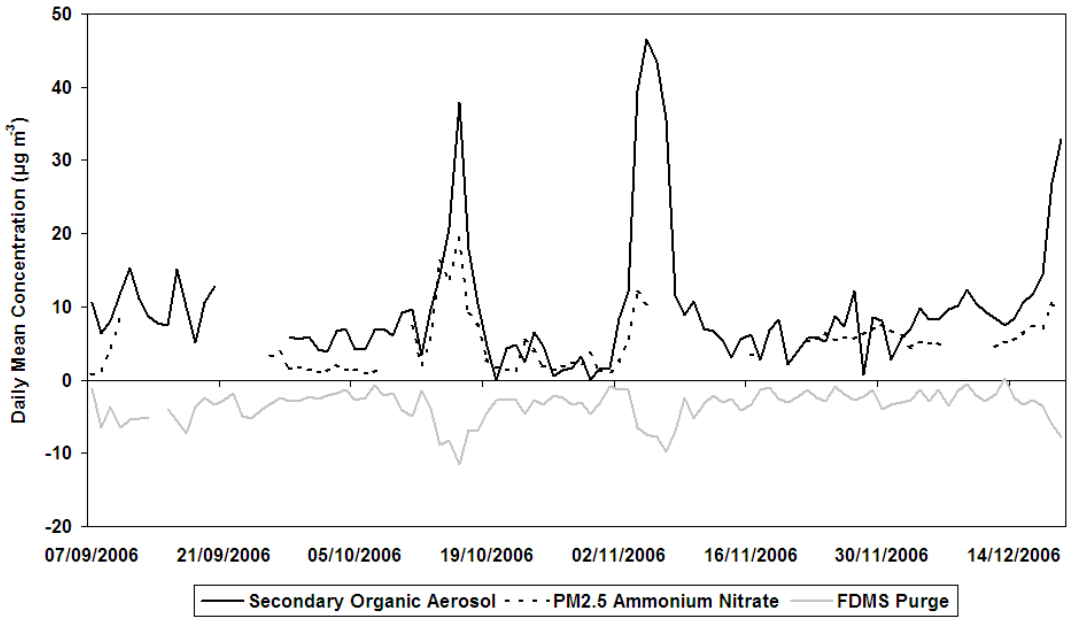

Figure 5: Time series of daily mean secondary organic aerosol (SOA), ammonium nitrate in $PM_{2.5}$ and PM_{10} FDMS purge measurements made at Marylebone Road between 7th September and 14th December 2006.

The influence of water due to condensation on the filter was expected to be minimal, as the dew point of both the TEOM and FDMS measurement filters remain low. The FDMS sample dew point was measured (at Marylebone Road between 2004 and 2006 the range was -11.7 to 1.8 ºC) and was constantly below the ambient dew point. The dew point of the TEOM filter at Marylebone Road was calculated every hour between 2004 and 2006 using the temperature and relative humidity recorded by the FDMS. The dew point at the filter was in the range -79 to 17 ºC and was at least always 20 ºC lower than the ambient temperature. However, influences from the evaporation of particle bound water after collection cannot be discounted.

The uniformity of the FDMS purge measurements between roadside and background sites demonstrated in Table 3 is perhaps surprising given the semi volatile nature of primary organic emissions (Robinson *et al.*, 2007). However, the 30 ºC sampling temperature of the FDMS may lead to the partition of these emissions into the gaseous phase.

The relationship derived between collocated TEOM and FDMS base measurements is also fundamental to the model. As discussed, the disparity between the FDMS base measurement and the TEOM measurement methodology existed predominantly in the sampling regime. There were three differences between the instruments in this area:

1. The FDMS switched between the base and purge measurement cycles every six minutes. It therefore only sampled ambient air for the base measurement only 50 per cent of the time.

2. The FDMS used a diffusion drier in the sample stream to remove particle bound water.

3. The FDMS heated the sample stream to 30 ºC, rather than the 50 ºC used by the TEOM, to provide a stable temperature environment for the microbalance.

Over shorter time periods and in rapidly changing environments, such as close to major roads, this switching may induce noise in this relationship. However, over the long time period and at the urban locations used in this study the 50 per cent sampling time of the FDMS was considered to be representative of ambient concentrations.

The diffusion dryer impacts on the chemical and physical characteristics of the sample. As well as removing water, the dryer removes other compounds such as alcohols, ammonia and amines. It can also convert carbonyl groups (-C=O) into hydroxyl groups through acid catalysis enolization and remove the compound in this way (PermaPureLLC, 2006). Furthermore, some attenuation of particles is recognised to occur in the dryer due to diffusional losses (small particles) and impaction (large particles) (Dick *et al.*, 1995). The impact of the dryer is difficult to quantify but may be responsible for some of the differences demonstrated at Marylebone Road and Thames Road that have a higher proportion of coarse particles ($PM_{2.5}$-PM_{10}) than other sites due to their kerbside and construction influenced environments respectively.

The major difference between the FDMS and TEOM instruments that affected mass concentrations was therefore the difference in sampling temperature. Semi volatile particulate matter that was volatile at 50 ºC but not at 30 ºC would have been measured by the FDMS but not by the TEOM; this is likely to be the same components identified as influencing the FDMS purge measurement.

Grover *et al* (2005) examined the difference between the TEOM and the total FDMS mass measurements alongside measurements of the ammonium nitrate and semi volatile organic material. The difference was mostly explained by ammonium nitrate measurements (as it is in this model), the remainder was accounted for (but in many samples shown to be less than) the measured semi volatile organic material. As the purge measurement was demonstrated to represent the ammonium nitrate concentration, the difference between the TEOM and the FDMS base measurements (described in the model as 0.87 times the purge measurement) may correspond to the semi volatile organic material measured by the FDMS base at 30 ºC but not by the TEOM at 50 ºC due to the gas-particle portioning effects described earlier. The model succeeded in describing the total mass difference as a function of the purge measurement as a large fraction of the semi volatile organic material, like ammonium nitrate, is secondary in origin (Turpin and Lim, 2001). Measurements of the semi volatile organic material and ammonium

nitrate are therefore key to providing a full understanding the difference between the two measurement techniques.

2.4 Statistical approaches

Several statistical approaches are used here in common with the field test procedure for the demonstration of equivalence as determined by EC Working Group on Guidance for the Demonstration of Equivalence (EC, 2005). We have sought to demonstrate:

1. The applicability of the VCM to hourly mean concentrations, for which there are no gravimetric reference measurements and there was no Limit Value pertaining.

2. Whether the AURN FDMS purge measurements were suitable for use in the VCM. The statistical approaches were therefore used to assess uncertainty rather than as part of the demonstration of equivalence.

2.4.1 Combined relative expanded uncertainty at the Limit Value (W_{CM})

The W_{CM} of the candidate ($TEOM_{VCM}$) measurements from the reference (FDMS) measurements 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 as described in EC Working Group on Guidance for the Demonstration of Equivalence (EC, 2005).

2.4.2 Between purge uncertainly (u_{purge})

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

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

Where:

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

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

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

2.5 Hourly mean $TEOM_{VCM}$ compared to hourly mean FDMS measurements

The $TEOM_{VCM}$ was treated as a candidate method and tested at an hourly mean resolution against the FDMS measurements in four steps, each used measurements made in the monitoring programmes listed in Section 2.2. In each case the model was tested against the criteria in the EC Working Group on Guidance for the Demonstration of Equivalence (EC, 2005). No reference methodology existed for hourly measurements. FDMS measurements were therefore used as the equivalent hourly reference measurement as they demonstrated the lowest W_{CM} in the UK Equivalence Programme (Harrison, 2006). As there was no gravimetric reference measurement, the 25 % W_{CM} threshold was only considered indicative of equivalence. As no Limit Value is set for hourly mean concentrations, the daily mean Limit Value concentration of 50 µg m^{-3} was used as an input into the W_{CM} calculation.

2.5.1 Testing the $TEOM_{VCM}$ at an hourly time resolution excluding the geographical aspects

This analysis was designed to test the equivalence of the $TEOM_{VCM}$ for hourly mean concentrations against the FDMS, *excluding* the regional aspects. This used measurements from collocated pairs of FDMS and TEOM instruments from the UK Equivalence Programme.

If we consider each equivalence site as having two TEOMs (A and B) from the 'home' site and two FDMS (C and D), also from the home site, we have four possible pairs of modelled hourly mean time series to test at each site:

$$TEOM_{VCM}\ PM_{10}\ 1A = TEOM\ PM_{10}\ A - 1.87\ FDMS\ PM_{10}\ purge\ C$$

$$TEOM_{VCM}\ PM_{10}\ 1B = TEOM\ PM_{10}\ B - 1.87\ FDMS\ PM_{10}\ purge\ C$$

$$TEOM_{VCM}\ PM_{10}\ 2A = TEOM\ PM_{10}\ A - 1.87\ FDMS\ PM_{10}\ purge\ D$$

$$TEOM_{VCM}\ PM_{10}\ 2B = TEOM\ PM_{10}\ B - 1.87\ FDMS\ PM_{10}\ purge\ D$$

$$TEOM_{VCM}\ PM_{10}\ 3A = TEOM\ PM_{10}\ A - 1.87\ FDMS\ PM_{10}\ purge\ C$$

$$TEOM_{VCM}\ PM_{10}\ 3B = TEOM\ PM_{10}\ B - 1.87\ FDMS\ PM_{10}\ purge\ D$$

$$TEOM_{VCM}\ PM_{10}\ 4A = TEOM\ PM_{10}\ A - 1.87\ FDMS\ PM_{10}\ purge\ D$$

$$TEOM_{VCM}\ PM_{10}\ 4B = TEOM\ PM_{10}\ B - 1.87\ FDMS\ PM_{10}\ purge\ C$$

Each pair of $TEOM_{VCM}$ PM_{10} 24 hour mean time series were subjected to the full equivalence test criteria (a total of 48 combinations).

2.5.2 Testing the $TEOM_{VCM}$ at an hourly time resolution including the geographical aspects

This analysis was designed to test the equivalence of the $TEOM_{VCM}$ for hourly mean concentrations against the FDMS, *including* the regional aspects. This used measurements from the collocated pairs of FDMS and TEOM instruments from the UK Equivalence Programme as described in section 2.5.1. However, the home TEOM measurements were corrected using FDMS purge measurements from remote sites; the 'away' sites.

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

$$TEOM_{VCM}\ PM_{10}\ 1A = TEOM\ PM_{10}\ A - 1.87\ FDMS\ PM_{10}\ purge\ Z$$

$$TEOM_{VCM}\ PM_{10}\ 1B = TEOM\ PM_{10}\ B - 1.87\ FDMS\ PM_{10}\ purge\ Z$$

The W_{CM} was calculated for each pair of $TEOM_{VCM}$ PM_{10} hourly mean time series (a total of 96 combinations). To aid the determination of the spatial applicability of the VCM the distance between each home and away site was also calculated.

2.5.3 Optimising the averaging time for the FDMS purge measurement

This analysis was designed to optimise the averaging period of the FDMS purge measurement used in the VCM.

In the initial development, the VCM was tested using daily mean concentrations; this smoothed the inherent spatial heterogeneity of the FDMS purge measurements. This variation leads to hourly FDMS purge measurements at one location, which are less representative of those at the limits of the model domain (up to 200 km away) than daily mean measurements. Conversely, the averaging period chosen also has to remain representative of the local hourly mean FDMS concentrations for the VCM to work over short distances.

To assess the competing effects of different averaging periods on VCM calculations using home and away FDMS purge measurements, a preliminary linear regression analysis study was undertaken. This allowed the later, more complex W_{CM} calculation to focus on the relevant averaging periods. A subset of the measurements was used during this preliminary analysis. February 2005 was chosen as this period included an episode characterised by long range transport, and hence volatile, particulate. It is important that the model can accurately account for these high concentrations over large distances. This analysis was made up of two parts:

1. Linear regression analysis of the hourly mean FDMS purge concentrations at Teddington and a rolling mean with an increasing averaging time (from 1 and 24 hours) of the purge concentrations from the same site.

2. Linear regression analysis of the hourly mean FDMS purge concentrations at Teddington and a rolling mean with an increasing averaging time (from 1 and 24 hours) of the purge concentrations from Birmingham (158 km distant).

The results of both these analyses are shown in Figure 6.

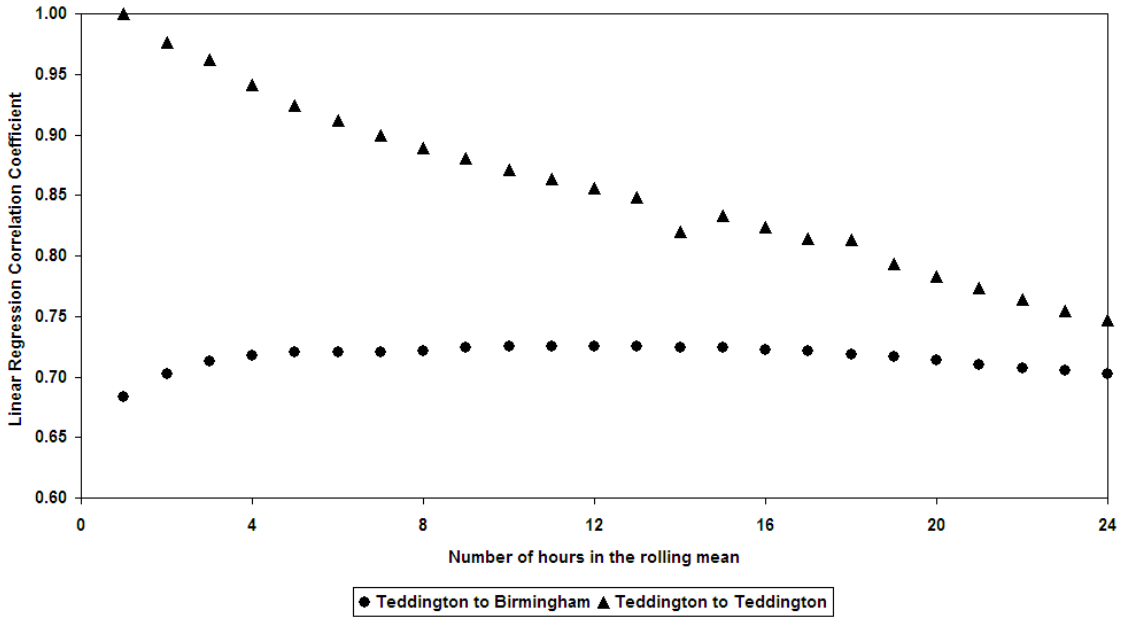

Figure 6: Linear regression correlation coefficients from a comparison of hourly mean FDMS purge concentrations at Teddington and FDMS purge concentrations from both Teddington and Birmingham with increasingly longer rolling mean. Measurements made during February 2005

Over a long distance (Teddington to Birmingham) the linear regression correlation coefficients in Figure 6 increased when the averaging period was increased up to four hours; after which the correlation coefficients plateaued. However, the analysis of collocated measurements showed that the linear regression correlation coefficients decreased rapidly with increased averaging time. Given this, the test should focus on rolling mean purge concentrations over 1 to 8 hours. Therefore, to assess the impact of these counteracting influences the W_{CM} was calculated for each pair of $TEOM_{VCM}$ hourly mean time series with an increasing number of hours in the rolling average, up to 8 hours (a total of 1176 combinations), for example:

$$TEOM_{VCM(2h)}\ A = TEOM\ PM_{10}\ A - 1.87 \times 2\ hour\ rolling\ mean\ FDMS\ PM_{10}\ purge\ Z$$

$$TEOM_{VCM(2h)}\ B = TEOM\ PM_{10}\ B - 1.87 \times 2\ hour\ rolling\ mean\ FDMS\ PM_{10}\ purge\ Z$$

2.5.4 Utilising the average of the FDMS purge measurements from up to three sites within 200 km at the optimised FDMS purge averaging time

This analysis was designed to test the final application of the VCM in the field.

When applied in the field, the VCM will correct the TEOM measurements from the home site using the FDMS purge concentrations from three away sites to produce $TEOM_{VCM}$. The average of three away sites at this distance was chosen because:

1. 200 km was the maximum distance between sites that the $TEOM_{VCM}$ passed the equivalence criteria in the first report (Green *et al.*, 2007)

2. Allows the VCM to operate when one or two FDMS instruments malfunction. Assuming a 90% data capture (randomly distributed) the VCM would produce a $TEOM_{VCM}$ 99.9 % of the time.

3. In the event of more than 3 instrument being available, choosing the three closest, rather than all sites less than 200 km, will ensure that the FDMS purge measurements are as representative of local sites as possible.

Again, if we consider each equivalence site as having two TEOMs (A and B), which we seek to 'correct' using the optimised rolling model mean ($\bar{z}$),(derived from the analysis described in section 2.5.3) and the contemporaneous hourly mean concentration from up to three away sites (Z_1, Z_2 and Z_3), we can produce the following $TEOM_{VCM}$ time series for each of the equivalence deployments.

$$TEOM_{VCM}\ PM_{10}\ 1A = TEOM\ A - 1.87\bar{z}$$

$$TEOM_{VCM}\ PM_{10}\ 1B = TEOM\ B - 1.87\bar{z}$$

Where:

$$\bar{Z} = \frac{1}{n}\sum_{i}^{n} Z_i \quad where \quad n \leq 3$$

The W_{CM} was calculated for each pair of $TEOM_{VCM}$ PM_{10} hourly mean time series (a total of 48 combinations). To aid the determination of the spatial applicability of the hourly $TEOM_{VCM}$, two distance parameters were calculated:

1. d_{mean}, the mean distance between each home and three away sites.

2. d_{max}, the furthest distance between the home site and any of the three away sites.

2.6 Review of the FDMS purge measurements from the first phase AURN deployment

This analysis was designed to determine if Defra's 2007 FDMS deployment would allow the VCM to be applied to all current UK AURN and local authority TEOM instruments. The analysis in the first report used measurements from the four UK Equivalence Programme sites to demonstrate that the $TEOM_{VCM}$ was equivalent to the gravimetric reference method (Green *et al.*, 2007). Unfortunately, gravimetric reference measurements of a similar quality were not available to test the ongoing equivalence of the $TEOM_{VCM}$. This lack of measurements was known at the time of writing the first report, consequently, a method of predicting W_{CM} was developed by comparing u_{purge} to W_{CM} to derive a u_{purge} at which the 25 % W_{CM} threshold would be breached; Figure 7 shows the results of this analysis. This demonstrated that $TEOM_{VCM}$ W_{CM} remained below 25% (except the Teddington to Westhorne Ave outlier) when the u_{purge} remained below 1.5 µg m^{-3}. A u_{purge} above 1.5 µg m^{-3} could therefore be assumed to lead to a $TEOM_{VCM}$ W_{CM} greater than the 25 % data quality objective.

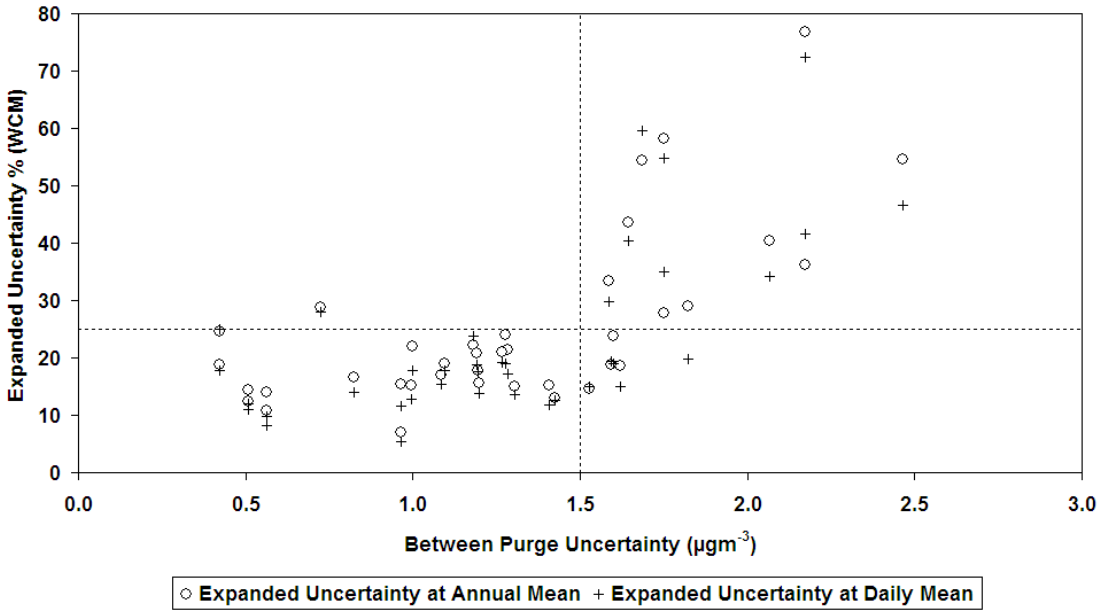

Figure 7: Scatter plot showing the u_{purge} and the $TEOM_{VCM}$ W_{CM} for the daily and annual mean limit values for the UK Equivalence Programme sites from Green *et al* (2007). The data quality objective of 25 % is shown as a dotted line.

2.6.1 Application of the VCM to AURN measurements at daily mean concentrations

The u_{purge} was calculated between each pair of FDMS sites and compared to the distance between sites. According to the equation shown in section 2.4.2.

2.6.2 Application of the model to AURN measurements at the three closest FDMS instruments under 200 km

To encompass the application of the model in the field the u_{purge} calculation was modified to use the home purge measurement and three FDMS instruments under 200 km distant (away sites). Therefore $p_{i,2}$ in the equation in section 2.4.2 is substituted with $\bar{p}_{i,2}$:

$$\bar{p}_{i,2} = \frac{1}{n}\sum_{i}^{n} p_i \quad where \quad n(sites) \leq 3$$

2.6.3 Feasibility of applying the VCM to correct AURN and local authority TEOMs

d_{mean} and d_{max} of the TEOMs currently in the AURN was calculated. It is acknowledged that the AURN is under review at the time of writing; this list is therefore restricted to sites on the AURN that used a TEOM to measure PM_{10} on 1st January 2008.

Furthermore, the feasibility of applying the VCM to correct local authority TEOMs was investigated. It was difficult to attain accurate geographical locations for all the local authority sites in the UK, a blanket approach was therefore taken to calculate all the locations in the UK that may require additional monitoring using FDMS instruments to use the VCM. This was achieved by assuming there was a local authority TEOM at the centre of every 1 km grid square in the UK. The d_{mean} and d_{max} of the TEOMs currently in the AURN and the three closest FDMS sites less than 200 km distant was calculated. If three FDMS sites were not within 200 km then the VCM was deemed not to be applicable for that 1 km grid square.

3 RESULTS AND DISCUSSION

This section details an examination of the AURN FDMS purge measurements and discusses the results of the uncertainty tests described in the method sections 2.5 and 2.6; these included 3,504 calculations of $TEOM_{VCM}$ W_{CM} and 9,091 calculations of u_{purge}.

3.1 AURN FDMS purge measurements

An additional sensibility check was made of the measurements provided by AEA Energy and Environment to ensure that the data the VCM used was representative of ambient conditions. This was based on FDMS purge ratification procedures developed by King's for the LAQN. This led to several additional periods of measurement being excluded from the dataset prior to analysis, these are listed in Table 4. Details of these periods were passed to the QA/QC unit so that they can review the measurements before the final ratification deadline for 2007 of 31st March 2008. Mostly, the type of faults identified in this dataset, especially those characterised by erratic and / or positive measurements, have been experienced on the LAQN and generally result from poorly fitted purge filters.

However, the Reading New Town site has a more serious problem that causes it to measure purge concentrations up to 5 µg m^{-3} lower than other sites. In the LAQN systematic differences over 1.5 µg m^{-3} are considered worthy of further investigation. The FDMS purge measurements made at Reading New Town were compared to the mean of the measurements made in the LAQN in Figure 8; the LAQN mean is made up of 11 FDMS sites. Again, this is a problem that has been previously identified in sites in the LAQN and is only quantifiable by comparing purge measurements between sites, as none of the instrument diagnostics, on-site LSO checks or on-site audits detect the problem. Replacing the dryer membrane has rectified malfunctions such as this and has been carried out on five instruments in the LAQN. The Reading New Town site has therefore not been included in this analysis.

Site	Start time	End time	Justification for excluding purge measurements
Hull Freetown	10/05/07 15:00	11/05/07 13:00	Filter equilibrating after filter change.
Leicester Centre	03/04/07 14:00	11/06/07 13:00	Positive measurements with a strong diurnal cycle. Some data already excluded by QA/QC unit.
Manchester Piccadilly	25/06/07 07:00	03/07/07 11:00	Erratic measurements of a magnitude far in excess of other sites, stops following filter change
Newcastle Centre	21/02/07 14:00	26/02/07 19:00	Erratic and positive measurements between installation and first filter change
Reading New Town	20/04/07 07:00	01/01/08 00:00	The FDMS purge measurements were up to 5 µg m^{-3} lower than the mean of the surrounding sites.
Southend-on-sea	11/04/07 06:00	20/04/07 12:00	Erratic measurements between filter changes.
Southend-on-sea	26/05/07 06:00	29/05/07 16:00	Sample dew point increased above the recommended 2 ºC.
Swansea Roadside	17/01/07 14:00	05/03/07 12:00	Erratic and positive measurements between filter changes

Table 4: Measurements excluded from the supplied dataset before analysis

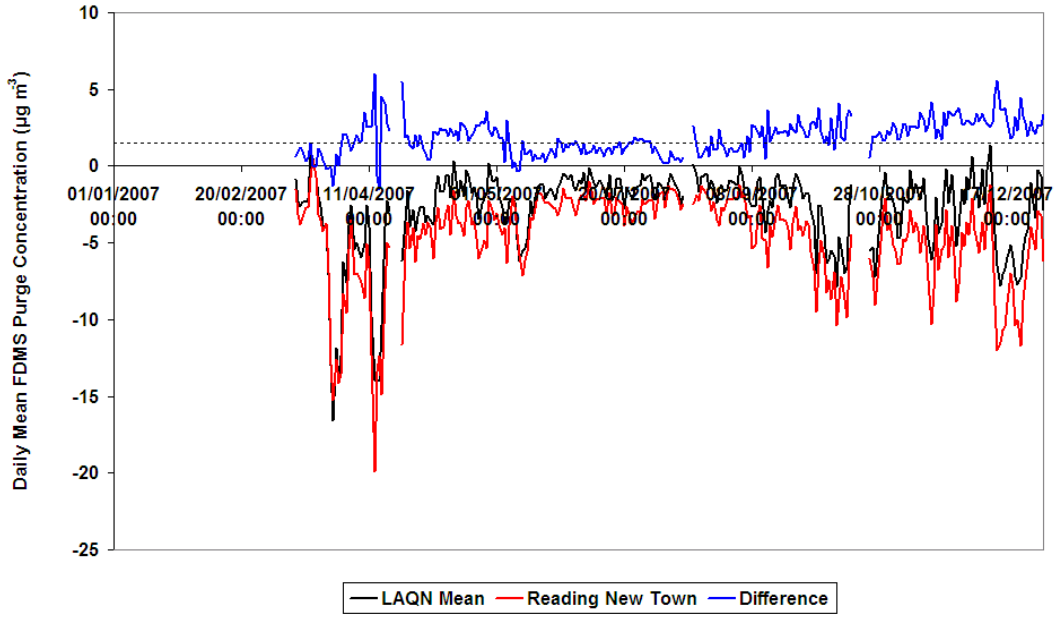

Figure 8: Time series graph showing the daily mean FDMS purge measurements made at Reading New Town and the mean of all the PM_{10} FDMS purge measurements made in the LAQN during 2007 and the difference between the Reading New Town and LAQN mean measurements. The dotted at 1.5 µg m^{-3} represents the maximum deviation expected between sites in the LAQN.

3.2 $TEOM_{VCM}$ hourly mean compared to FDMS hourly mean measurements

This set of tests followed a stepwise approach to examine the impact of using the VCM at an hourly time resolution. The hourly $TEOM_{VCM}$, comprising inputs from the TEOM at the equivalence site and the FDMS purge measurements from the equivalence and LAQN sites, were compared to the FDMS PM_{10} mass measurements from the equivalence site using the full equivalence methodology described in EC Working Group on Guidance for the Demonstration of Equivalence (EC, 2005).

3.2.1 Testing the VCM at an hourly time resolution excluding the geographical aspects

This compared the hourly mean FDMS measurements at equivalence sites with hourly mean $TEOM_{VCM}$ concentrations and used FDMS purge concentrations from the same equivalence site as described in section 2.5.1. The results are shown in full in Table 9 and Table 10; a summary is presented in Figure 9.

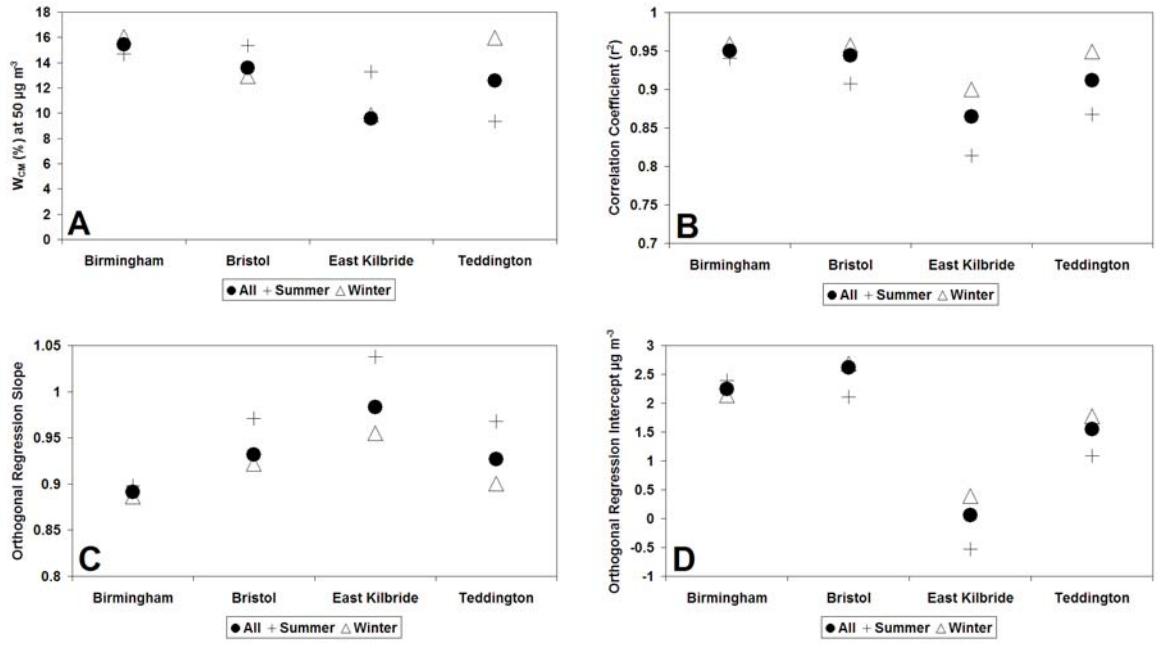

Figure 9: Summary of the results from section 3.2.1, the comparison between the hourly mean $TEOM_{VCM}$ concentrations and the hourly mean FDMS PM_{10} measurements at the four UK equivalence sites. A is the W_{CM} at 50 µg m^{-3}, B is the orthogonal regression correlation coefficient, C is the orthogonal regression slope and D is the orthogonal regression intercept. All points are the mean of the four combinations.

The VCM performed well at all sites and the W_{CM} between the $TEOM_{VCM}$ and the FDMS on an hourly basis at all sites and during all seasons were low. The mean $TEOM_{VCM}$ concentrations differed from the FDMS measured concentration for each potential combination by between -2.1 and 1.1 µg m^{-3}; the mean difference was -0.3 µg m^{-3} (σ = 0.6 µg m^{-3}); the mean difference is therefore not significant at a 95 % confidence interval. The W_{CM} of the $TEOM_{VCM}$ at 50 µg m^{-3} was generally low, the mean of all 48 tests was 13 % (σ = 4 %). The W_{CM} was between 5 and

18 % except for the summer at East Kilbride, which resulted in a W_{CM} of 29 %, which utilised the purge measurements from FDMS 04443. A closer look at the measurements from this instrument reveals that there were large positive and negative deviations in these purge measurements before and after gaps in the data; these are indicative of instrument malfunction and / or poor purge filter conditioning. On one occasion the FDMS 04443 hourly mean purge concentration descended to -36 µg m^{-3} while the other instrument remained at -5 µg m^{-3}. This individual comparison can therefore be discounted.

The results of the orthogonal regression analysis yielded slopes between 0.88 and 1.16 with a mean of 0.94 (σ = 0.05); this was not significant at a 95 % confidence interval. The intercept varied between -2.59 and 3.16 µg m^{-3}, the mean was 1.54 µg m^{-3} (σ = 1.18 µg m^{-3}); this was not significant at a 95 % confidence interval. The mean correlation coefficient was 0.91 (σ = 0.05), this varied between 0.66 and 0.96. Again, the single comparison using FDMS 04443 at East Kilbride was an exception; removing this from the comparison yielded a mean slope of 0.93 (σ = 0.04, min = 0.88, max = 1.03), a mean intercept of 1.63 µg m^{-3} (σ = 1.02, min = -1.36 µg m^{-3}, max = 3.16 µg m^{-3}) and a mean correlation coefficient of 0.92 (σ = 0.04, min = 0.78, max = 0.96). Neither the slope nor the intercept were significant at a 95 % confidence interval.

3.2.2 Testing the VCM at an hourly time resolution including the geographical aspects

This compared the hourly mean FDMS measurements at equivalence sites with the hourly mean $TEOM_{VCM}$ concentrations, which used FDMS purge concentrations from away sites as described in section 2.5.2. The results are summarised in Figure 10. The aim of this and the following set of tests was to demonstrate the applicability of the VCM at an hourly time resolution and to optimise the parameters used in its application, rather than to demonstrate equivalence. Therefore, results for the entire monitoring period are reported rather than split into summer and winter.

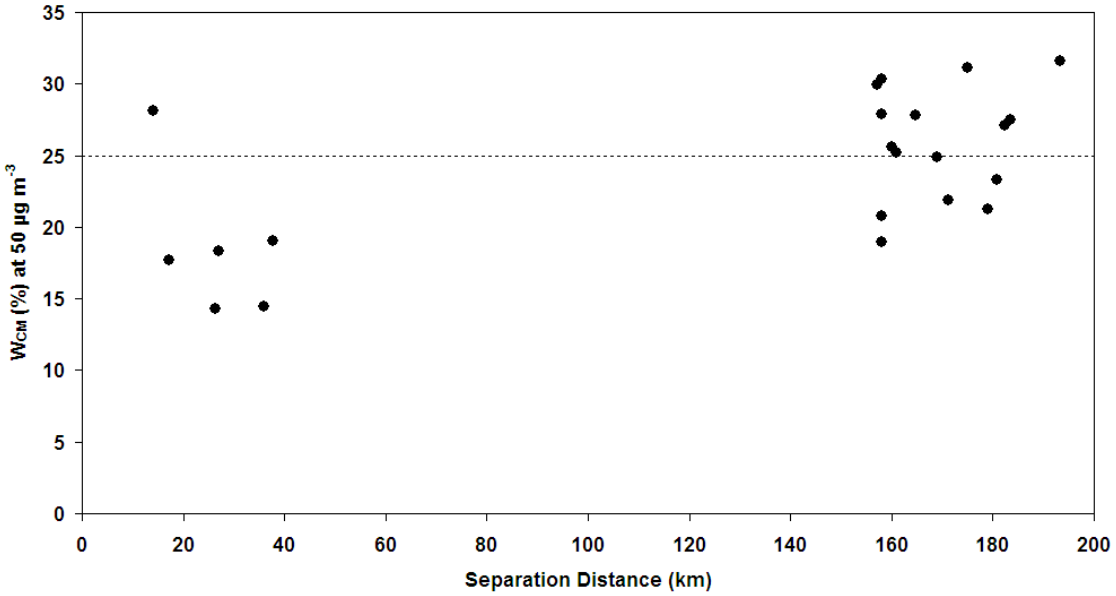

Figure 10: Scatter plot showing the W_{CM} at 50 µg m^{-3} for the hourly mean FDMS measurements at equivalence sites with hourly mean $TEOM_{VCM}$ concentrations using one hour mean FDMS purge concentrations from single away sites.

Due to the spatial distribution of the UK Equivalence Programme and LAQN sites these calculations resulted in two clusters of distances. The sites with a separation distance of less 40 km distance were the comparisons between Teddington FDMS measurements and the $TEOM_{VCM}$ using Teddington TEOM measurements and purge measurements from the neighbouring London sites. The sites with a distance between 150 and 200 km were:

1. Those that use Birmingham or Bristol FDMS and the $TEOM_{VCM}$ using Birmingham or Bristol TEOM measurements and purge measurements from the London sites.

2. Those that use Teddington FDMS measurements and the $TEOM_{VCM}$ using Teddington TEOM measurements and purge measurements from Birmingham.

At distances of less than 40 km the $TEOM_{VCM}$ produced a W_{CM} at 50 µg m^{-3} between 14 and 28 %. This is within the 4 - 29 % range produced when the instruments were collocated. The $TEOM_{VCM}$ that used the Teddington TEOM and the North Kensington FDMS was a single clear outlier at 28%. A closer examination of the FDMS measurements from North Kensington showed a degree of variation in the hourly mean purge concentrations that was not present in other hourly mean purge measurements. This variation led to the increased uncertainty displayed in Figure 10 but was not manifested in the comparison at daily time resolution (Green *et al.*, 2007) and was therefore assumed to be a random noise artefact.

At sites with a distance between 150 and 200 km the comparison between $TEOM_{VCM}$ and the FDMS PM_{10} measurements at the equivalence sites led to a larger W_{CM}; between 19 and 32 %. This was unsurprising given the greater heterogeneity of the air masses across this distance.

3.2.3 Optimising the averaging time for the FDMS purge measurement

This analysis compared the hourly mean FDMS measurements at equivalence sites with hourly mean $TEOM_{VCM}$ concentrations which used rolling mean FDMS purge concentrations from away sites with averaging times between one and eight hours, $TEOM_{VCM(1h)}$ to $TEOM_{VCM(8h)}$, as described in section 2.5.3.

This analysis produced the $TEOM_{VCM}$ W_{CM} between 21 different site combinations over 20 different distances for each of the eight hours; a total of 3360 tests. These have been summarised in Figure 11 by grouping them into 10 km distance bins and plotting them with increasing FDMS purge averaging time. Although there was not a clear linear relationship between W_{CM} and distance, there was a tendency for comparisons performed over a larger distance to produce larger uncertainties. Figure 11 shows that after four hours the 0 to 40 km comparisons are grouped in the 13-18 % W_{CM} range while the comparisons in the 150-200 km range are grouped in the 25-30 % W_{CM} range.

In Figure 6 the correlation coefficient between local sites was shown to decrease with an increased averaging time, while the correlation coefficient between away sites was shown to increase. Some of these effects are apparent in the W_{CM} in Figure 11. The W_{CM} for the sites separated by between 150 and 200 km all reduced as the number of hours incorporated in the rolling mean increased. However, at the sites separated by less than 40 km only those less than 10 km apart and those between 20 and 30 km apart showed the expected rise in W_{CM}. The other two distance bins below 40 km showed a reduction in W_{CM}. The 10-20 km bin contained the Teddington and North Kensington combination and as discussed in section 3.2.2, the North Kensington FDMS purge measurements displayed a large degree of noise in the hourly mean purge concentration. This noise in the hourly mean purge concentration would reduce as the averaging time increased and would therefore explain the decrease in the W_{CM}. The 30-40 km bin contained the Teddington and Thames Road combination, an examination of the Thames Road FDMS purge measurements shows some noise but to a lesser degree than that seen at North Kensington, nevertheless, this would explain the initial decrease in W_{CM} as averaging time increased. Therefore an additional benefit of increasing the averaging time would be to reduce the impact of hour-by-hour noise in one instrument when compared to another.

Overall, the reductions in W_{CM} with increasing averaging time were modest; they were clearly largest over the first few hours after which any improvement tailed off. To obtain the optimum number of hours for the rolling average, the rolling average that provided the minimum W_{CM} for each of the nine different distance bins was calculated and is indicated by a black dot in Figure

11. These ranged between one and seven hours; the mean was four hours. $TEOM_{VCM(4h)}$ was therefore chosen as the optimum configuration for the model.

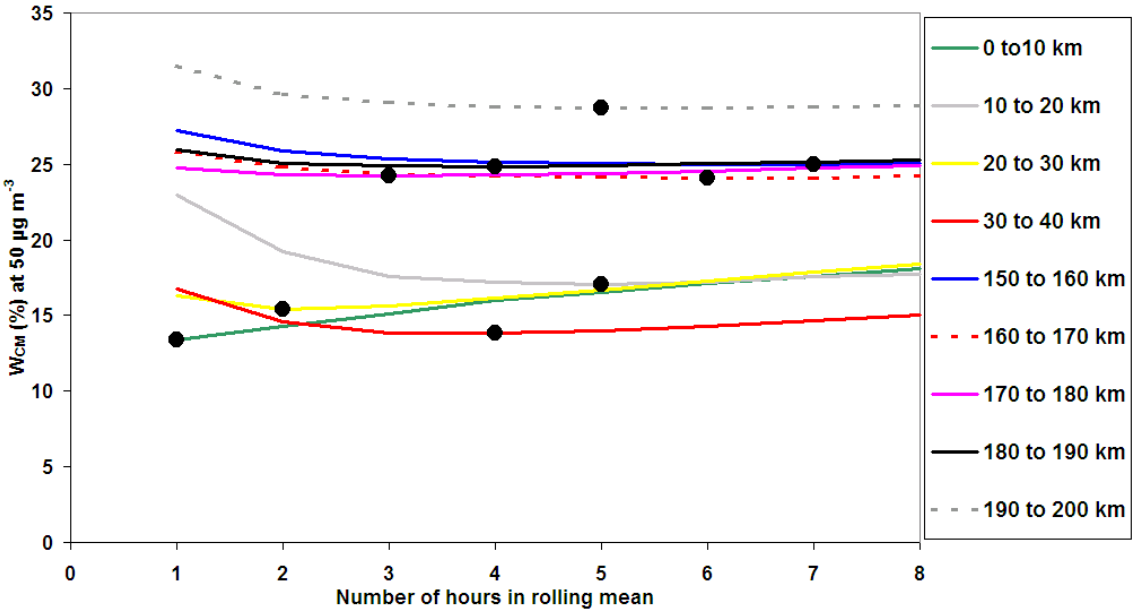

Figure 11: W_{CM} at 50 µg m^{-3} for the hourly mean FDMS measurements at equivalence sites with $TEOM_{VCM(1h)}$ to $TEOM_{VCM(8h)}$. Results were averaged in 10 km distance bins. The black dots indicate the rolling mean that had the lowest W_{CM} for each distance bin.

To calculate the change in W_{CM} (ΔW_{CM}) that would result from $TEOM_{VCM(4h)}$ compared to $TEOM_{VCM(1h)}$, the ΔW_{CM} ($\Delta = TEOM_{VCM(4h)} W_{CM} - TEOM_{VCM(1h)} W_{CM}$) was calculated and is shown in Figure 12. ΔW_{CM} was between +3 and -11 %, the mean ΔW_{CM} is -1%. This was a modest reduction and the use of the $TEOM_{VCM(4h)}$ should be carefully considered as this would result in an inconsistency between the hourly and daily resolution of the VCM. It is clearly desirable for the two time resolutions to be compatible so that the hourly modelled concentrations are the same as the daily modelled concentrations.

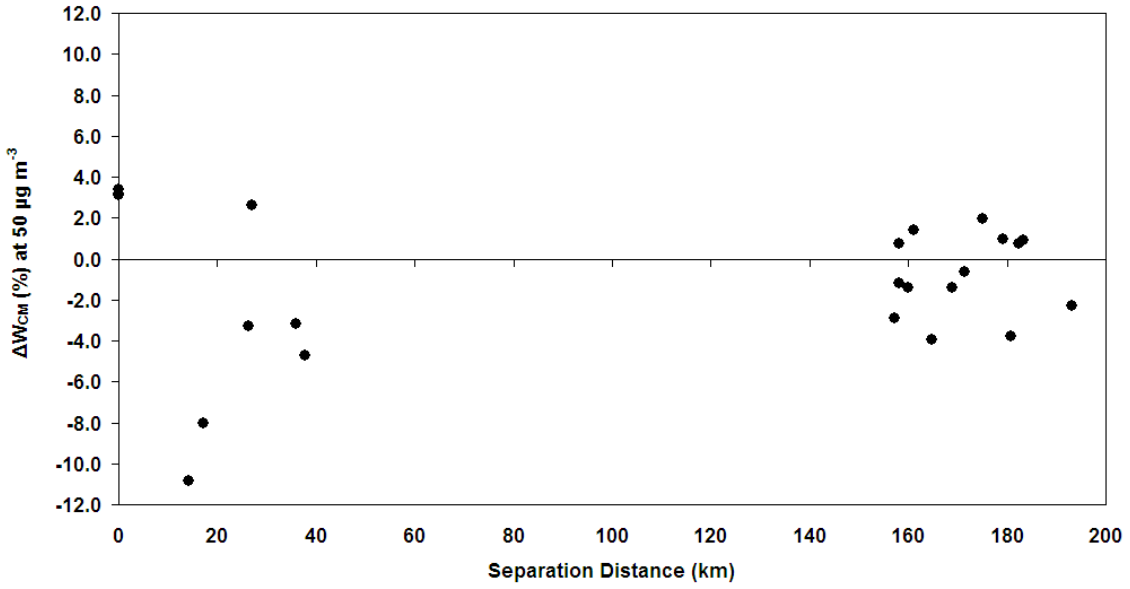

Figure 12: Scatter plot showing the difference (Δ) between the W_{CM} at 50 µg m^{-3} for the hourly mean FDMS measurements at the home equivalence sites with $TEOM_{VCM(4h)}$ and $TEOM_{VCM(1h)}$. Δ = $TEOM_{VCM(4h)}$ W_{CM} – $TEOM_{VCM(1h)}$ W_{CM}.

3.2.4 Utilising the average of the FDMS purge measurements from up to three sites within 200 km

This analysis calculated the W_{CM} using the hourly mean FDMS measurements at equivalence sites (home) and the hourly mean $TEOM_{VCM}$ concentrations using the mean FDMS purge concentrations from the three away sites and was described in section 2.5.4. This analysis was undertaken using $TEOM_{VCM(1h)}$ and $TEOM_{VCM(4h)}$; this is the optimised rolling mean from section 3.2.3.

Figure 13 shows the $TEOM_{VCM(1h)}$ W_{CM} at 50 µg m^{-3} with the hourly mean FDMS measurements at equivalence sites. These ranged between 10 and 32 %, the mean was 19 %. Figure 14 shows the $TEOM_{VCM(4h)}$ W_{CM} at 50 µg m^{-3} with the hourly mean FDMS measurements at equivalence sites. These ranged between 12 and 31 %, the mean was 20 %. This is lower than the $TEOM_{VCM}$ W_{CM} calculated when single sites were used (shown in Figure 10); using three sites therefore improves the VCM performance. There was a clear linear trend relating $TEOM_{VCM}$ W_{CM} at 50 µg m^{-3} with the d_{mean}, regardless of whether a one hour or four hour FDMS purge mean was used. Indeed, the difference in W_{CM} was very small.

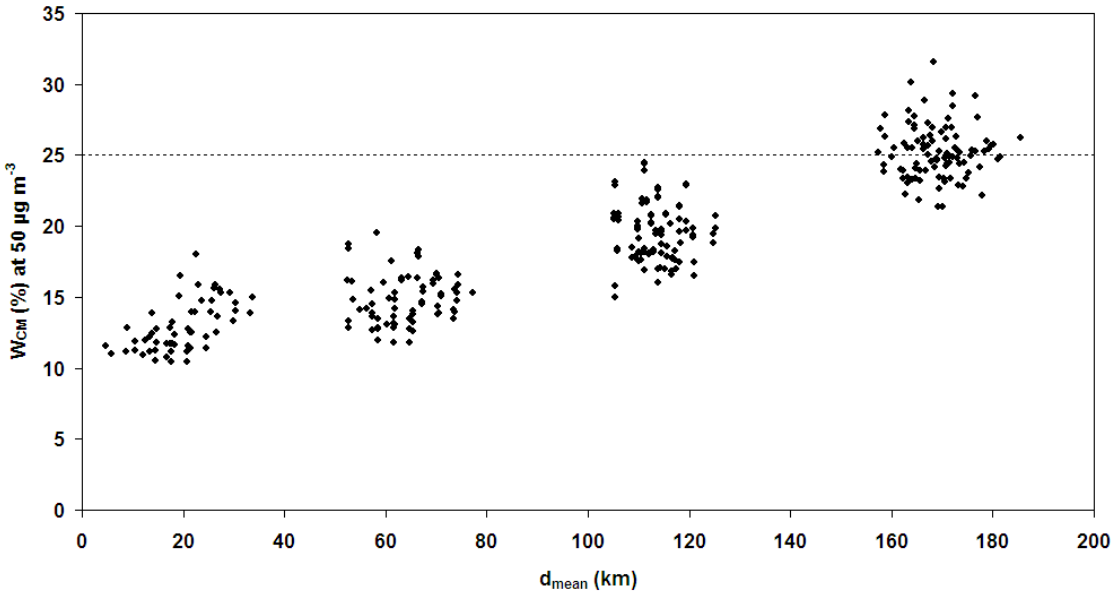

Figure 13: Scatter plot showing the $TEOM_{VCM(1h)}$ W_{CM} at 50 µg m^{-3} with the hourly mean FDMS measurements at equivalence sites against the d_{mean}.

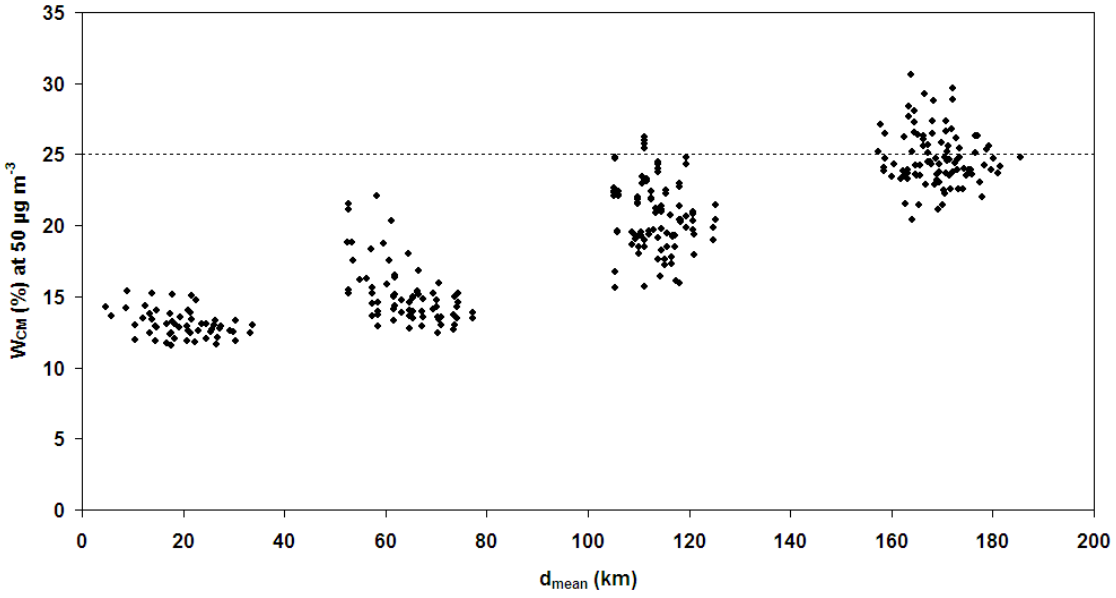

Figure 14: Scatter plot showing the $TEOM_{VCM(4h)}$ W_{CM} at 50 µg m^{-3} with the hourly mean FDMS measurements at equivalence sites against the d_{mean}.

To calculate the change in ΔW_{CM} that would result from applying the VCM_{4h} with 3 away sites compared to the VCM_{1h}, the ΔW_{CM} (Δ = $TEOM_{VCM(4h)}$ W_{CM} – $TEOM_{VCM(1h)}$ W_{CM}) was calculated and is shown in Figure 15. This demonstrates that ΔW_{CM} is between ±3 %, the mean ΔW_{CM} is +0.24 %.

Over short distances, averaging the contemporaneous hourly measurement from three sites caused the same increase in W_{CM} as the change from $TEOM_{VCM(1h)}$ to $TEOM_{VCM(4h)}$ at a single site; it reduced W_{CM} caused by instrument noise. The four hour rolling mean reduced transient spikes in data due to noise artefacts, however, it also smoothed short-term peaks that were representative of ambient conditions and therefore also increased the uncertainty.

Therefore the $TEOM_{VCM(1h)}$ from the three away sites should be used as it marginally decreases the W_{CM} and, most importantly, is consistent with the $TEOM_{VCM(24h)}$. At distances greater than 125 km the $TEOM_{VCM(1h)}$ W_{CM} increased above 25% in many of the calculations; this is shown in Figure 13. Therefore, although the FDMS is not a reference methodology and a 25% limit of the W_{CM} can only be considered indicative, it may be necessary to review the limit of the model domain.

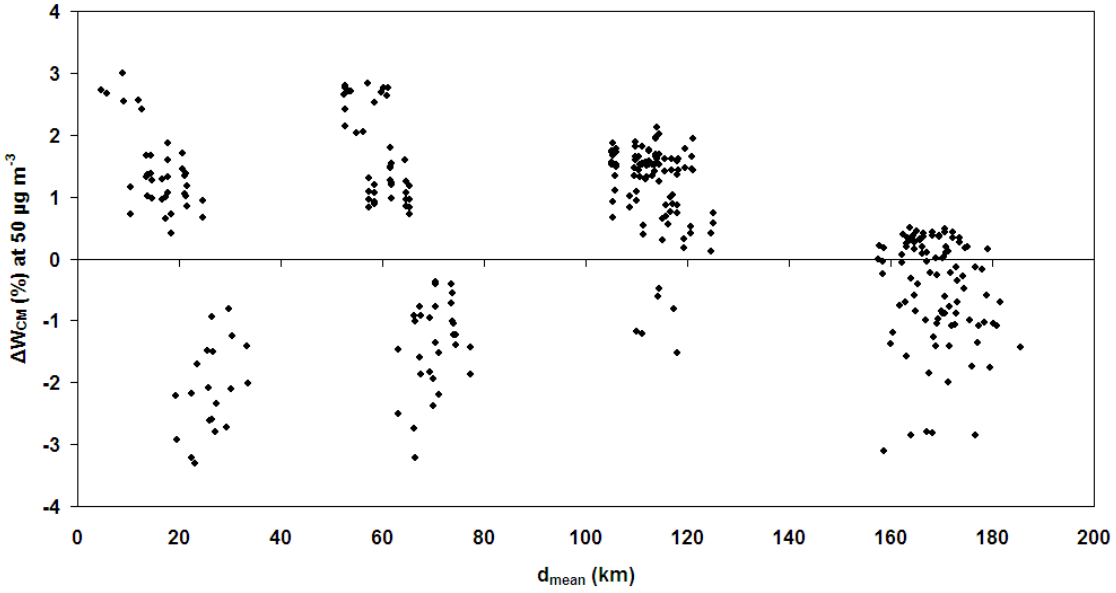

Figure 15: Scatter plot showing the difference (Δ) between the W_{CM} at 50 µg m^{-3} for the hourly mean FDMS measurements at equivalence sites with $TEOM_{VCM(1h)}$ and $TEOM_{VCM(1h)}$ using the mean FDMS purge concentrations from three away sites against the mean distance between the sites. Δ = $TEOM_{VCM(4h)}$ W_{CM} – $TEOM_{VCM(1h)}$ W_{CM}.

3.3 Review of the FDMS purge measurements from the first phase AURN deployment

The analysis in this section was designed to determine if Defra's 2007 FDMS deployment would allow the VCM to be applied to all current UK AURN and local authority TEOM instruments.

3.3.1 Application of the VCM to AURN FDMS purge measurements at daily mean concentrations

In the first report (Green *et al.*, 2007), it was demonstrated that the $TEOM_{VCM}$ W_{CM} remained below the EU data quality threshold of 25 % when the u_{purge} was below 1.5 µg m^{-3} at both the

annual and daily mean limit values; this is shown in Figure 7. The relationship of u_{purge} for all possible FDMS site pairs in the AURN with distance is shown in Figure 16. u_{purge} above 1.5 µg m^{-3}, where the distance between the sites is less than 200 km, is shaded in Figure 16 and sites are listed in Table 5.

There were a total of 300 combinations between the 25 AURN sites, 225 of which had 40 or more daily mean pairs. Of these 122 site pairs were separated by less than 200 km; this was the maximum separation distance shown in Green *et al* (2007) for the $TEOM_{VCM}$ to provide a W_{CM} less than 25 %. Of these 122 site pairs 5 sites (4 %) had u_{purge} greater than 1.5 µg m^{-3}; these are shown in Table 5. These site pairs marginally exceed the 1.5 µg m^{-3} threshold (maximum 1.58 µg m^{-3}) and were all separated by more than 132 km. There was a clear relationship between separation distance and the u_{purge}. It would therefore appear that if **individual** sites from the AURN were used in the VCM then a small number of marginal breaches of the 25 % W_{CM} threshold could be expected at distances greater than 132 km.

The u_{purge} between the Reading New Town site and other sites on the AURN has also been calculated and are shown as crosses in Figure 16. It is clear that many of the u_{purge} results are higher than other sites. This may therefore be used as a ratification tool.

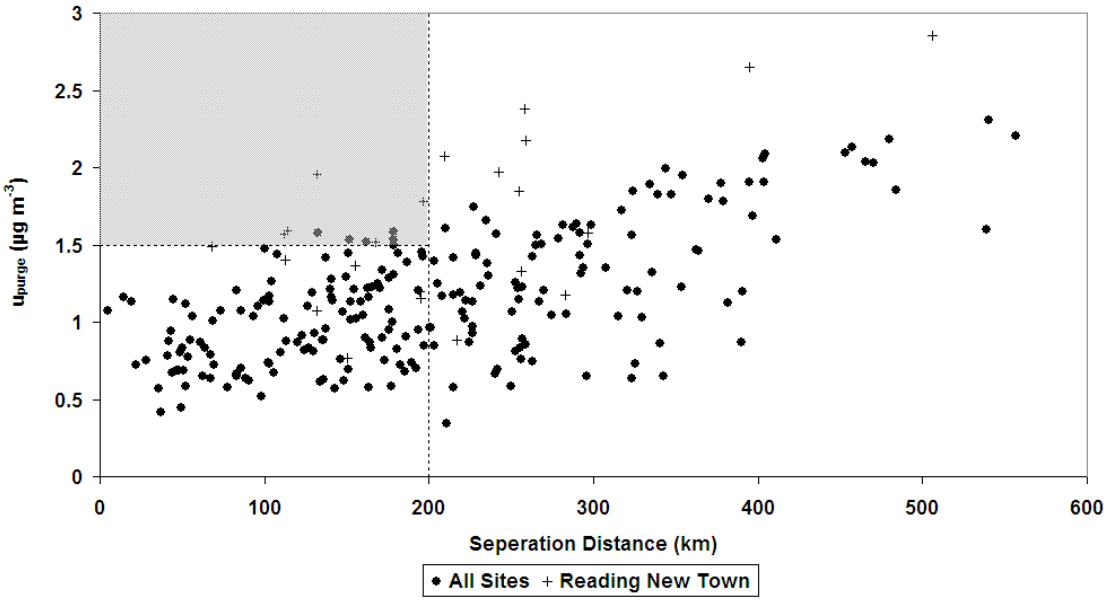

Figure 16: Scatter plot showing the u_{purge} for single FDMS site combinations in the AURN against distance where the number of daily mean pairs is greater than 40. The grey area highlights sites less than 200 km apart with a u_{purge} greater than 1.5 µg m^{-3}; the maximum shown to result in a W_{CM} greater than 25 %.

Home site	Away site	Separation distance (km)	u_{purge} (µg m^{-3})	n	Home site mean (µg m^{-3})	Away site mean (µg m^{-3})
Birmingham Centre	Port Talbot	162	1.52	135	2.44	3.26
Hull Freetown	Liverpool	179	1.58	166	1.75	1.59
Liverpool	Nottingham Centre	133	1.58	154	1.48	2.87
Newcastle Centre	Preston	152	1.53	82	0.25	1.92
Newcastle Centre	Sheffield Centre	178	1.53	67	0.07	1.96

Table 5: Site combinations and separation distances where, the distance between the sites was less than 200 km and the u_{purge} was greater than 1.5 µg m^{-3}

3.3.2 Application of the VCM to AURN FDMS measurements at the three closest FDMS instruments under 200 km

The VCM will be employed using FDMS purge measurements from the three closest instruments under 200 km as described in section 2.5.4.

Each of the AURN FDMS home sites had an optimum combination of three other FDMS sites, i.e. the three closest away sites. The u_{purge} at the home site and the average of the contemporaneous hourly measurements from the three closest away sites was calculated. A minimum of one measurement was required from any one of the three away sites for a valid away average. This test of the effect of missing measurements due to instrument malfunction was therefore included. Results are detailed in Table 6 and are plotted against the d_{mean} in Figure 17 as large red dots. The u_{purge} for every possible combination of a home and any three away sites less than 200 km (8124 combinations) was also calculated, 6995 had over 40 data pairs. These are shown as small black dots in Figure 17. Neither Auchencorth Moss nor Edinburgh St Leonards have three other FDMS monitoring sites within 200 km; these were therefore not included as home FDMS purge sites. However, both were included in potential combinations with the Newcastle Centre site.

It is clear that when an AURN FDMS purge measurement was compared with the mean FDMS purge measurement from its nearest three neighbours the u_{purge} was less than the 1.5 µg m^{-3} threshold. When every possible combination of a home and any three away sites were considered, 25 combinations breach the 1.5 µg m^{-3} threshold. However, this was only 0.4 % of the combinations; these breeches are shown in Table 7. Twenty-three of these occurred when Liverpool was the home site, which had FDMS purge concentrations lower than the surrounding sites. This is inconsistent with faults experienced in the LAQN, which tend to lead to elevated concentrations due to leaks or incomplete drying and may be indicative of a previously uncharacterised fault or a microscale suppression of volatile material not experienced elsewhere; assuming all audit diagnostics such as flow are within tolerance. The two other

breeches are site combinations with larger mean separation distances of 159 km and 175 km; the 175 km combination also used Liverpool as an away site.

It is clear that the relationship between d_{mean} and u_{purge} is not as strong with the average of three away sites as with single FDMS site combinations (Figure 16) because d_{mean} can be made up of one very distant site and two closer sites or visa versa. d_{max} was therefore also calculated and is shown in Table 6 and Table 7, these results show that the u_{purge} threshold of 1.5 µg m^{-3} is breeched before the 200 km model domain identified in the first study (Green *et al.*, 2007).

It was therefore necessary to consider a revision of the 200 km model domain concluded in the first study, however, the relative merits of the analysis methods in the first report and here should be reviewed. The first study used PM_{10} samples on Emfab filters and weighed to the criteria laid down in EN14907 (CEN, 2003) and showed a direct relationship between distance and W_{CM}. However, that study was limited by the geographical spread of sites, the number of sites used and data capture. This study has a far larger geographical coverage, number of sites and data capture but relied on the relationship derived between W_{CM} and u_{purge} in the first study. **Without gravimetric reference measurements made to the high standard of the first study and a geographical coverage of sites the maximum model domain cannot be definitively concluded.** In the meantime a review of the model domain should be considered at the first identified point of failure, d_{max} = 133 km, until the maximum model domain cannot be definitively concluded.

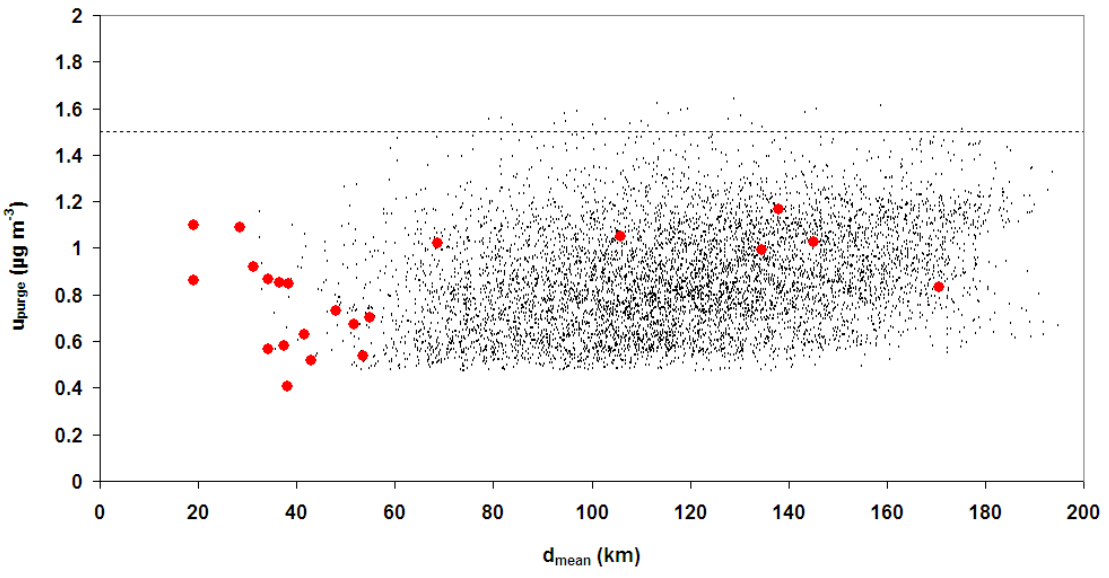

Figure 17: Scatter plot showing the u_{purge} against d_{mean}. The red dots show the combination of sites that provides the minimum d_{mean} (i.e. the optimum combination) while the small black dots show all 6995 potential combinations between the AURN sites with over 40 data pairs.

Home Site	Away Site 1	Away Site 2	Away Site 3	Mean separation distance (d_{mean}) (km)	Maximum distance between sites (d_{max}) (km)	u_{purge} (µg m^{-3})	n	Home site mean (µg m^{-3})	Distant site mean (µg m^{-3})
Birmingham Centre	Wolverhampton Centre	Leicester Centre	Coventry Memorial Park	34	55	0.87	201	1.76	2.57
Blackpool	Wirral Tranmere	Preston	Liverpool	38	48	0.41	116	1.03	1.23
Bristol St Paul's	Port Talbot Margam	Port Talbot	Cardiff Centre	69	83	1.02	219	2.25	2.77
Cardiff Centre	Port Talbot Margam	Port Talbot	Bristol St Paul's	42	42	0.63	207	2.71	2.51
Coventry Memorial Park	Wolverhampton Centre	Leicester Centre	Birmingham Centre	37	47	0.58	201	2.38	2.25
Hull Freetown	Sheffield Centre	Nottingham Centre	Manchester Piccadilly	106	129	1.05	194	1.61	2.55
Leicester Centre	Nottingham Centre	Coventry Memorial Park	Birmingham Centre	43	55	0.52	100	1.98	1.55
Liverpool	Wirral Tranmere	Preston	Blackpool	31	44	0.92	116	0.35	1.50
Manchester Piccadilly	Stoke-on-Trent Centre	Preston	Liverpool	48	51	0.73	186	1.87	1.84
Newcastle Centre	Preston	Edinburgh	Auchencorth Moss	145	152	1.03	185	0.91	1.11
Nottingham Centre	Sheffield Centre	Leicester Centre	Coventry Memorial Park	52	67	0.67	182	2.72	2.54
Plymouth Centre	Port Talbot Margam	Port Talbot	Cardiff Centre	138	141	1.17	209	2.37	2.80
Preston	Manchester Piccadilly	Liverpool	Blackpool	36	44	0.85	116	1.85	0.79
Port Talbot	Swansea Roadside	Port Talbot Margam	Cardiff Centre	19	42	0.86	150	3.08	2.84
Port Talbot Margam	Swansea Roadside	Port Talbot	Cardiff Centre	19	41	1.10	63	2.12	0.95
Southend-on-sea	Southampton Centre	Leicester Centre	Coventry Memorial Park	171	173	0.83	164	1.87	1.76
Sheffield Centre	Stoke-on-Trent Centre	Nottingham Centre	Manchester Piccadilly	55	61	0.70	101	1.99	1.26
Southampton Centre	Southend-on-sea	Cardiff Centre	Bristol St Paul's	135	161	0.99	178	2.12	2.33
Stoke-on-Trent Centre	Wolverhampton Centre	Sheffield Centre	Manchester Piccadilly	54	61	0.54	102	1.40	1.69
Swansea Roadside	Port Talbot Margam	Port Talbot	Cardiff Centre	28	56	1.09	150	1.90	3.11
Wirral Tranmere	Preston	Liverpool	Blackpool	34	49	0.57	73	1.38	0.74
Wolverhampton Centre	Stoke-on-Trent Centre	Coventry Memorial Park	Birmingham Centre	38	49	0.85	108	2.09	1.03

Table 6: u_{purge}, d_{mean} and d_{max} with the minimum d_{mean} for all site combinations

Home site	Away site 1	Away site 2	Away site 3	Mean distance (d_{mean}) (km)	Maximum distance between sites (d_{max}) (km)	u_{purge} (µg m^{-3})	n	Home site mean (µg m^{-3})	Distant site mean (µg m^{-3})
Liverpool	Wirral Tranmere	Sheffield Centre	Nottingham Centre	79	179	1.55	185	1.24	2.77
Liverpool	Wolverhampton Centre	Wirral Tranmere	Nottingham Centre	82	151	1.56	185	1.24	2.78
Liverpool	Wirral Tranmere	Stoke-on-Trent Centre	Hull Freetown	84	179	1.53	197	1.34	1.81
Liverpool	Sheffield Centre	Preston	Nottingham Centre	92	133	1.53	185	1.24	2.80
Liverpool	Wirral Tranmere	Sheffield Centre	Hull Freetown	95	179	1.58	197	1.34	1.95
Liverpool	Wolverhampton Centre	Preston	Nottingham Centre	95	179	1.55	185	1.24	2.82
Liverpool	Wolverhampton Centre	Wirral Tranmere	Hull Freetown	97	133	1.59	197	1.34	1.97
Liverpool	Stoke-on-Trent Centre	Sheffield Centre	Nottingham Centre	100	179	1.53	185	1.24	2.72
Liverpool	Wolverhampton Centre	Stoke-on-Trent Centre	Nottingham Centre	103	179	1.55	185	1.24	2.75
Liverpool	Sheffield Centre	Preston	Hull Freetown	108	133	1.54	197	1.34	2.06
Liverpool	Wolverhampton Centre	Preston	Hull Freetown	110	179	1.55	197	1.34	2.07
Liverpool	Wirral Tranmere	Leicester Centre	Hull Freetown	112	179	1.53	197	1.34	1.84
Liverpool	Wolverhampton Centre	Sheffield Centre	Nottingham Centre	114	151	1.62	185	1.24	2.88
Liverpool	Stoke-on-Trent Centre	Sheffield Centre	Hull Freetown	116	179	1.58	197	1.34	1.94
Liverpool	Wolverhampton Centre	Stoke-on-Trent Centre	Hull Freetown	118	133	1.60	197	1.34	1.97
Liverpool	Wolverhampton Centre	Sheffield Centre	Leicester Centre	120	179	1.60	113	0.28	2.32
Liverpool	Sheffield Centre	Nottingham Centre	Leicester Centre	128	151	1.56	185	1.24	2.78
Liverpool	Wolverhampton Centre	Sheffield Centre	Hull Freetown	129	196	1.64	197	1.34	2.09
Liverpool	Wolverhampton Centre	Nottingham Centre	Leicester Centre	130	133	1.57	185	1.24	2.79
Liverpool	Stoke-on-Trent Centre	Leicester Centre	Hull Freetown	133	179	1.54	197	1.34	1.86
Liverpool	Wolverhampton Centre	Sheffield Centre	Newcastle Centre	135	133	1.52	199	1.33	1.63
Liverpool	Sheffield Centre	Leicester Centre	Hull Freetown	143	179	1.59	197	1.34	1.99
Liverpool	Wolverhampton Centre	Leicester Centre	Hull Freetown	146	133	1.60	197	1.34	2.01
Newcastle Centre	Sheffield Centre	Preston	Edinburgh St Leonards	159	178	1.61	86	0.27	2.13
Newcastle Centre	Sheffield Centre	Preston	Liverpool	175	196	1.51	169	0.95	2.10

Table 7: u_{purge}, d_{mean} and d_{max} where the u_{purge} was higher than the 1.5 µg m^{-3} threshold

The d_{mean}, d_{max} and d_{min} between the TEOMs currently in the AURN and the three closest FDMS sites was also calculated; these are shown in Table 8. The AURN is being reorganised at the time of writing; this list is therefore restricted to sites on the AURN that used TEOMs on 1st January 2008. As discussed in (Green *et al.*, 2007), when the single nearest site at less than 200 km was considered, the only TEOM AURN sites without three FDMS instruments within 200km were in Scotland and Northern Ireland. These sites were Aberdeen, Belfast Centre and Derry. Several sites (Glasgow Kerbside, Lough Navar, Grangemouth, Norwich Centre, Rochester and Thurrock) had a d_{max} greater than the 133 km. On this basis, areas outside Scotland and Northern Ireland (already highlighted) that require additional FDMS instruments are East Anglia and the South East. As discussed, three available sites is considered good practice for network design to maximise data capture and remain representative of the air shed. However, as shown in Figure 16, a single site at distances of less than 133 km is also representative of the regional volatile particulate matter concentration. This interpretation reduced the areas that that require additional FDMS instruments to the north of Scotland and Northern Ireland (as shown in Figure 20), specifically, the only AURN sites with TEOM instruments outside these geographical limits are Aberdeen, Derry and Lough Navar.

The position of the AURN FDMS instruments in the UK has clear implications for local authorities if they wish to use the model to correct their TEOM measurements and for Defra when installing FDMS instruments. The maps in Figure 18 and Figure 19 show the areas in the UK that are adequately covered in by three AURN FDMS instruments for the 200 km and 133 km model domains respectively. To provide adequate coverage for all areas of the UK with a model domain of 200 km, additional AURN FDMS instruments are required in Scotland, Northern Ireland and the far southwest. To provide adequate coverage for all areas of the UK with a model domain of 133 km, additional AURN FDMS instruments are required in Scotland, Northern Ireland and the northeast, East Anglia, the southeast, the southwest and the western most points of north and south wales. As discussed, a single site at distances of less than 133 km is also representative of the regional volatile particulate matter concentration Figure 20 shows the areas in the UK that are adequately covered using this interpretation.

It is worth noting that neither local authority FDMS instruments in the LAQN and elsewhere are not included in this assessment, nor are proposed Defra FDMS deployments. If these were included, the model coverage would be more comprehensive.

Site	Mean Distance (d_{mean}) (km)	Maximum Distance Between Sites (d_{max}) (km)	Minimum Distance Between Sites (d_{min}) (km)
Aberdeen	-	-	151
Belfast Centre	-	-	
Bury Roadside	29	43	7
Camden Kerbside	75	111	54
Derry	-	-	-
Glasgow Kerbside	109	194	64
Grangemouth	82	175	33
Haringey Roadside	78	120	52
Harwell	64	88	30
Leamington Spa	31	47	12
Leeds Centre	60	75	48
London Bloomsbury	75	112	56
London Haringey	77	116	56
London Harlington	69	93	35
London Marylebone Road	74	110	55
London N. Kensington	73	107	51
Lough Navar	-	-	-
Middlesbrough	97	131	52
Narberth	78	110	54
Norwich Centre	153	166	128
Portsmouth	74	127	25
Rochester	91	154	10
Salford Eccles	28	39	6
Scunthorpe Town	55	78	27
Southwark Roadside	75	113	52
Stockton-on-Tees Yarm	94	120	55
Thurrock	83	135	26

Table 8: AURN sites that were using a TEOM to measure PM_{10} on 1st January 2008, the d_{mean} d_{max} and d_{min} between the home and one of the three away sites where the maximum distance between any site is 200km

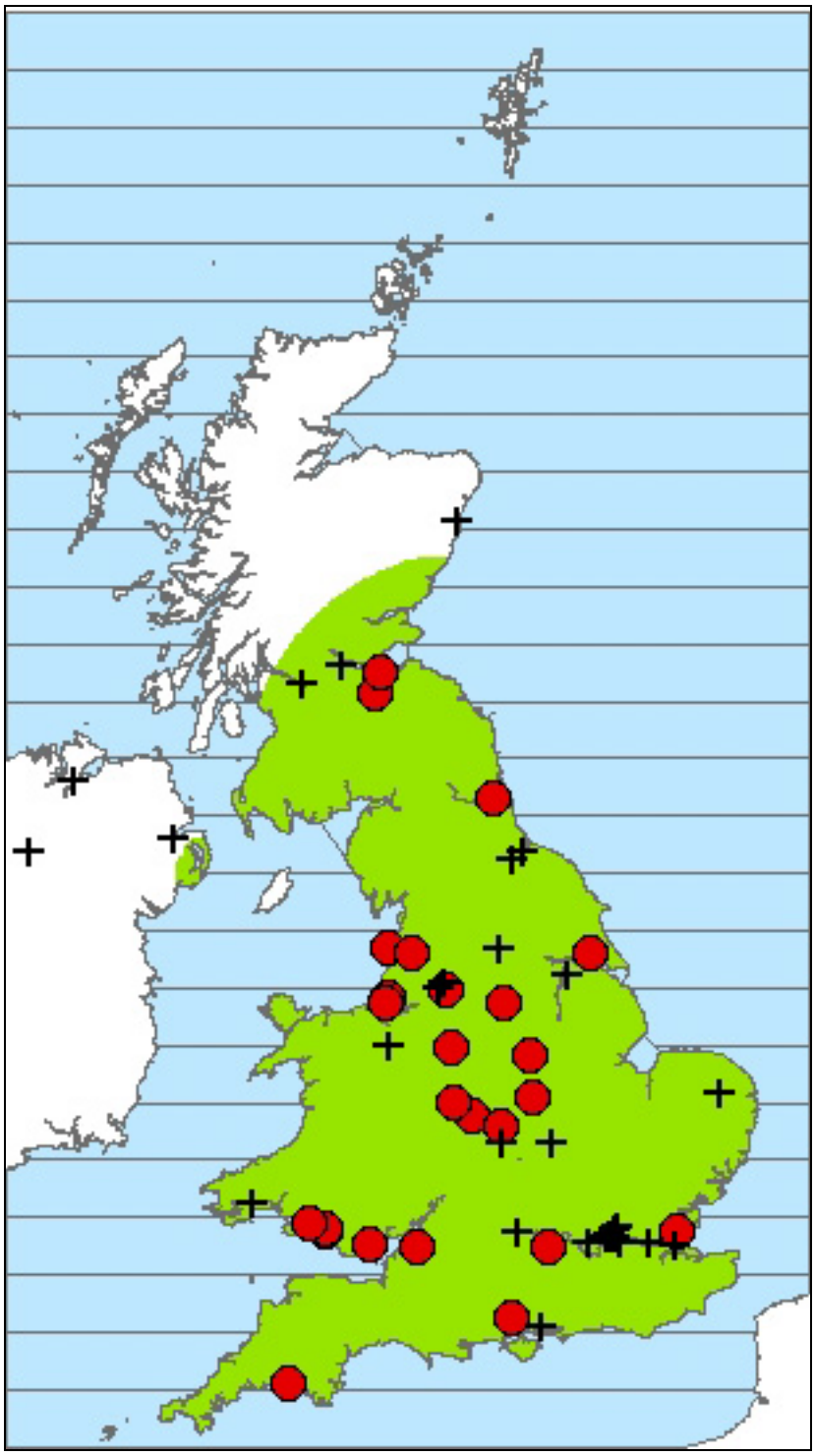

Figure 18: Map of the UK showing the locations which have three AURN FDMS instruments within 200km. FDMS sites are shown as red circles, TEOM sites are marked with a cross.

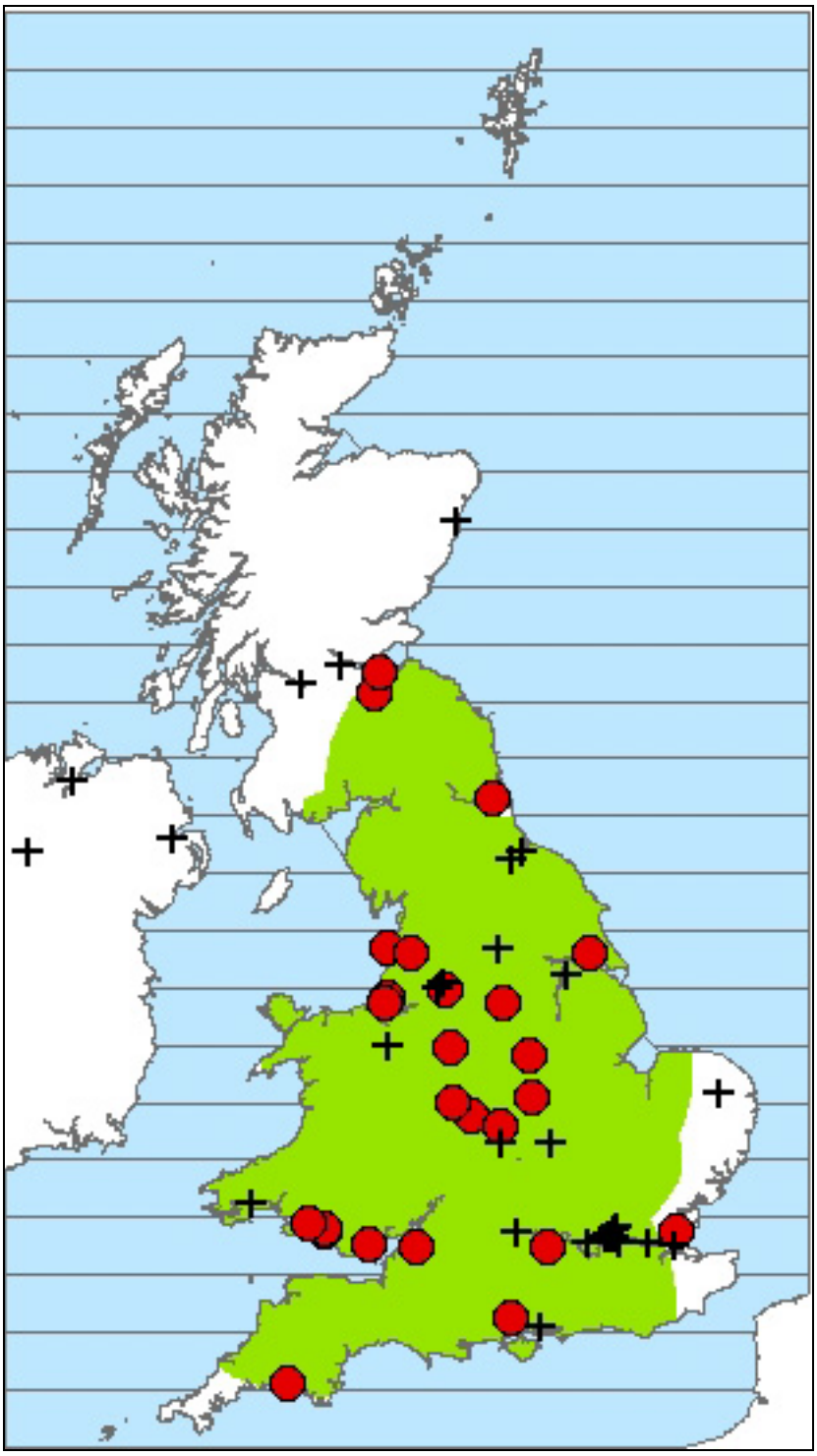

Figure 19: Map of the UK showing the locations which have three AURN FDMS instruments within 133km. FDMS sites are shown as red circles, TEOM sites are marked with a cross.

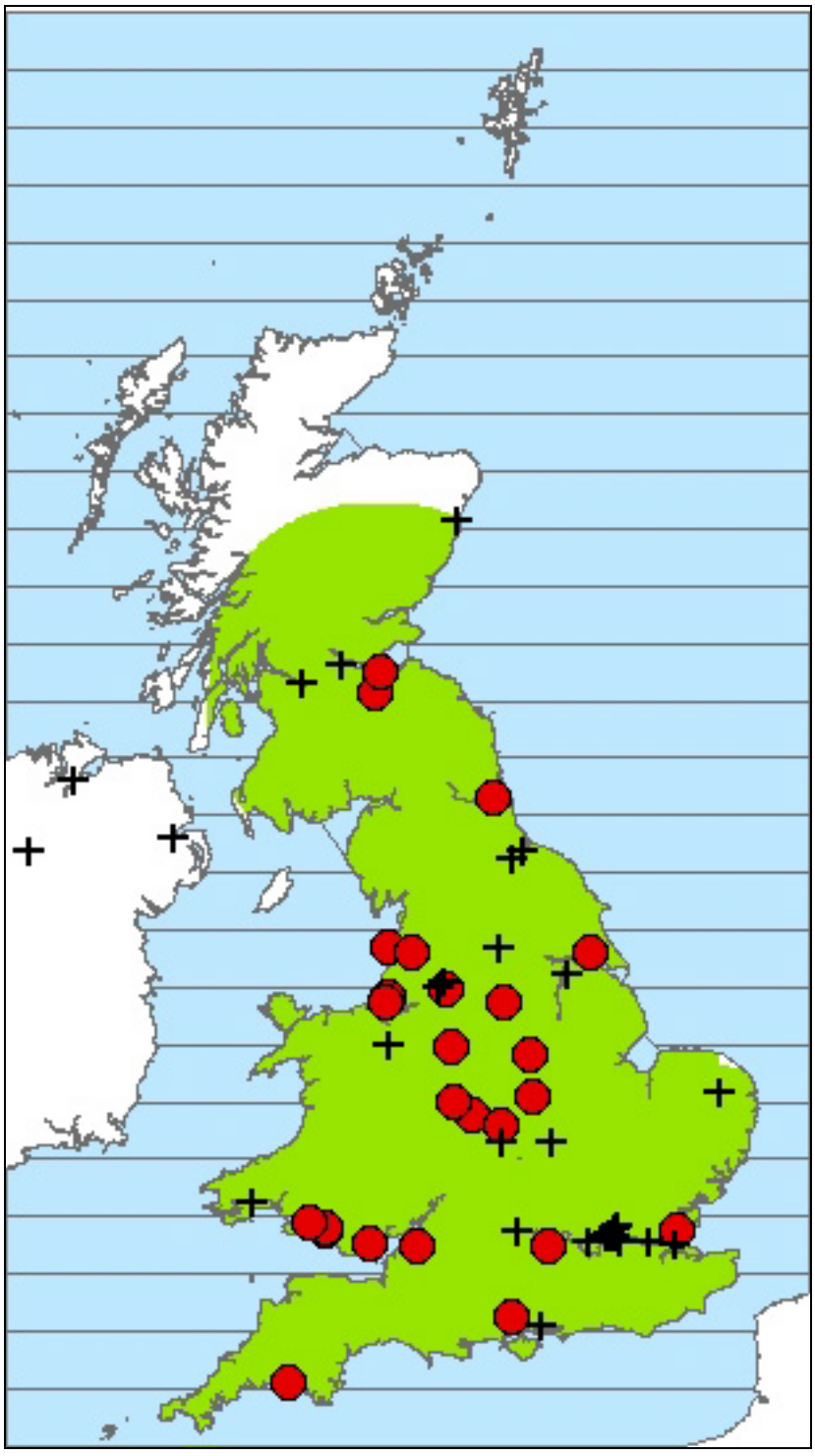

Figure 20: Map of the UK showing the locations which have one AURN FDMS instruments within 133km . FDMS sites are shown as red circles, TEOM sites are marked with a cross.

4 CONCLUSIONS

The VCM was tested at an hourly time resolution by calculating the $TEOM_{VCM}$ W_{CM} compared to the FDMS PM_{10} measurements made at the UK Equivalence Programme sites. These tests used FDMS hourly mean concentrations as the 'reference' method as hourly mean gravimetric reference concentrations were not available. As there was no gravimetric reference measurement, the 25 % W_{CM} threshold was only considered indicative of equivalence. It should also be noted that the VCM equation used here ($TEOM_{VCM}$ PM_{10} = TEOM PM_{10} - 1.87 FDMS PM_{10} purge) was optimised in the first report to produce $TEOM_{VCM}$ measurements that were equivalent to the gravimetric reference method, not the FDMS (Green *et al.*, 2007).

The $TEOM_{VCM}$ had a very low uncertainty when compared to the FDMS measurements at an hourly mean time resolution. This demonstrated that the model was suitable for use at this time resolution. The $TEOM_{VCM}$ W_{CM} rose as function of separation distance between the TEOM (home) site and FDMS (away) site; it reached 25 % at 125 km.

To counteract the heterogeneity in hourly mean FDMS purge measurements likely over the model domain the use of a mean FDMS purge measurement in the VCM was proposed. The optimum number of hours for this mean was estimated by calculating the W_{CM} between FDMS measurements and the $TEOM_{VCM}$. The minimum W_{CM} resulted from using a four hour rolling mean ($TEOM_{VCM(4h)}$), however, the difference between $TEOM_{VCM(1h)}$ and $TEOM_{VCM(4h)}$ was negligible.

To maintain high data capture in the event of instrument failure, and to remain representative of the regional volatile particulate matter concentration it was important that the VCM did not rely on single FDMS instruments to provide purge measurements. It was therefore proposed that the model would calculate $TEOM_{VCM}$ concentrations using the nearest three FDMS instruments in the model domain. The impact of this methodology at the hourly time resolution was assessed by calculating the W_{CM} of the $TEOM_{VCM}$ using the mean of the three away sites for both the $TEOM_{VCM(1h)}$ and $TEOM_{VCM(4h)}$. The difference between them was shown to be very small (±3 % W_{CM}). Overall, using $TEOM_{VCM(1h)}$ caused a decrease of 0.24 % in the W_{CM}. To avoid inconsistencies between the hourly and daily VCM the $TEOM_{VCM(1h)}$ should be used at an hourly time resolution.

There were 25 PM_{10} and 2 $PM_{2.5}$ FDMS instruments in the AURN during 2007. AEA Energy and Environment ratified the measurements from the instrument installation dates until 30th September 2007. Additional ratification was undertaken as part of this study to ensure that valid measurements were input into this study. Several, generally short-term, periods from a number of sites were identified as being influenced by erratic and / or positive measurements. Similar issues have been experienced on the LAQN in recent years and generally result from poorly fitted purge filters. Furthermore, one site was suspected to have a malfunctioning dryer

throughout 2007. These measurements have not been included in this analysis and the AURN QA/QC unit have been informed.

In the first report, it was shown that the $TEOM_{VCM}$ W_{CM} remained below the EU data quality threshold of 25 % when the u_{purge} was below 1.5 µg m^{-3} at both the annual and daily mean limit values. A method for assessing the W_{CM} without gravimetric reference measurements is achieved by assuming that a u_{purge} above 1.5 µg m^{-3} would lead to W_{CM} greater than the 25 % data quality objective. The u_{purge} between every combination of two AURN FDMS sites therefore was calculated and compared to the distance between the two sites. This demonstrated that the u_{purge} increased linearly with distance. The minimum distance at which the 1.5 µg m^{-3} threshold was breached when comparing individual sites was 133 km.

The u_{purge} for the AURN FDMS sites were then calculated using a home site and three away sites; analogous to how the model will be used in practice. This resulted in 8124 site combinations of sites, 6995 had over 40 data pairs. Within these 6995 combinations there is a minimum d_{mean} between the home site and the three away sites for each AURN site; the optimised site combination. None of the optimised site combinations exceeded the 1.5 µg m^{-3} u_{purge} threshold, however, a small percentage (0.4 %) of the 6995 potential combinations did breach the threshold. The first breach of the threshold occurred when the d_{max} between one of the away sites and the home site was 133 km. However, breeches were almost exclusively due to the Liverpool site; further investigation of the measurements at this site by the QA/QC unit is therefore recommended.

Given that these tests had indicated that the model domain was smaller than the 200 km concluded from the initial study, a review of the geographical limit of the model was considered necessary. Three pieces of evidence from this study indicated that the model domain was reduced:

1. The W_{CM} between the $TEOM_{VCM}$ and the FDMS on an hourly basis exceeded 25 % at 125 km.

2. The u_{purge} between individual sites on the AURN first exceeded 1.5 µg m^{-3} at 133 km.

3. The u_{purge} between one home and three away AURN sites first exceeded 1.5 µg m^{-3} at 133 km.

The assessment of the model domain in the first study was more direct as it used PM_{10} samples on Emfab filters and weighed to the criteria laid down in EN14907 (CEN, 2003). This showed a direct relationship between distance and W_{CM}. However, it was limited by the geographical spread of sites, the number of sites used and data capture. This study has a far larger geographical coverage, number of sites and data capture but model domain assessment relied

on the relationship derived between W_{CM} and u_{purge} in the first study and the indicative 25 % W_{CM} threshold at the hourly time resolution.

Without gravimetric reference measurements made to the high standard of the first study **and** a geographical coverage of sites, the maximum model domain cannot be definitively concluded. In the meantime a review of the model domain should be considered at the first identified point of failure from the analysis of the AURN FDMS measurements (133 km) until the maximum model domain can be definitively concluded.

A key output of this study was the use of the VCM to correct AURN TEOMs. At the start of 2008 there were 31 sites in the AURN measuring PM_{10} using TEOMs. Of these, neither Aberdeen, Belfast Centre nor Derry had three FDMS sites within the original 200 km model domain; indeed the closest sites were 150, 210, 170 km respectively. With a model domain of 133 km, several sites (Glasgow Kerbside, Lough Navar, Grangemouth, Norwich Centre, Rochester, Thurrock) fall outside the model domain. However, only Lough Navar has no sites within 133 km. Therefore, Scotland and Northern Ireland, East Anglia and the South East require additional FDMS instruments.

To assess the implications of the model for local authority TEOMs, a blanket approach was taken to calculate all the locations in the UK that require additional monitoring using FDMS instruments to be able to use the model (at both 200 km and 133 km model domains) by assuming the centre of every 1 km grid square was a potential TEOM location. Using a 200 km model domain, Scotland, Northern Ireland and the far southwest required additional FDMS instruments for a full UK coverage. Using a 133 km model domain the northeast, East Anglia, the southeast, the southwest and the western most points of north and south wales also required additional FDMS instruments.

Neither of these assessments included local authority FDMS instruments that could be used in the model calculation. For instance, including the FDMS instruments in the LAQN would reduce the required additional coverage to areas outside the southeast and much of East Anglia.

In summary, a model domain of 133 km is consistent with the analysis of the $TEOM_{VCM}$ W_{CM} at an hourly time resolution and from the analysis of the u_{purge} between single and multiple AURN FDMS measurements. However, both these methods are inferior compared with the direct relationship derived between the W_{CM} of the $TEOM_{VCM}$ and gravimetric reference method with separation distance in the first report. Reducing the model domain to 133 km does not adversely affect the application of the model in the UK substantially as the FDMS coverage is adequate in most areas, especially when supplemented by the LAQN. Furthermore, using only a single FDMS instruments in the model has also been shown to work successfully; this method could be applied at the remaining locations.

Looking forward, 2008 will see the establishment of gravimetric reference measurements at six sites in the UK and the start of the MCerts trials to demonstrate equivalence; these measurements need to be undertaken a similarly high standard as those in the UK Equivalence Programme. If so, this will provide an opportunity to undertake an assessment of the $TEOM_{VCM}$ W_{CM} using gravimetric reference measurements and the geographical spread provided by the AURN FDMS measurements.

Outputs from this study will feed into the design of the local authority web portal which will allow local authorities to download a time resolved, site specific correction factor to calculate $TEOM_{VCM}$ for local authority air quality management purposes.

5 RECOMMENDATIONS FOR FURTHER WORK

Several areas of the model could be improved and clarified with further work.

Analysis of high quality gravimetric measurements and AURN FDMS measurements

The lack of gravimetric reference measurements undertaken on Emfab filters to EN14907 standard (CEN, 2003) has hampered the validation of the model on a wider UK scale and necessitated the use of the u_{purge} as a surrogate for model applicability. Gravimetric reference measurements are proposed at six sites in the UK as part of established Defra monitoring programmes and at two sites in the UK as part of ongoing equivalence work. If these are of a high enough quality, these will enable a wider on-going validation of the VCM with reference measurements, collocated TEOMs (where available) and distant FDMS purge measurements.

Collocated TEOM and FDMS measurements

The VCM factor (1.87) needs to be clarified and monitored over time at a range of site: roadside, urban background and rural sites. At present, the only collocated TEOM and FDMS measurements are made at LAQN sites.

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

The physical / chemical basis of the VCM requires further investigation to understand how the model will react to future changes in volatile particulate; especially in relation to the semi volatile organic fraction and ammonium nitrate.

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8 APPENDIX

Dataset				Distance Between Sites (km)	FDMS Mean (µg m^{-3})	Modelled Mean (µg m^{-3})	Hourly means		Orthogonal Regression				Daily Limit Value
Equivalence 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} (%)
Birmingham	25053	04443	A	0	20	20	4006	2.05	3660	0.96	0.88 ± 0.00	2.29 ± 0.07	15
Birmingham	25053	25053	A	0	20	20	4006	2.05	3660	0.94	0.89 ± 0.00	2.35 ± 0.08	16
Birmingham	04443	04443	A	0	20	20	4006	2.05	3660	0.94	0.89 ± 0.00	2.04 ± 0.08	16
Birmingham	04443	25053	A	0	20	20	4006	2.05	3660	0.96	0.88 ± 0.00	2.29 ± 0.07	15
Birmingham	25053	04443	S	0	20	20	1961	2.03	1618	0.94	0.89 ± 0.00	2.42 ± 0.12	14
Birmingham	25053	25053	S	0	20	21	1961	2.03	1618	0.94	0.89 ± 0.00	3.04 ± 0.13	13
Birmingham	04443	04443	S	0	20	19	1961	2.03	1618	0.93	0.90 ± 0.00	1.66 ± 0.14	17
Birmingham	04443	25053	S	0	20	20	1961	2.03	1618	0.94	0.89 ± 0.00	2.42 ± 0.12	14
Birmingham	25053	04443	W	0	20	20	2045	2.07	2042	0.96	0.88 ± 0.00	2.18 ± 0.09	16
Birmingham	25053	25053	W	0	20	19	2045	2.07	2042	0.95	0.88 ± 0.00	1.82 ± 0.10	18
Birmingham	04443	04443	W	0	20	20	2045	2.07	2042	0.95	0.89 ± 0.00	2.35 ± 0.10	15
Birmingham	04443	25053	W	0	20	20	2045	2.07	2042	0.96	0.88 ± 0.00	2.18 ± 0.09	16
Bristol	24431	24431	A	0	26	27	3218	1.58	3077	0.93	0.93 ± 0.00	3.15 ± 0.13	15
Bristol	24431	24447	A	0	26	27	3218	1.58	3077	0.95	0.92 ± 0.00	2.67 ± 0.11	13
Bristol	24447	24431	A	0	26	27	3218	1.58	3077	0.95	0.92 ± 0.00	2.67 ± 0.11	13
Bristol	24447	24447	A	0	26	26	3218	1.58	3077	0.95	0.93 ± 0.00	1.97 ± 0.12	14
Bristol	24431	24431	S	0	23	25	1164	1.56	1097	0.91	0.96 ± 0.00	2.98 ± 0.23	15
Bristol	24431	24447	S	0	23	24	1164	1.56	1097	0.91	0.96 ± 0.00	2.14 ± 0.23	15
Bristol	24447	24431	S	0	23	24	1164	1.56	1097	0.91	0.96 ± 0.00	2.14 ± 0.23	15
Bristol	24447	24447	S	0	23	23	1164	1.56	1097	0.90	0.98 ± 0.00	1.13 ± 0.25	16
Bristol	24431	24431	W	0	27	29	2054	1.59	1980	0.94	0.93 ± 0.00	3.06 ± 0.16	14
Bristol	24431	24447	W	0	27	28	2054	1.59	1980	0.96	0.91 ± 0.00	2.74 ± 0.13	12
Bristol	24447	24431	W	0	27	28	2054	1.59	1980	0.96	0.91 ± 0.00	2.74 ± 0.13	12
Bristol	24447	24447	W	0	27	27	2054	1.59	1980	0.96	0.91 ± 0.00	2.18 ± 0.13	13

Table 9: Results from section 3.2.1, the comparison between the hourly mean modelled concentrations and the hourly mean FDMS PM_{10} measurements; all measurements from either Birmingham or Bristol. Season is denoted as All (A), Summer (S) and Winter (W). W_{CM} > 25% are highlighted in red.

Dataset				Distance Between Sites (km)	FDMS Mean ($\mu g\ m^{-3}$)	Modelled Mean ($\mu g\ m^{-3}$)	Hourly means		Orthogonal Regression				Daily Limit Value
Equivalence 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 (%)
East Kilbride	25053	25053	A	0	13	13	3320	2.06	3080	0.90	0.96 ± 0.00	1.03 ± 0.08	7
East Kilbride	25053	04443	A	0	13	13	3320	2.06	3080	0.89	0.96 ± 0.00	0.28 ± 0.08	9
East Kilbride	04443	25053	A	0	13	13	3320	2.06	3080	0.89	0.96 ± 0.00	0.28 ± 0.08	9
East Kilbride	04443	04443	A	0	13	12	3320	2.06	3080	0.78	1.03 ± 0.00	-1.35 ± 0.13	14
East Kilbride	25053	25053	S	0	12	13	1197	2.10	1187	0.90	0.98 ± 0.00	0.70 ± 0.13	5
East Kilbride	25053	04443	S	0	12	12	1197	2.10	1187	0.85	1.00 ± 0.01	-0.12 ± 0.16	9
East Kilbride	04443	25053	S	0	12	12	1197	2.10	1187	0.85	1.00 ± 0.01	-0.12 ± 0.16	9
East Kilbride	04443	04443	S	0	12	12	1197	2.10	1187	0.66	1.15 ± 0.01	-2.58 ± 0.27	29
East Kilbride	25053	25053	W	0	13	14	2123	2.04	1893	0.90	0.95 ± 0.00	1.26 ± 0.11	8
East Kilbride	25053	04443	W	0	13	13	2123	2.04	1893	0.92	0.94 ± 0.00	0.51 ± 0.09	10
East Kilbride	04443	25053	W	0	13	13	2123	2.04	1893	0.92	0.94 ± 0.00	0.51 ± 0.09	10
East Kilbride	04443	04443	W	0	13	12	2123	2.04	1893	0.87	0.97 ± 0.00	-0.73 ± 0.12	12
Teddington	24431	24431	A	0	20	20	4543	2.42	4186	0.91	0.94 ± 0.00	1.53 ± 0.10	11
Teddington	24431	24447	A	0	20	20	4543	2.42	4186	0.92	0.92 ± 0.00	1.60 ± 0.09	12
Teddington	24447	24431	A	0	20	20	4543	2.42	4186	0.92	0.92 ± 0.00	1.60 ± 0.09	12
Teddington	24447	24447	A	0	20	20	4543	2.42	4186	0.90	0.91 ± 0.00	1.44 ± 0.10	14
Teddington	24431	24431	S	0	19	20	2235	3.23	2108	0.87	0.99 ± 0.00	1.06 ± 0.17	9
Teddington	24431	24447	S	0	19	20	2235	3.23	2108	0.88	0.96 ± 0.00	1.16 ± 0.16	8
Teddington	24447	24431	S	0	19	20	2235	3.23	2108	0.88	0.96 ± 0.00	1.16 ± 0.16	8
Teddington	24447	24447	S	0	19	19	2235	3.23	2108	0.85	0.95 ± 0.00	0.94 ± 0.17	12
Teddington	24431	24431	W	0	21	21	2308	1.21	2078	0.95	0.90 ± 0.00	1.71 ± 0.11	15
Teddington	24431	24447	W	0	21	21	2308	1.21	2078	0.95	0.89 ± 0.00	1.81 ± 0.1	16
Teddington	24447	24431	W	0	21	21	2308	1.21	2078	0.95	0.89 ± 0.00	1.81 ± 0.1	16
Teddington	24447	24447	W	0	21	20	2308	1.21	2078	0.95	0.89 ± 0.00	1.75 ± 0.11	17

Table 10: Results from experiment 3.2.1, the comparison between the hourly mean modelled concentrations (home purge) and the hourly mean FDMS PM_{10} measurements; all measurements from either East Kilbride or Teddington. Season is denoted as All (A), Summer (S) and Winter (W).