Characterising the PM climate in the UK for Equivalence Testing

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Executive Summary-

Defra require evidence to assist with decisions around the experimental conditions for field tests for the declaration of equivalence for PM analysers within the MCERTS framework. To enable this, an understanding of the UK (and to some extend the European) PM 'climate' is needed with respect to concentration and composition; especially in relation to semi-volatile PM. Defra have highlighted several objectives for investigation:

1. The importance of climatic and meteorological effects in selecting a test site.
2. Seasonal effects and variation – ideally when should tests be carried out, what would represent value for money for manufacturers as year round testing is unfeasible?
3. Spatial variation and influence of choice of site – e.g. roadside, background.
4. How the pollution climate might vary in the future. This could mean that instruments which are equivalent now might not be in future.
5. An awareness of the extent to which the consideration of these metrics should be prioritised for different monitoring techniques.

The report is divided into two sections, the first seeks to describe UK PM climate through the assembly and analysis of a reference dataset of the available PM measurements. The availability of these measurements varied over time as the monitoring networks expanded and instrument methodologies changed; the reference dataset was therefore focused on a limited number of sites to minimise these effects. The methodology for choosing these sites has been documented so that the process can be repeated in subsequent years as further measurements become available. An analysis of the reference dataset was undertaken to summarise the UK PM climate and identify any trends or seasonality which would affect the field tests for equivalence for PM analysers within the MCERTS framework. The available literature was reviewed to examine how PM concentrations varied across Europe and how concentrations are expected to change in the future.

The second section uses the reference datasets assembled to address the specific requirements from the Guide to the Demonstration of Equivalence for Ambient Air Monitoring Methods (GDE) (EC 2010). A methodology was proposed to assess whether sites used in equivalence trials are typical of UK conditions, based on the geometric annual mean concentration. This is used to identify existing sites and areas in Europe which could be considered to have a similar PM Climate to the UK. The reference dataset is also used to identify high and low thresholds for composition and meteorology required by the GDE. These are used to propose the best times and locations to undertake equivalence field tests in the UK.

The tests the assess whether field trials locations should be considered representative of typical UK conditions and whether they have been performed in different climatic seasons to represent the different concentrations of semi volatile PM and a range of meteorological conditions as recommended by the GDE. There tests are laid out below:

Long term geometric mean PM_{10} concentration from equivalence field test site

The long term (preferably annual) geometric mean PM_{10} concentration should lie within the minimum and maximum range shown in the table below.

Site Type	Geometric Mean PM_{10} Range ($\mu g\ m^{-3}$)
Background (urban or suburban)	11.9 – 25.7
Traffic	10.9 – 42.3
Rural	4.3 – 7.9
Industrial	14.3 – 24.6

High and low thresholds for semi-volatile PM and meteorological conditions

For each of the parameters in the table below a threshold and a percentage of daily means either above the high threshold or below the low threshold is set.

Threshold	Semi-volatile PM (or $PM_{2.5}$ nitrate) ($\mu g\ m^{-3}$)		Wind speed (m/s)							Ambient Temperature (°C)		Ambient Dew Point (°C)	
	Threshold	%	Threshold						%	Threshold	%	Threshold	%
			10m		5m		2.5m						
			Urban	Rural	Urban	Rural	Urban	Rural					
Low	3.2	5	2.9	6.0	0.7	5.1	0.3	4.2	10	6.6	10	3.7	10
High	6.3	5	5.2	12.4	1.2	10.6	0.6	8.8	10	13.6	10	10.6	10

Measurements from equivalence field trials already undertaken in the UK and Germany were compared to the ranges and thresholds proposed. They were found, excepting a lack of available data in some cases, to be representative of typical UK conditions. The trials were also found to have been undertaken in different climatic seasons to represent the different concentrations of semi volatile PM and a range of meteorological conditions as recommended by the GDE.

Section A – Summarising PM Climate in the UK

1. Introduction

To achieve Defra's objectives a characterisation of the PM and meteorological climate in the UK needed to be undertaken. This required the assimilation of the available data into reference datasets which were representative of the UK for each parameter.

This section of the report details the development of a methodology to create the reference datasets. This methodology creates datasets which are consistent geographically and free from interferences from changes to sites and instrumentation. Due to changes to the national networks (in terms of sites, PM fractions measured and instruments used) some of the datasets are limited. The methodology described can therefore be used to update these datasets as more data becomes available.

Some of the datasets produced are used in section B of this report to define UK PM_{10} conditions and propose thresholds for PM and meteorological concentrations.

A detailed description of the measurements is beyond the scope of this report, however, additional charts and tables are included in the appendix.

1.1 Note on box and whisker plots

Data is presented throughout this report as box and whisker plots. In all plots the rectangle shows the interquartile range (IQR); it goes from the first quartile (the 25th percentile) to the third quartile (the 75th percentile). The mean is shown by the line that subdivides the box. The arithmetic mean is represented by an X. The width of the box represents the proportion of data in each subset. The whiskers go from the minimum value to the maximum value unless the distance from the minimum value to the first quartile is more than 1.5 times the IQR. In that case the whisker extends out to the smallest value within 1.5 times the IQR from the first quartile. A similar rule is used for values larger than 1.5 times IQR from the third quartile. A circle shows the values which are smaller or larger than the whiskers. These values would be determined as outliers if the data were expected to follow a normal distribution but in this case help to highlight the log normal tendency of these datasets.

2. UK PM measurement availability

The term climate is generally characterised by a long time scale; the Intergovernmental Panel on Climate Change (IPCC) define this as 30 years (IPPC 2003). This longer timescale accounts for seasonal and inter-annual meteorological variability. It would ensure that atypical PM pollution conditions such as those encountered in 1996 and 2003 are considered, but do not skew, any evaluation. This consideration has to be balanced against our changing PM composition over this timescale which is affected by a range of emissions abatement policies and interventions. Furthermore, the availability of measurements to enable a detailed characterisation is somewhat limited; for instance widespread PM_{10} measurements extend back to early 90's while measurements of semi-volatile PM are only available for last six or seven years. The analysis therefore needs to ensure that the PM climate characterised is valid for the present time, taking into consideration changes in emissions (and therefore changes in concentrations and composition) which may take place in the next 10-15 years, with the measurements available.

Many attributes of PM can be measured, including mass, chemical composition, number concentrations and surface area. These can be further differentiated by PM size fraction (PM_{10}, $PM_{2.5}$ or PM_1). Here we are concerned with PM_{10} and $PM_{2.5}$ mass and the attributes of these fractions which impact on the ability of the instruments used to measure these metrics.

PM mass was measured using TEOM, FDMS and gravimetric methodologies in the UK over the last 10-15 years. However, the gravimetric measurements are limited to a few sites and have been subject to a change in filter media during this time (Maggs, Harrison et al. 2009). The analysis was therefore limited to TEOM and FDMS measurements.

In particular, the capability of instruments to sample and/or measure the semi-volatile components of PM is of concern due to both active and/or ambient heating of the sample. This attribute of PM is measured directly using the Thermo Scientific Filter Dynamics Measurement System (FDMS) and has been shown to be well correlated with $PM_{2.5}$ nitrate concentrations, in both the US (Hering, Fine et al. 2004) and the UK (Green, Fuller et al. 2009), which are a key component of semi-volatile PM. This measurement is widely available in the UK and other European Countries; where this is not the case $PM_{2.5}$ nitrate concentrations could be used instead.

Representative datasets for the following PM fractions and metrics were assimilated:

- PM_{10}
- $PM_{2.5}$
- PM_{coarse}
- Semi-volatile PM (exclusively PM_{10})
- $PM_{2.5}$ nitrate

PM_{10} and $PM_{2.5}$ were further subdivided into TEOM and FDMS datasets.

2.1 Data sources

A characterisation of this kind requires a large database of measurements of consistent quality, ideally traceable to national metrological standards, so that they are representative both spatially and temporally. Several PM databases were available for this analysis:

Airbase

Data from the AURN are reported annually to Airbase, this was used as the primary source of PM_{10}, $PM_{2.5}$, coarse PM (PM_{10}- $PM_{2.5}$) denoted here as PM_{coarse}. 2009 data was still marked as 'interim'. Data can be found at http://acm.eionet.europa.eu/databases/airbase/

Automatic Urban and Rural Network (AURN)
Semi volatile PM_{10} as measured by the FDMS is retained separately on www.airquality.co.uk.
London Air Quality Network (LAQN)
PM_{10} and semi volatile PM_{10} as measured by the FDMS is measured to a high level for QA/QC through the LAQN and is available through www.londonair.org.uk
UK Particle Number and Concentration Network
This network measures number concentrations and some aspects of the chemical composition of PM. It was used as the source of nitrate in $PM_{2.5}$. Data can be found at http://uk-air.defra.gov.uk/data/particle_data.

2.2 Time period

A subset of measurements from these databases has been chosen so that they are representative of a climatic period, geographical variation and source variation. Measurements of PM_{10} only started in the UK in 1992. However, this lack of long term data should also be considered alongside the change in emissions and PM concentrations which the UK has experienced over the last 40 years. UK PM_{10} emissions have reduced from over 500 kilotonnes in 1970 (Goodwin, Salway et al. 1999), to under 100 kilotonnes in 2008 (MacCarthy, Li et al. 2010).

The aim of this study was to provide a PM climate assessment that is valid for the present time, taking into consideration changes in emissions (and therefore changes in concentrations and composition) which may take place in the next 10-15 years. A long term data set which encompassed PM concentrations which were representative of conditions when the sources had different strengths would not be applicable to present and future conditions. The last 10-15 years represents a period of relative stability in the emissions and in the concentrations of black smoke; which is the only PM measurement available over a similar time period in the UK. The PM data available over the last 10-15 years would therefore appear to be a good compromise between examining a long term dataset and avoiding a bias to historic, and currently unrepresentative, emissions.

2.3 Site selection

The sites chosen should be representative of a range of UK conditions both geographically and by site type. The PM_{10} concentrations in the UK vary considerably from location to location; this is illustrated by the box and whisker chart in Figure 1; which contrasts concentrations at an industrial site (Port Talbot) with a remote rural site (Auchencorth Moss).

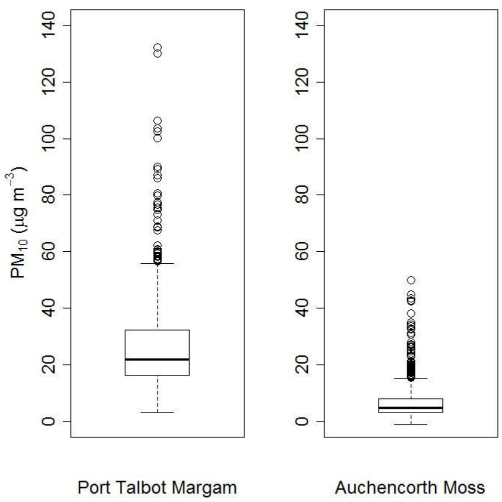

Figure 1: Box and whisker chart showing the measurements from the rural background site in Auchencorth Moss, Scotland and the industrial site in Port Talbot

The sites which report data have changed over the last 10-15 years. Principally, we have more sites now than we did when the networks were first implemented. Automatic measurements of air pollutants started with research work in the early 1970s. The Statutory Urban Network was created in 1987 to monitor compliance to EU Directives on air quality. The Enhanced Urban Network was commissioning by the government in 1992 and consisted of 12 sites monitoring CO, NO_X, SO_2, O_3 and PM_{10} using TEOMs. A subsequent expansion through directly funded sites and the affiliation of local authority sites saw the AURN increase to 119 sites, 69 monitoring PM_{10} (DEFRA 2003). A further reorganisation in response to the Air Quality Directive requirements (EU 2008) and the UK Equivalence Programme (Harrison 2006) resulted in the upgrade of TEOM instruments to FDMS.

2.4 Changes in instrument type

Dealing with the change in PM_{10} methodology from TEOM to FDMS, which occurred from 2006 onwards is challenging. PM_{10} measurements, made using TEOM instruments, began in 1992. These continued until 2007 when the introduction of FDMS instruments into the AURN saw the gradual replacement of the TEOM; the phasing in of these instruments continued until 2010. This presented practical and methodological challenges for this study as TEOMs are not equivalent to the EU reference method, whereas the FDMS has been shown to be equivalent (Harrison 2006). As this change in monitoring methodology produces a step change in measurement, PM_{10} measurements were therefore separated into TEOM, reported at TEOM x 1.3 (Defra 2009) and referred to here as TEOM, and FDMS. The opportunities for the application of the Volatile Correction Model (Green, Fuller et al. 2009) on a national scale to extend the time period of equivalent measurements available was limited by the widespread deployment of FDMS instruments. This deployment began in 2006 and while it may have extended the equivalent measurements back a further year for some sites, it was felt that the benefits of the additional sites were outweighed by the addition of a different measurement metric into the core set of measurements used.

As there is no widely accepted correction factor for the TEOM $PM_{2.5}$ these are reported without any correction factor. This leads to inconsistencies when calculating PM_{coarse} concentrations using TEOM measurements as the sum of TEOM $PM_{2.5}$ and TEOM PM_{coarse} would not equal TEOM PM_{10}. Therefore only the FDMS PM_{coarse} concentrations are used in this study.

2.5 Creating reference datasets in a changing network

The reference datasets have to be free from changes in instrument type, as long as possible, representative of the chosen period (high data capture), representative of all site types and representative of the UK as a whole.

To account for changes in the available measurements due to the opening and closing of monitoring sites and instrument changes, a methodology was developed to identify the optimum dataset. This methodology also provides the basis on which to update the reference datasets in the future.

To combine the importance of length of data set and number of sites, a simple availability factor (R) was calculated to quantify how representaive periods of data were. This factor was designed to assess the number of sites with high data capture operating for as long as possible. R was calculated as follows:

$$R = S_n \times n$$

where:

S_n = number of sites with data capture greater than 75% for n years

n = number of years

This is a simple way of quantifying whether, for example, three sites operating over five years is more representative that four sites over three years. A value of R was calculated at yearly intervals from the start of the first year when data was available. However, the number of sites available for different instruments and fractions followed different growth and contraction patterns. For instance, the number of TEOM instruments first expanded as the AURN grew in the late 1990's and then contracted as they were replaced with FDMS instruments from 2006 onwards. The optimum dataset for the measurements from this instrument has a start date and an end date. Conversely, the number of FDMS instruments on the network was continuing to grow quickly in the latest available dataset, therefore the last year was the most representative by this measure.

To reflect these different patterns, a start date (1) and an end date (2) for the reference datasets were calculated based on the following stepwise approach.

1. The start date (1) was found by calculating R for each dataset starting on 1st Jan each year and finishing at the end of the available data (31st Dec 2009); this is shown as R1 in the figures below. The date where R_A was at its maximum was chosen as the most representative start date (1).
2. If A was less than the latest year, the end date (2) was found by calculating R from date A to the end of the available data (31st Dec 2009) moving forward in yearly intervals; this is shown as R2. The date where R_B was at its maximum was chosen as the most representative end date (2).
3. The distribution of sites was checked for:
    a. Similar proportions of site types to available sites where possible
    b. Good geographical spread (no obvious bias shown in maps included in Appendix)

If either of these conditions are not satisfied, additional sites were sought from other quality assured datasets and R was recalculated if necessary. Values of R for each data set are shown in Figure 2, the start and end dates of the reference datasets (A and B) are listed in Table 1. The derivation of each dataset using this process is detailed in the Appendix.

Table 1: Start and end dates (A and B) for the reference datasets

Dataset	Start date(A)	End date (B)
TEOM PM_{10}	1st Jan 1997	31st Dec 2008
FDMS PM_{10}	1st Jan 2007	31st Dec 2009
TEOM $PM_{2.5}$	1st Jan 1999	31st Dec 2008
FDMS $PM_{2.5}$	1st Jan 2009	31st Dec 2009
FDMS PM_{coarse}	1st Jan 2009	31st Dec 2009
Semi-volatile PM	1st Jan 2007	31st Dec 2009
$PM_{2.5}$ nitrate	1st Jan 2004	31st Dec 2009

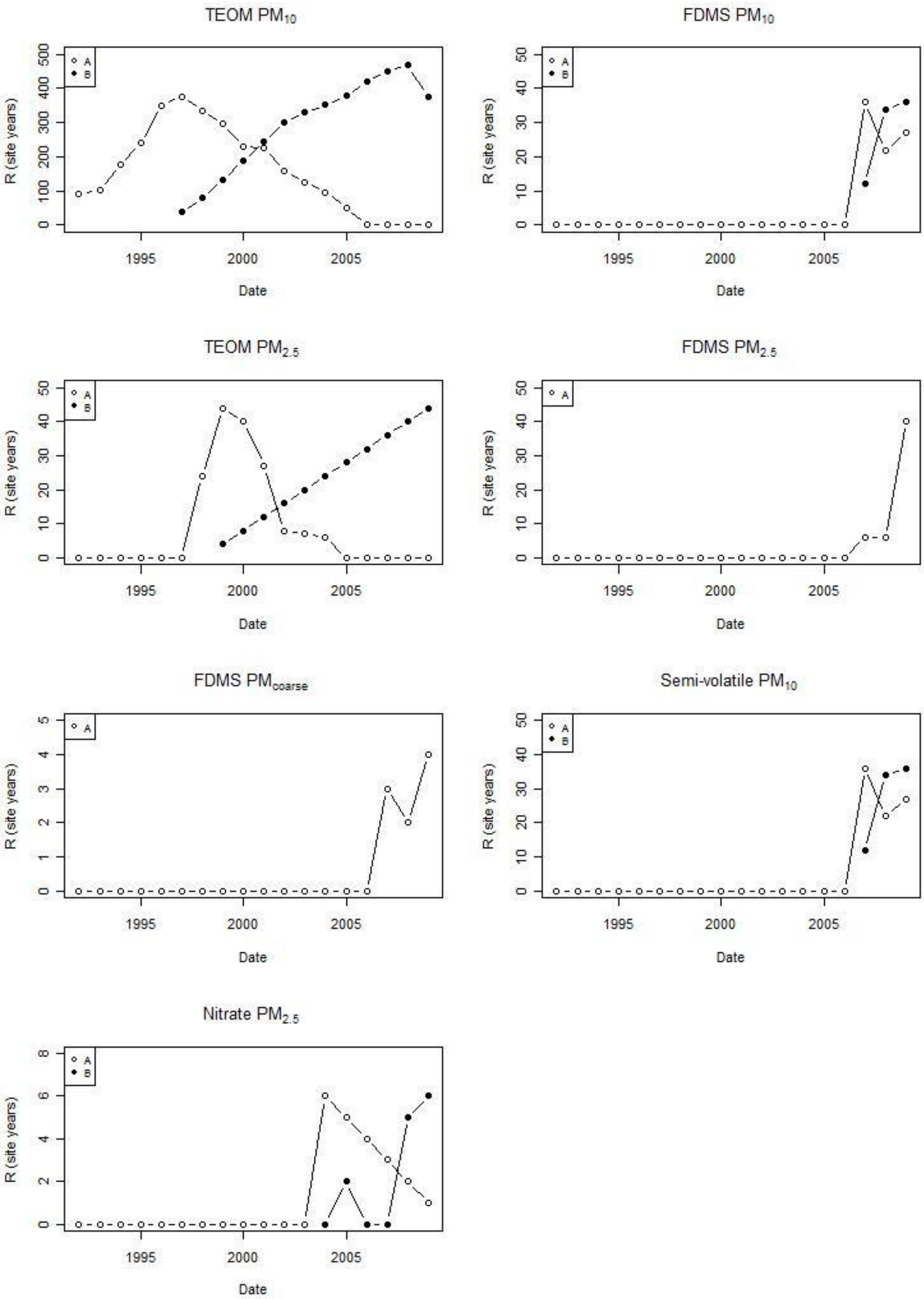

Figure 2: R values for PM_{10}, $PM_{2.5}$, PM_{coarse}, Semi-volatile PM and $PM_{2.5}$ nitrate

3. UK PM concentration

The PM concentrations are summarised by fraction / composition using box and whisker plots in Figure 3, the key statistics are shown in Table 2. Each fraction / composition is differentiated by year to highlight any inter-annual variation or trends in these statistics and by site type in Appendix II; only a summary of the concentrations measured is reported here.

Comparisons between reference datasets are difficult as they are representative of different periods and some have issues regarding geographical or site type representation. However, some differences and similarities are clear.

The TEOM PM_{10} concentration is higher that the FDMS PM_{10} concentration. This is to be expected as the 1.3 factor used in an attempt to make the TEOM data equivalent is known to overestimate at most locations (Green, Fuller et al. 2001).

The TEOM $PM_{2.5}$ concentration is slightly higher than the FDMS $PM_{2.5}$ concentration. No factor has been applied to the TEOM measurements for this fraction, however the internal correction factors present in all TEOM measurements by default (3 µg m^{-3} offset and 1.03 scale) have not been removed.

The semi-volatile PM and the $PM_{2.5}$ nitrate have similar medians, means and inter quartile ranges. This is supportive of the use of $PM_{2.5}$ nitrate as a surrogate for semi-volatile PM if necessary. The semi-volatile PM has a substantial negative minimum due to its susceptibility to the adsorption of gases or incomplete drying on occasion.

Dataset	Start date	End date	Mean	Median	1st Quartile	3rd Quartile	Min	Max
TEOM PM_{10}	1st Jan 1997	31st Dec 2008	25.3	22.1	16.5	30.6	0	196.1
FDMS PM_{10}	1st Jan 2007	31st Dec 2009	19.8	15.7	10.5	24.8	-1.1	138.6
TEOM $PM_{2.5}$	1st Jan 1999	31st Dec 2008	14.3	12	8.7	18	2.7	68
FDMS $PM_{2.5}$	1st Jan 2009	31st Dec 2009	11.8	9.2	6.3	14.6	-1	91.1
FDMS PM_{coarse}	1st Jan 2009	31st Dec 2009	10.6	8.1	3.6	14.4	-1.8	74.1
Semi-volatile PM	1st Jan 2007	31st Dec 2009	2.8	2.1	1	3.9	-4.2	22.1
$PM_{2.5}$ nitrate	1st Jan 2007	31st Dec 2009	2.6	1.9	0.8	3.4	0.1	34.1

Table 2: Summary of concentrations in each reference dataset

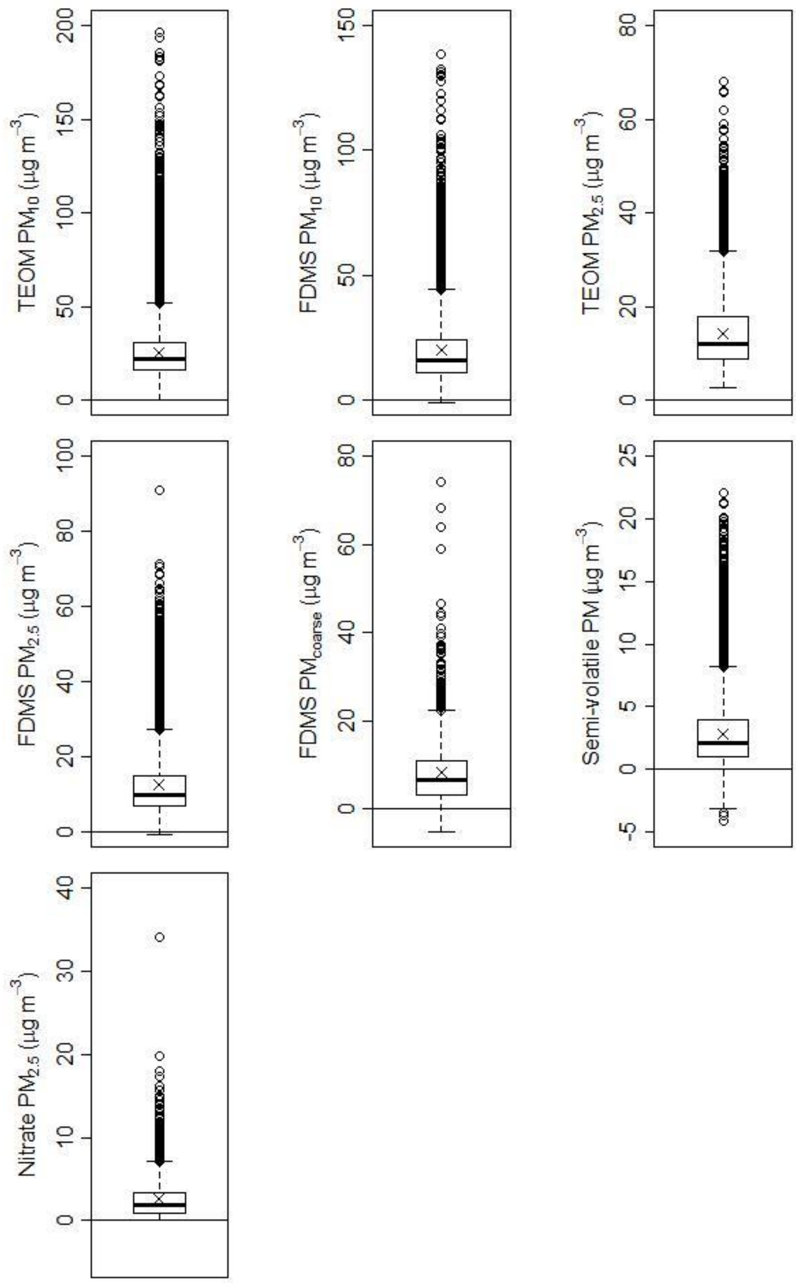

Figure 3: Box and whisker plot of each reference dataset

4. UK meteorological measurements

This section assesses the availability of meteorological measurements of PM in the UK to produce datasets for this project. Meteorological conditions are closely coupled to PM concentrations through particle formation processes and dispersion. However, in this study we are concerned with the effect of meteorological conditions on the measurement of PM.

Meteorological conditions can affect the sampling in three key ways:

1. High wind speed on PM size selection
2. High temperatures leading to the loss of semi-volatile PM
3. High aerosol water content leading to poor sample conditioning

There are many other interactions between the PM and meteorological conditions prior to, during and after sampling which will undoubtedly affect the measurement. However, these can be subtle and are often related to particular components in both the particle and gaseous phase and are beyond the scope of this study.

The three keys issues listed above are dealt with in the GDE:

- *Air humidity and temperature (high and low) to cover any conditioning losses of semi-volatiles during the sampling process.*
- *Wind speed (high and low) to cover any dependency of inlet performance due to deviations from ideal behaviour as dictated by mechanical design, or deviations from the designated sampling flow rate.*

Air humidity can be measured in a number of ways. Relative humidity is commonly used; it measures how much water vapour is in the air compared with the maximum that can be in the air at the temperature the air happens to be when you measure it. This means that the relative humidity goes down as the temperature of the parcel of air goes up even though the amount of water vapour in it remains the same. The dew point is the temperature to which air needs to be cooled for water vapour to condense. This is a much clearer measurement of the amount of water vapour because it only changes when the amount of water vapour in the air changes. Some of the instruments used to measure PM in real-time utilise dryers to reduce the water in the sample stream and therefore reduce its impact on the PM measurement. The ambient dew point is commonly used to assess the efficiency of these dryers and is therefore used in this study.

Measurements of wind speed, ambient temperature and ambient dew point have been taken from the 30 sites in the UK Meteorological Office's Regional Basic Synoptic Network (RBSN) between 1st January 2000 and 31st December 2009. These sites are shown in Figure 4 and are geographically representative of the UK. Measurements are all taken at 10 m and are subjected to standardised quality assurance procedures; as such they represent the best uniform dataset to compare meteorological conditions across the UK for this purpose. However, within the 29 sites the overwhelming majority of sites are in open, rural locations and many are coastal; only one is in an urban location (London Heathrow). These rural locations will experience higher wind speeds, especially closer to the ground, than urban areas due to surface roughness conditions. This creates a rural bias in the dataset and it is therefore important to examine the urban site separately to the rural locations. Unfortunately, further meteorological measurements made at 10 m and subjected to the same quality assurance procedures were not available from UK urban areas.

As with the PM reference datasets, the metrological reference dataset should be updated as more data becomes available although as there are 10 years available this is less important.

Figure 4: UK Meteorological Office's Regional Basic Synoptic Network sites

4.1 Wind Speed adjustment for height

Many meteorological measurements associated with air quality monitoring stations are made at heights other than the standard 10m due to practical issues. However, wind speed varies with height over the first few hundred meters above ground. In neutral stability the wind speed change is given by the well known 'log law' and is demonstrated in Figure 5. It is therefore important that wind speeds measured at the sites are comparable to the reference dataset.

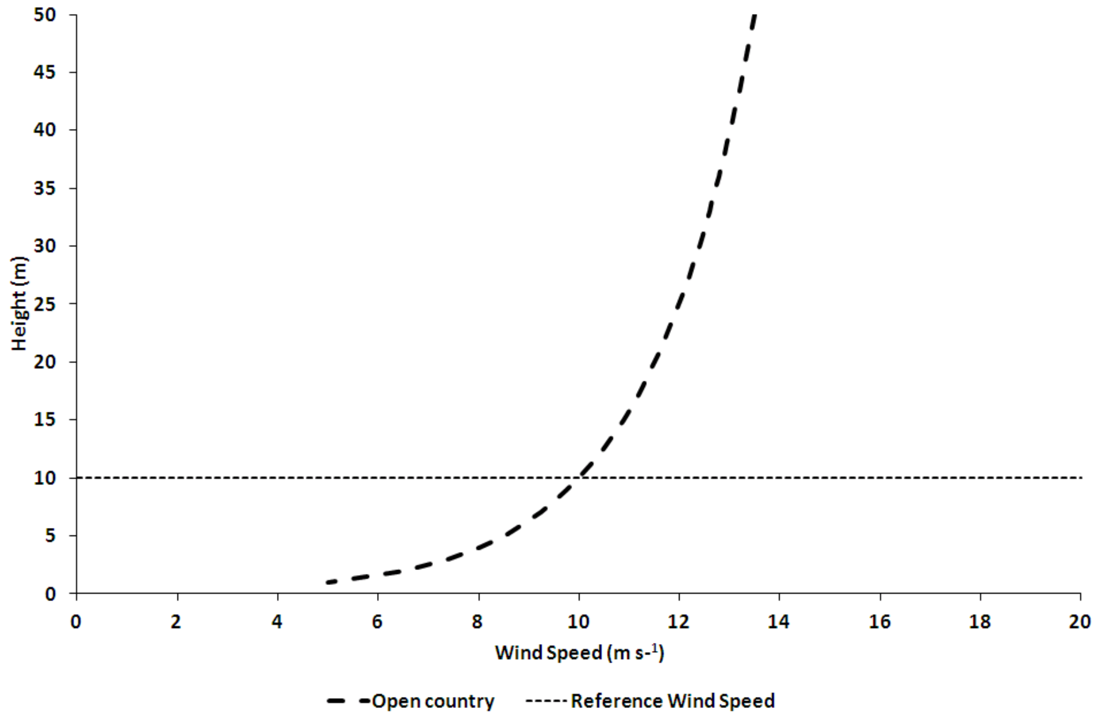

Figure 5: Vertical wind speed profile at 10 ms$_{-1}$ and 10m height

The wind speeds measured on the RSBN are measured at 10m, these have been adjusted to 5m and 2,5m heights using separate equations for urban and non-urban locations.

In non urban locations the following equation is used (Hall and Spanton 2011) where two values of wind speed u_1 and u_2 at respective heights z_1 and z_2 where d is the surface displacement (effect of surface clutter) and z_0 is the roughness length to provide a ratio of the wind speed at the reference height.

$$\frac{u_1}{u_2} = \frac{ln\left[\frac{z_1 - d}{z_0}\right]}{ln\left[\frac{z_2 - d}{z_0}\right]}$$

In urban locations, where the wind speed is required within the urban canopy and therefore below the heights of the surface roughness elements the previous equation does not hold true. Although wind flows will be very site specific, a good fit to the experimental data was found by Macdonald (Macdonald 2000); the same equation was used here for urban sites.

$$u = u(H)\exp\left(-\alpha\left(1 - \frac{z}{H}\right)\right)$$

Where u(H) is the wind speed at the canopy height, H. α is derived from experimental data by (Macdonald 2000) as:

$$\alpha = 9.6\lambda_p$$

Where λ_p is the area density. In this study λp was estimated from satellite images.

4.2 Meteorological measurement summary

The box and whisker plots Figure 6, Figure 7 and Figure 8 summarise the daily mean the range of meteorological conditions used in this study, the statistics are also shown in Table 3.

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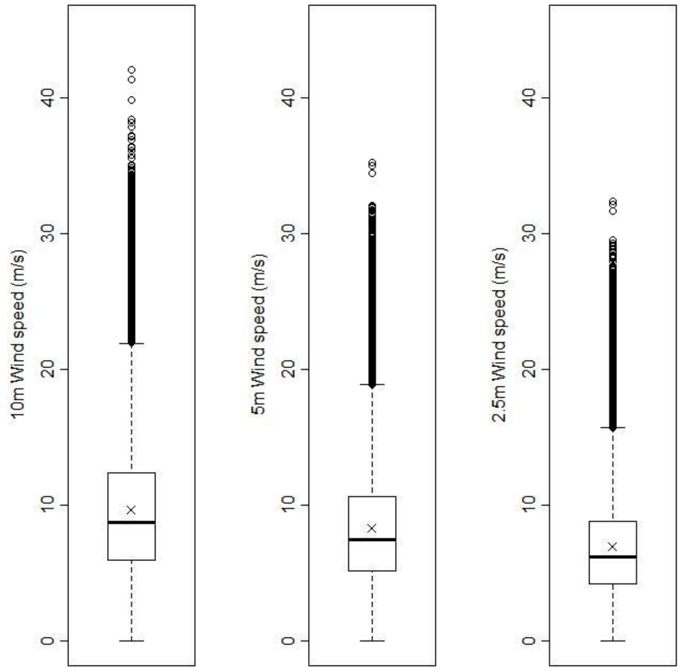

Figure 6: Box and whisker plot of daily mean wind speed measurements at different heights at rural locations between 2000 and 2010

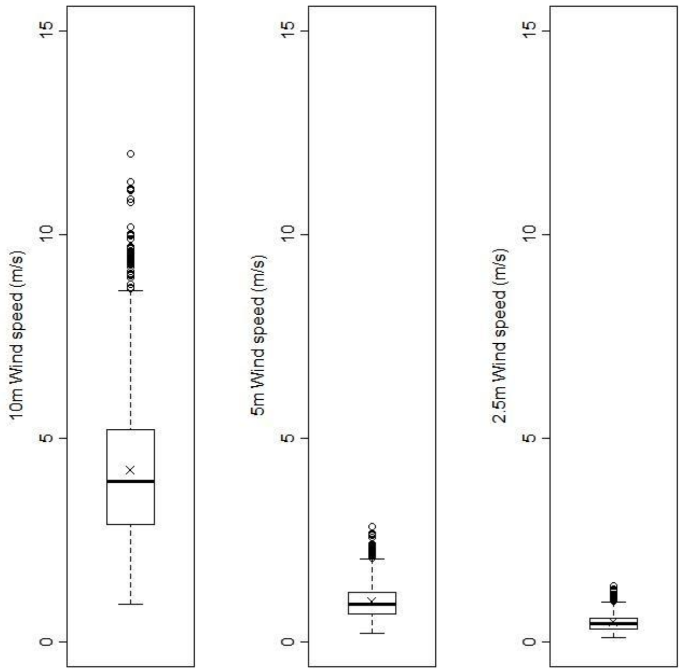

Figure 7: Box and whisker plot of daily mean wind speed measurements at different heights at urban locations between 2000 and 2010

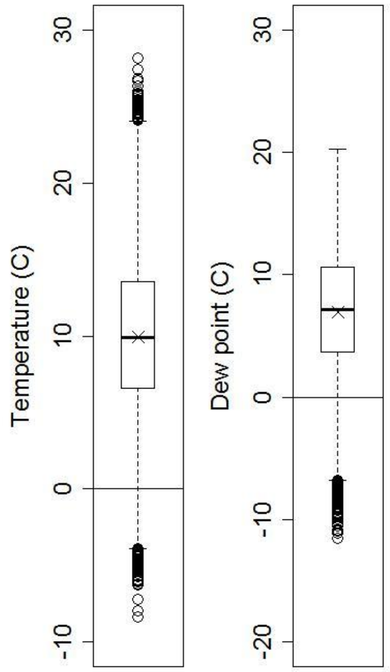

Figure 8: Box and whisker plot of daily mean ambient temperature and dew point measurements between 2000 and 2010

Table 3: Summary statistics for meteorological measurements between 2000 and 2010

Dataset	Wind speed (m/s)						Ambient temperature (°C)	Dew Point (°C)
Start date	1st Jan 2000		1st Jan 2000		1st Jan 2000		1st Jan 2000	1st Jan 2000
End date	1st Jan 2010		1st Jan 2010		1st Jan 2010		1st Jan 2010	1st Jan 2010
Height	10m		5m		2.5m		N/A	N/A
Location	Urban	Rural	Urban	Rural	Urban	Rural	N/A	N/A
Mean	4.2	9.7	1.0	8.3	0.5	6.9	9.9	6.9
Median	3.9	8.7	0.9	7.5	0.5	6.2	9.9	7.1
1st Quartile	2.9	6.0	0.7	5.1	0.3	4.2	6.6	3.7
3rd Quartile	5.2	12.4	1.2	10.6	0.6	8.8	13.6	10.6
Min	0.9	0.0	0.2	0.0	0.1	0.0	-8.3	-11.5
Max	12.0	42.0	2.8	35.3	1.4	32.4	28.2	20.2

5. Trends in PM concentration

Trends in pollutant concentrations depend on changes in emissions and atmospheric chemistry; a full investigation of these issues is beyond the scope of this study. However, the trend in measured pollutant concentration in the years which make up the concentrations used to assess the PM climate is important. Furthermore, the years preceding this needs to be considered to put the assessment period into context. In particular, we are using the FDMS measurements from a small number of years to construct a reference dataset, the presence of an underlying trend may be masked by seasonal and inter-annual variation. It is therefore important to assess whether there was an underlying trend in the longer dataset of TEOM measurements in the years preceding the switch to FDMS measurements.

Trends have been calculated from monthly means using the non-parametric Mann-Kendall approach via the openair tool; data was de-seasonalised, a 75% data threshold specified and the confidence intervals set to 95%.

Figure 9 shows the monthly mean PM_{10} concentrations from the TEOM and FDMS PM_{10} reference datasets with the Mann Kendall trend line running through them, 95% confidence intervals are also shown. The trend in the TEOM PM_{10} measurements was calculated between the start of the reference data set and the end. To assess the impact of the starting date on the trend calculation, the trend was also calculated using a start date of 1st Jan 2000. The trend in the FDMS PM_{10} measurements was calculated between the start of the reference data set and the end. The slopes and the 95% confidence intervals are summarised in Table 4

Instrument	Start Date	End Date	Trend ($\mu g\ m^{-3}$/annum)	Lower CI ($\mu g\ m^{-3}$/annum)	Upper CI ($\mu g\ m^{-3}$/annum)
TEOM	1st Jan 1997	31st Dec 2008	-0.31	-0.48	-0.11
TEOM	1st Jan 2000	31st Dec 2008	-0.03	-0.25	0.16
FDMS	1st Jan 2007	31st Dec 2009	-0.48	-2.81	1.54

Table 4: Mann Kendall trend slopes and the 95% confidence intervals in PM_{10} dataset

The TEOM PM_{10} reference data set between 1st Jan 1997 and 31st Dec 2008 showed a significant downwards trend of -0.31 $\mu g\ m^{-3}$/annum. However, this trend was expected to be unduly influenced by the reduction in concentrations between 1st Jan 1997 and 1st Jan 1999 at the start of dataset. The TEOM PM_{10} trend calculation between 1st Jan 2000 and 31st Dec 2008 support this assumption; this showed no significant trend. There is therefore no significant trend in PM_{10} concentration as measured by the TEOM going into the period measured by the FDMS. This is consistent with a number of studies (Fuller and Green 2006; Harrison, Stedman et al. 2008).

There was no significant trend in the FDMS PM_{10} concentrations between 1st Jan 2007 and 1st Jan 2010.

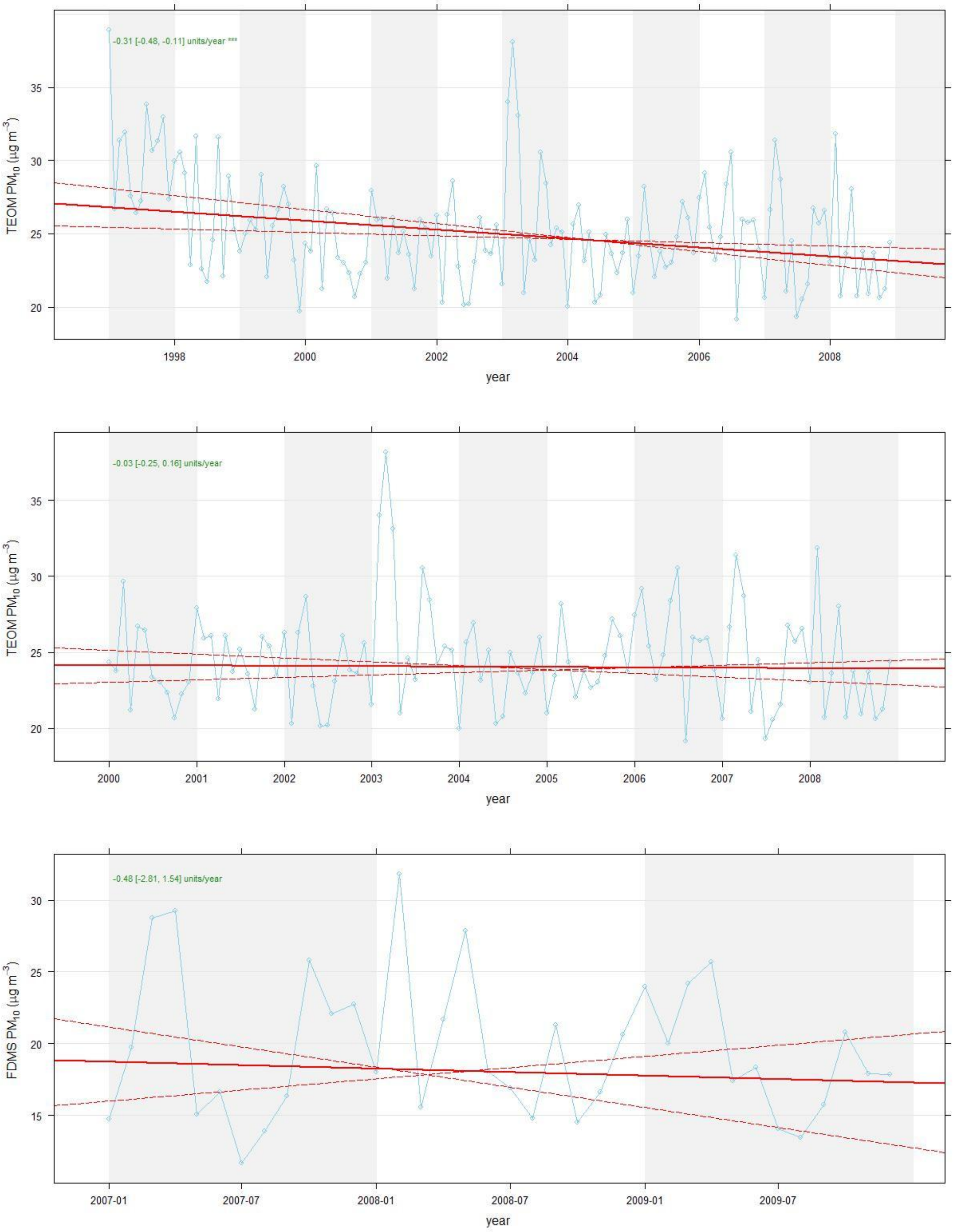

Figure 9: PM_{10} trends using Mann Kendall

6. Seasonality in PM and meteorological metrics

Seasonality in PM metrics is driven by changes in emissions, meteorology and atmospheric processes. The most simple of these drivers is the seasonality in ambient temperature, increases in which lead to higher ambient humidity (Oke 1987), increases in biogenic secondary organic (Marelli 2007) and the evaporation of semi-volatile PM (Seinfeld and Pandis 1998). Synoptic weather patterns also influence PM metrics, high wind speeds over the sea, such as those associated with low pressure systems from the south west, increase the concentration of marine aerosol.

6.1 Seasonality of meteorological measurements

The degree of seasonal variation in daily mean wind speed, ambient temperature and ambient dew point at all rural and urban sites is shown in Figure 10, Figure 11 and Figure 12.

Wind speed has a seasonal variation; the individual monthly means vary between 8.6 and 10.4 m/s while the mean wind speed was 9.5 m/s. It should be noted that the whiskers extend further during the winter, indicating that both windy and calm conditions are more prevalent during this season.

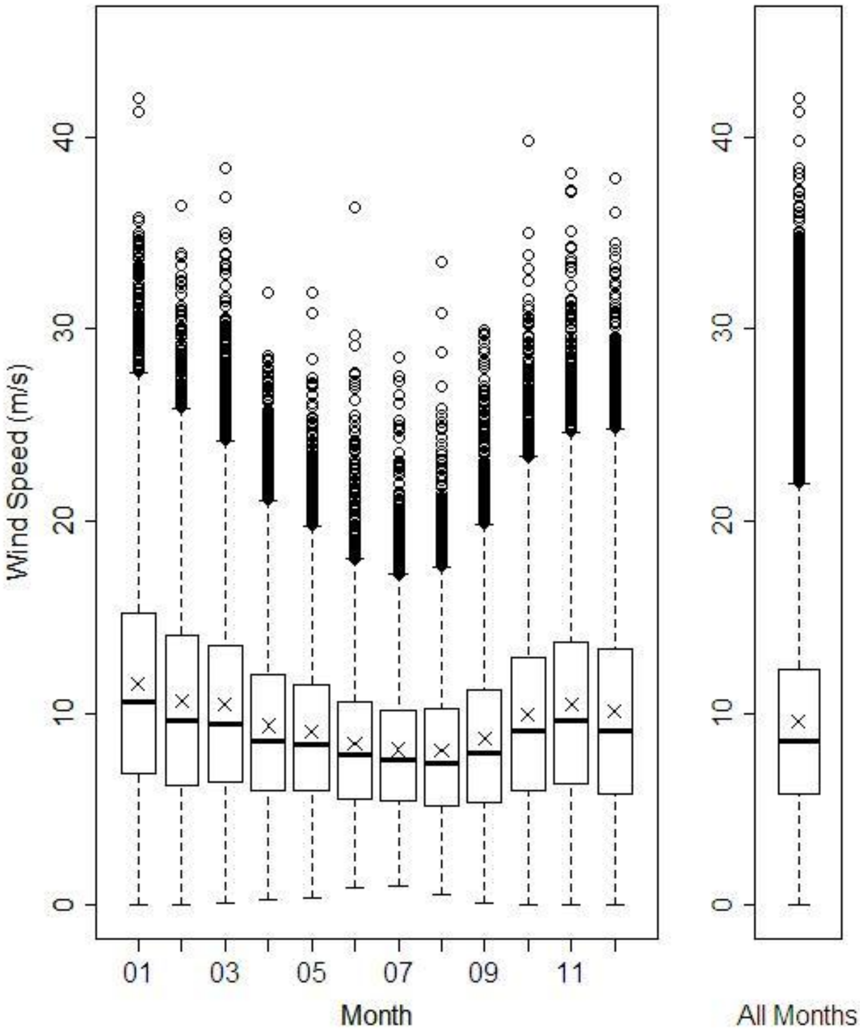

Figure 10: Wind speed measurements for each month and as a mean of all measurements

Ambient temperature has a significant seasonal variation; the individual monthly means vary between 5.1 and 15.5 ºC while the mean ambient temperature was 9.9 ºC.

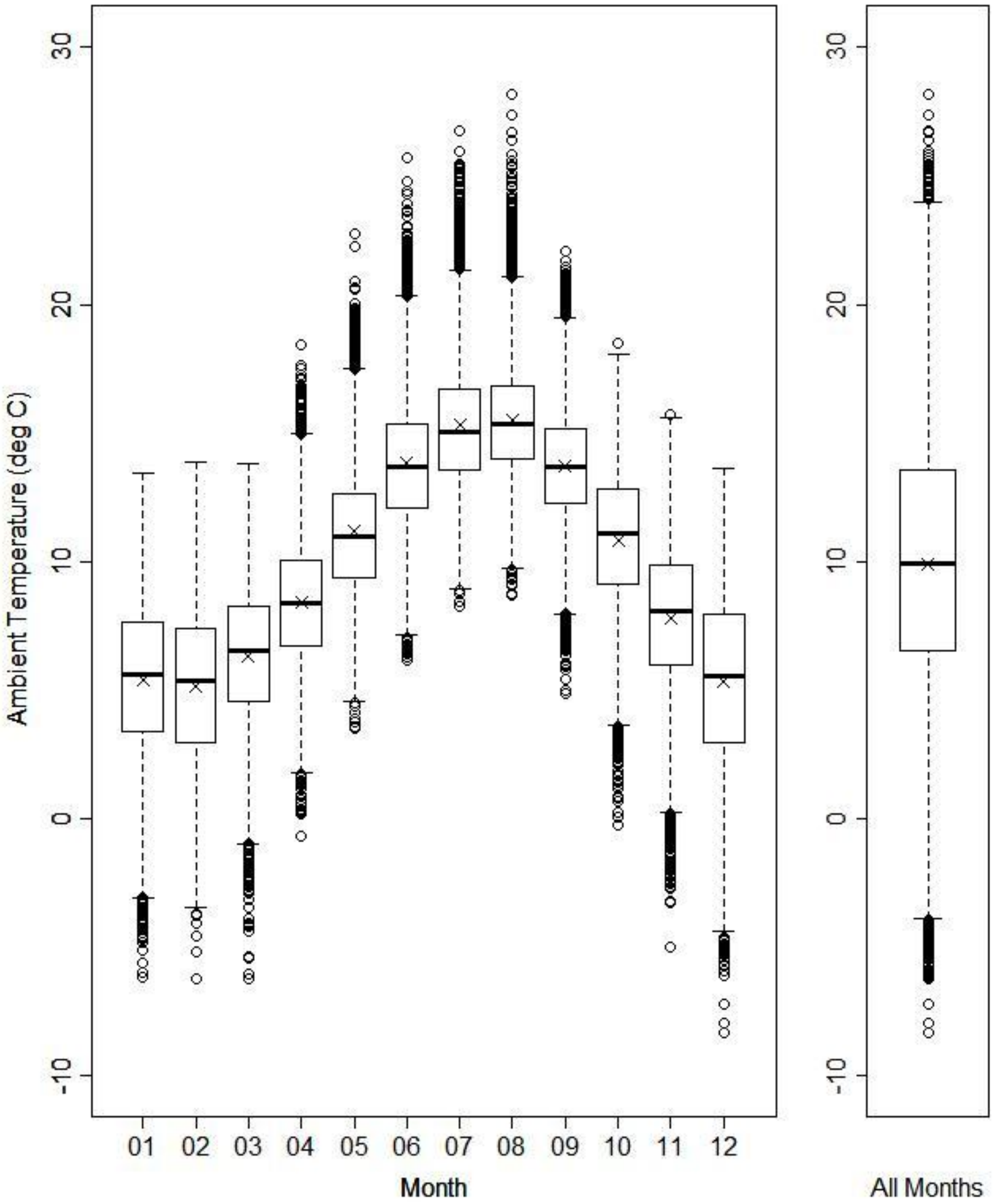

Figure 11: Ambient temperature measurements for each month and as a mean of all measurements

Ambient dew point also has a significant seasonal variation (driven by the changes in ambient temperature); the individual monthly means vary between 2.5 and 12.5 ºC while the mean ambient temperature was 7.0 ºC.

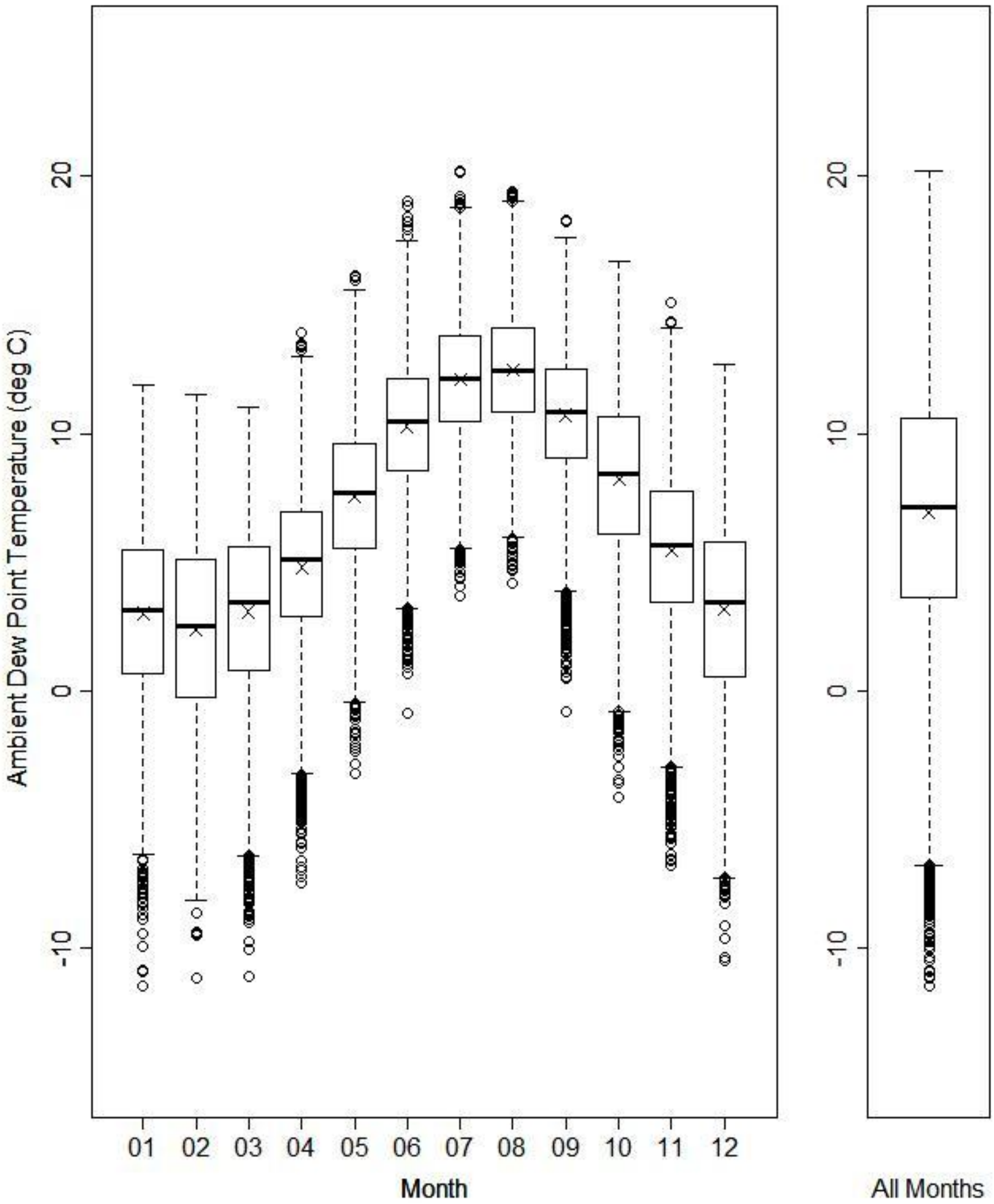

Figure 12: Ambient dew point measurements for each month and as a mean of all measurements

6.2 PM_{10} measurements

There is a limited PM_{10} dataset available from which to draw robust conclusions regarding seasonality however, a distinct seasonality can be seen in the daily mean FDMS PM_{10} measurements. A minimum is apparent in the summer in Figure 13; individual monthly means vary between 13.1 and 23.5 µg m^{-3} while the mean PM_{10} concentration was 18.1 µg m^{-3}. This was not noted by Bigi et al. (2010), who found the seasonal cycle from a London background site to be extremely weak when examining it over a 13 year period. This may have been due to looking at mean and median statistics; the seasonality is accentuated in Figure 13 as it includes the higher percentiles and measurements above the 95^{th} percentile. It may also reflect the ability of the FDMS to measure the semi-volatile PM which peaks in the spring months as shown in Figure 14. The difference between the 13 year period examined by Bigi et al. (2010) and the four years available here will undoubtedly have an effect.

The seasonality of PM_{10} in the UK is not characterised by a summer and winter cycle. Instead, the highest mean concentrations occur in late-winter / early-spring and autumn / winter. During these conditions secondary PM is being formed but the semi-volatile components of this are not being partitioned into the gaseous phase. Peak daily means occur due to the these episodes but also due to Guy Fawkes events in October/November and due to temperature inversions and the resulting lack of dispersion in the winter months.

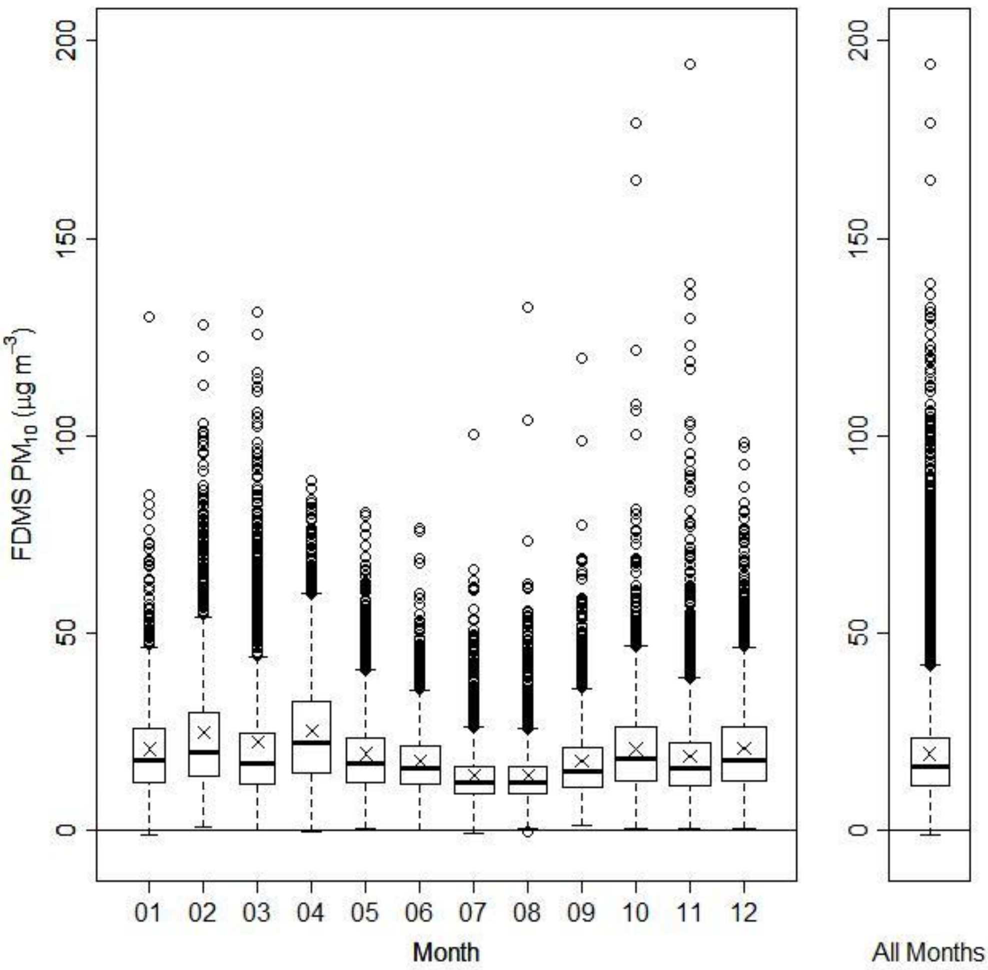

Figure 13: FDMS PM_{10} measurements for each month and as a mean of all measurements

6.3 Semi-volatile PM

It is clear from Figure 14 that the seasonality in the semi-volatile PM concentrations is similar to the FDMS PM_{10} seasonality (Figure 13), although the autumn / winter peak is not so pronounced. Individual monthly means vary between 1.6 and 4.5 µg m^{-3} while the mean was 2.8 µg m^{-3}. It somewhat reflects the inverse of the temperature seasonality shown in Figure 11 as the semi-volatile components in the PM remain in, or are moved into, the gaseous phase at higher ambient temperatures. It is also influenced by the prevalence of easterly winds in the spring time which, combined with relatively low temperatures and high photochemical activity, lead to the production of large amounts of semi-volatile PM and its advection into the UK. The increase in PM_{10} concentrations in winter (Figure 13) is likely to be caused by increased local emissions and limited dispersion rather than semi-volatile PM advected into the UK.

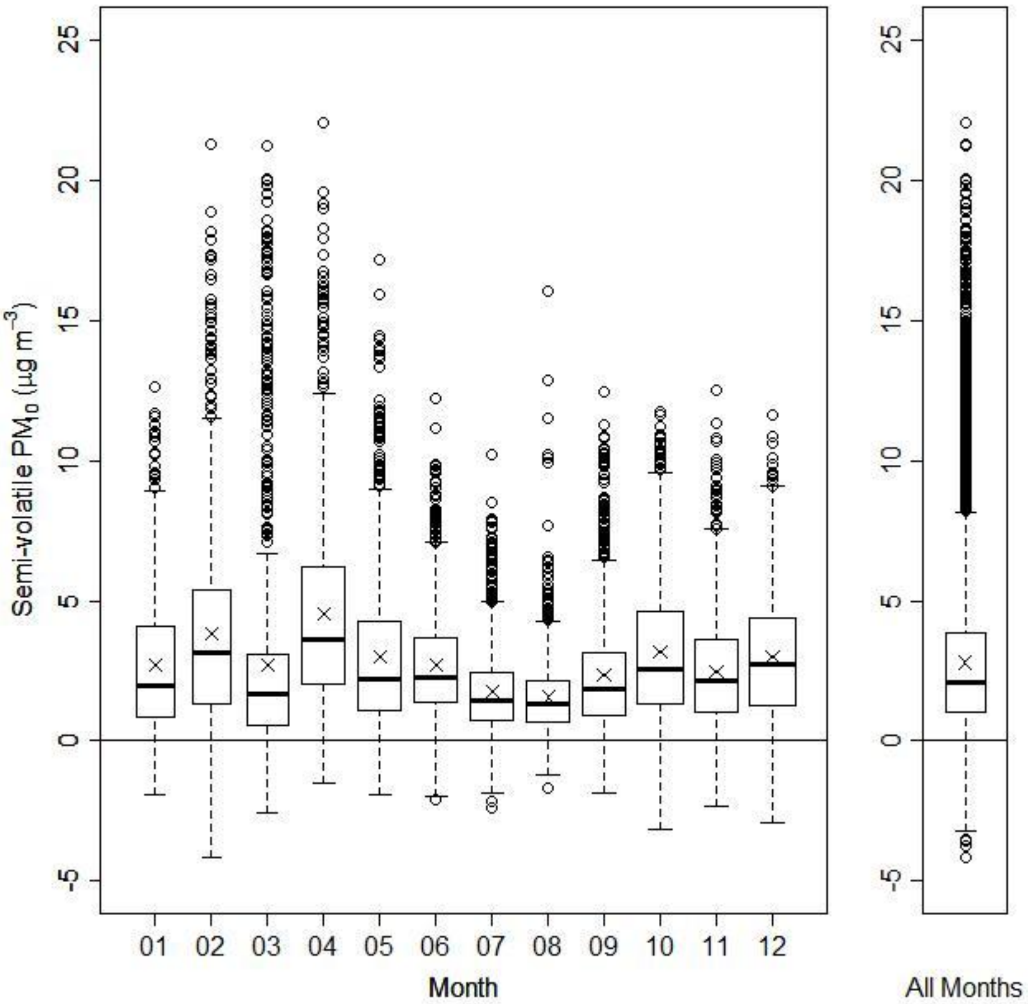

Figure 14: Semi-volatile PM measurements for each month and as a mean of all measurements

7. Future PM Climate

7.1 Changes in the concentration and composition of PM in the UK

Different components of PM_{10} and $PM_{2.5}$ provide a range of measurement challenges. Different sensitivities to PM components, coupled with changes in PM composition may mean that equipment that is reference equivalent today may not be equivalent in the future. Additionally, future changes in PM composition may cause factors derived from equivalence tests to change. This section therefore considers the probable changes in PM composition in the UK in the decade from 2010 to 2020, mainly with respect to PM volatility.

7.2 Projected changes in PM components

A range of emissions reduction measures are in place across the EU and neighbouring countries to decrease air pollution emissions to reduce both ecosystem and health impacts. Total emissions of key pollutants from each EU member state are subject to the National Emissions Ceilings Directive (NECD) (2001/81/EC) and also to international obligations under the United Nations Convention for Economic Commission for Europe's Convention on Long Range Transport of Air Pollution; the so-called Gothenberg protocol.

Looking forward, the EU's Thematic Strategy on Air Pollution, provides a strategic approach towards cleaner air in Europe with interim objectives for 2020. To consider emissions changes between 2010 and 2020, projected 2010 emissions (EEA, 2010) have been combined with projections of EU emissions and emissions from surrounding areas between 2000 and 2020 (Wagner, Amann et al. 2010) using economic and energy projections and also projections of the EU emissions controls. Projected emission changes from sea areas around the EU have also been included reflecting the clear impact of these areas on PM in the UK (NILU 2010). These changes from annual 2010 emissions to annual 2020 emissions are shown in Table 5.

Table 5: Projected annual emission changes from EU 27 and adjacent sea areas 2010 to 2020, relative to 2010

	SO_2	NO_X	Primary $PM_{2.5}$	NH_3	VOC
Change	-50%	-30%	-10%	-11%	-20%

Due to atmospheric chemistry and source location changes in emissions of primary PM_{10} and PM precursors do not result in linear decreases in PM components in the UK. A prime example is the competition between SO_2 and NO_X for available NH_3; decreases in SO_2 can therefore lead to increased concentrations of fine mode NO_3. The sensitivity of UK PM concentrations to emissions changes in Europe were modelled by Derwent et al. (2009). Applying these sensitivity factors, in turn to each emission it is possible to project concentrations changes for UK PM components for 2010 to 2020, as shown in Table 6. Concentrations of other PM components were assumed to be unchanged.

Table 6: Projected changes in annual mean PM between 2010 and 2020.

	SO_4^-	Fine NO_3^-	Coarse NO_3^-	Primary $PM_{2.5}$
Mean concentration change concentration	-46%	+8%	-31%	-10%

Expected concentration changes in each PM component were applied to measured concentrations at three UK sites: Marylebone Road (Kerbside London), North Kensington (Background Inner London) and Harwell (Rural SE England) from 2007 to 2009 using measurements from the UK Particle Concentrations and Numbers network and the Automated Rural and Urban Network. Measurement methods for each component are shown in Table 7. Particle bound water is calculated as proposed by (Frank 2006). Unaccounted PM_{10} is a combination of PM components that are not measured; metal rich

PM_{10} and windblown dust for example and also uncertainty in the sum of the individual component concentrations.

Table 7: Measurement methods for PM components

Component	Measurement Method	Notes
$(NH_4)_2SO_4$	Ion chromatography on daily PM_{10} filters	SO_4^{2-} * 1.46 to account for cation.
Coarse NO_3	Difference between PM_{10} NO_3 from ion chromatography measurements and $PM_{2.5}$ NO_3	NO_3^- * 1.37 to account for cation.
Fine NO_3	R&P 8400 ($PM_{2.5}$)	NO_3^- * 1.35 to account for cation.
NaCl	Ion chromatography on daily PM_{10} filters	Cl^- * 1.65 to account for cation
EC	Sunset analysis of daily PM_{10} filters	
OM	Sunset analysis of daily PM_{10} filters	OC * 1.6
Particle bound water	(Frank 2006)	Depends on SO_4^{2-} and NO_3^-
Unaccounted PM	By difference	Windblown dust and metals, uncertainty in mass closure.
PM_{10}	TEOM (VCM)	Green et al 2009

Concentrations of each PM_{10} component measured in 2010 and projected in 2020 are shown in Table 8. The overall PM_{10} is projected to decrease at each of the three sites. This decrease is mainly caused by a decrease in SO_4^{2-} coarse NO_3^- and to a lesser extend decreases in EC and OM concentrations. By contrast the concentration of fine NO_3^- is expected to increase at each of the three sites.

Table 8: Mean concentrations of PM components at three monitoring sites in 2010 and 2020. Direction of change is indicated by an arrow.

	Rural SE England 2010	Rural SE England 2020	Back ground inner London 2010	Background inner London 2020	Kerbside London 2010	Kerbside London 2020
$(NH_4)_2SO_4$ (µg m^{-3})	3.5	1.9(↓)	3.9	2.1(↓)	4.5	2.4(↓)
Coarse NO_3 (µg m^{-3})	1.4	1.0(↓)	1.1	0.8(↓)	0.2	0.1(↓)
Fine NO_3 (µg m^{-3})	2.7	2.9(↑)	3.7	4.0(↑)	5.6	6.1(↑)
NaCl (µg m^{-3})	2.6	2.6(=)	3.2	3.2(=)	3.9	3.9(=)
EC (µg m^{-3})	0.5	0.4(↓)	1.4	1.3(↓)	8.2	7.4(↓)
OM (µg m^{-3})	4.5	4.1(↓)	6.9	6.2(↓)	11.1	10.0(↓)
Unaccounted (µg m^{-3})	2.2	2.2(=)	-0.5	-0.5(=)	1	1.0(=)
PM_{10} µg m^{-3})	17.3	15.0(↓)	19.7	17.0(↓)	34.5	30.9(↓)

The relative concentrations of each component are shown in Table 9. These relative concentrations are critical to measurement challenges that are posed by semi-volatile PM components and by particle bound water. The greatest change in relative concentration is exhibited by $(NH_4)_2SO_4$ which decreases at all sites. The relative concentration of coarse NO_3 is also expected to decrease at each site. The relative concentration of fine NO_3 shows an increase at each of the sites with other components being stable or increasing.

Table 9: Relative concentrations of PM components at three monitoring sites in 2010 and 2020. Direction of change is indicated by an arrow.

	Rural SE England 2010	Rural SE England 2020	Back ground inner London 2010	Background inner London 2020	Kerbside London 2010	Kerbside London 2020
$(NH_4)_2SO_4$ ($\mu g\ m^{-3}$)	20%	13%(↓)	20%	13%(↓)	13%	8%(↓)
Coarse NO_3 ($\mu g\ m^{-3}$)	8%	7%(↓)	6%	5%(↓)	1%	0%(↓)
Fine NO_3 ($\mu g\ m^{-3}$)	16%	19%(↑)	19%	23%(↑)	16%	20%(↑)
NaCl ($\mu g\ m^{-3}$)	15%	17%(↑)	16%	19%(↑)	11%	13%(↑)
EC ($\mu g\ m^{-3}$)	3%	3%(↑)	7%	8%(↑)	24%	24%(~)
OM ($\mu g\ m^{-3}$)	26%	27%(↑)	35%	37%(↑)	32%	32%(~)
Unaccounted ($\mu g\ m^{-3}$)	12%	14%(↑)	-3%	-3%(↑)	3%	3%(~)

8. European PM Climate

The PM mass concentrations in Europe, including measurements from the UK, have been summarised in reports by the European Environment Agency (EEA 2007). Figure 15 is reproduced from their report which covers 1999-2004; this was constructed by combining rural and urban maps using population density and the measurement points were superimposed on interpolated concentrations. It demonstrates the range of annual mean concentrations experienced across Europe which is attributed to a range of factors including the extent and scale of long-range atmospheric transport, natural sources, the size of cities/agglomerations, distance between neighbouring major cities, density of traffic, the main PM sources in the urban area, national PM control measures and the formation of 'secondary' PM within a country.

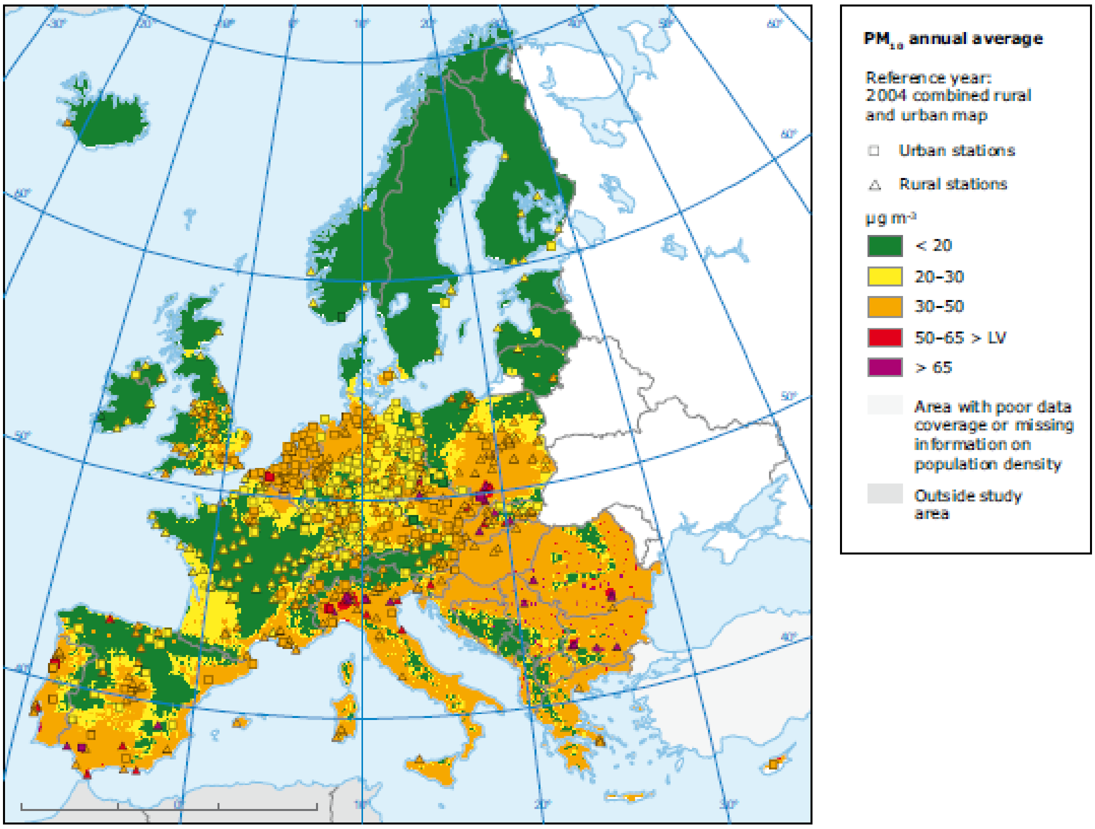

Figure 15: PM10 concentrations in Europe 2004, showing annual average concentrations

Two key academic papers have also sought to assess the physical aspects of PM in Europe (Van Dingenen, Raes et al. 2004; Putaud, Van Dingenen et al. 2010); a third (Putaud, Raes et al. 2004) looked solely at the chemical characteristics. Two figures from Putaud et al., 2010 are reproduced here. The first, Figure 16, shows how the authors divided Europe into geographical sectors: Northwestern, Southern, and Central Europe. In contrast, Figure 17 shows the large range of PM_{10} annual mean concentrations (5-54 µg m^{-3}); there was substantial overlap between regions. The authors did, however, observe significantly larger mean and median PM_{10} concentrations in southern Europe compared to NW and Central Europe. This zonal approach potentially provides a basis for choosing locations which may experience similar conditions to the UK. However, the degree of variation within each member state shown in both Figure 15 and Figure 16 indicates that it is difficult to choose regions or member states with similar PM climates.

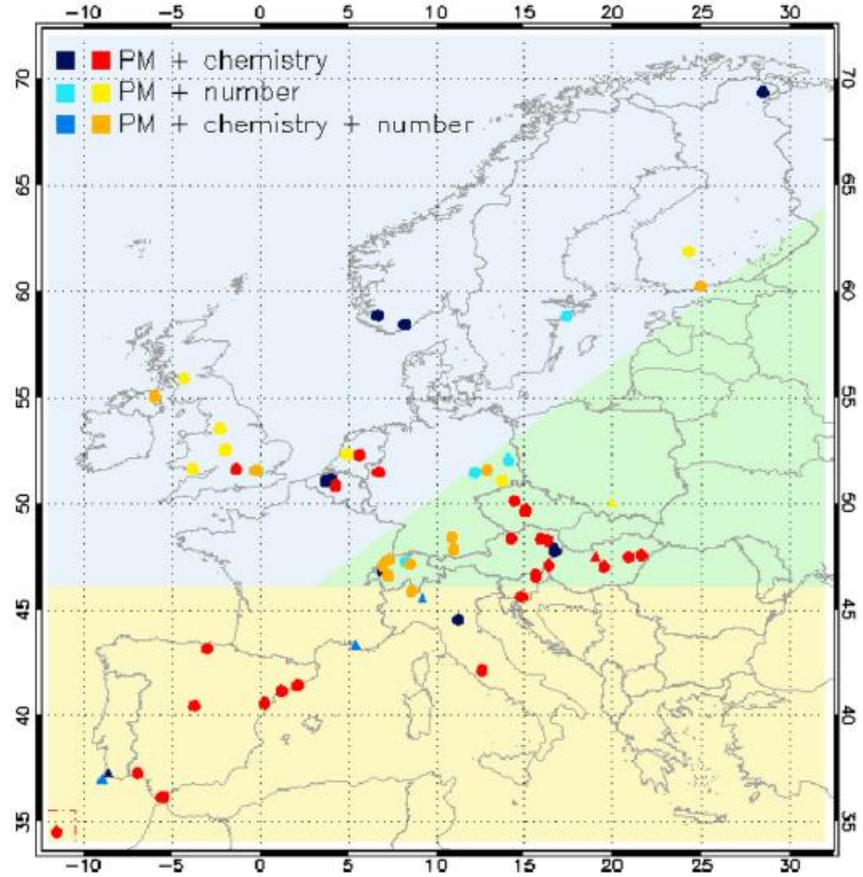

Figure 16: Delineation of Europe into 3 geographical sectors (Northwestern (blue), Southern (yellow), and Central Europe (green)) by Putaud et al. 2010

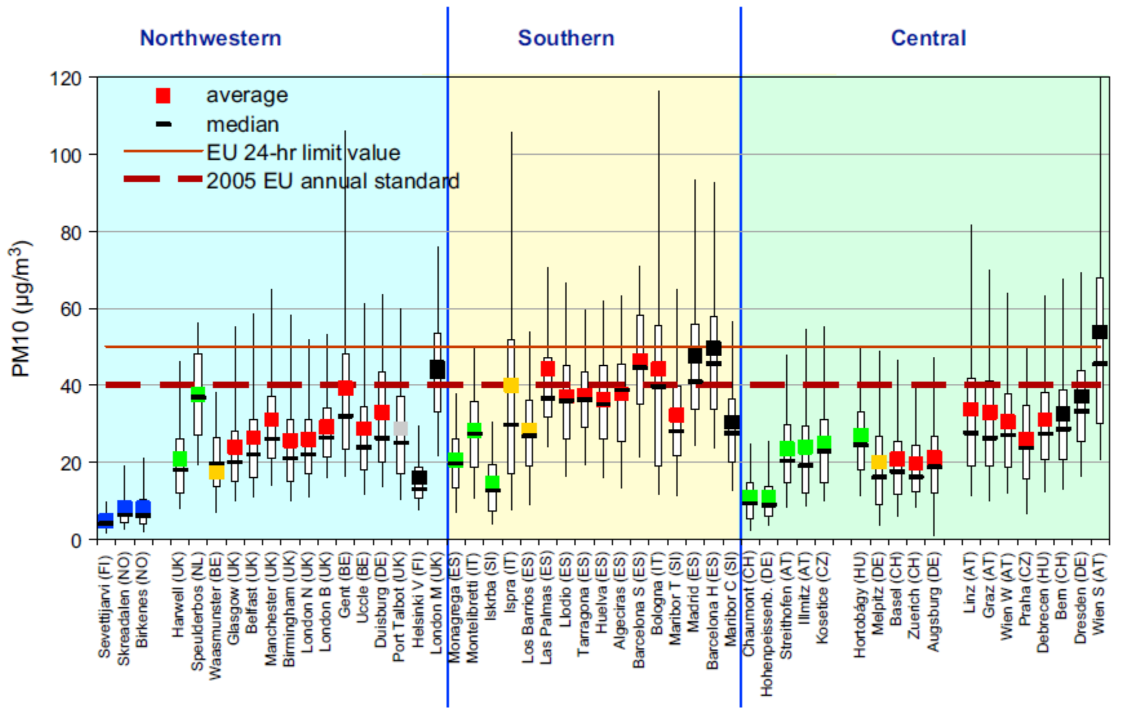

Figure 17: Annual averages of PM_{10} concentrations, including the 5, 25, 50 (median), 75, and 95% percentiles of their 24-h integrated concentrations. Symbol colours indicate the type of site (blue: natural background, green: rural background, yellow: near-city, red: urban background, grey: industrial, black: kerbside).

Section B – Applicability of equivalence test sites and field trial data to the UK PM climate

1. Introduction

Section A described the assembly and attributes of reference datasets. The data sets assembled were of varying lengths from 1 year to 12 years and the number of sites in each dataset varied from only 3 sites to 61 sites; the usefulness of these datasets therefore also varied. For the purposes for the GDE, only meteorological data, PM_{10}, $PM_{2.5}$ and semi volatile are of interest. The $PM_{2.5}$ data, although having 61 sites, only spans a single year and is therefore not considered to be representative of interannual variation. Only PM_{10} is taken forward in the analysis in this section to assess UK PM climate; although some estimates regarding $PM_{2.5}$ are made in section 7.

This section of the report details the statistical analysis proposed to demonstrate whether sites used for equivalence field tests are representative of typical PM_{10} conditions for the UK. It also proposes high and low threshold for semi-volatile PM and meteorological factors referred to in the GDE. To assist equipment manufacturers, locations and seasons which are most likely to achieve the proposed thresholds are identified.

It is important that measurements compared against these thresholds are made under the same conditions as those used to set the thresholds. PM_{10} concentrations should be measured using methods which have shown equivalence to the reference method. Semi-volatile PM measurements (or $PM_{2.5}$ nitrate measurements) should be made using robust QA/QC and as far as possible using the same methodology as the UK. Meteorological measurements should be quality assured and free from local influences such as buildings which may result in shading for both temperature measurements and wind speed.

1.1 Guide to the Demonstration of Equivalence

The Guide to the Demonstration of Equivalence describes the principles and methodologies used for the demonstration of the equivalence of methods other than the EU reference methods. It is intended for use by laboratories nominated by National Competent Authorities (see Directive 2008/50/EC) to perform the tests relevant to the demonstration of equivalence of ambient-air measurement methods (EC 2010).

Special consideration is given the text from the Guide to the Demonstration of Equivalence for Ambient Air Monitoring Methods (GDE) (EC 2010); in particular that reproduced from page 58 in Figure 18.

"Test sites shall be representative for typical conditions for which equivalence will be claimed, including possible episodes of high concentrations.

A minimum of 4 comparisons at a minimum of 2 sites shall be performed preferably in different climatic seasons with particular emphasis on the following variables, if appropriate:

- *Composition of the PM fraction, notably high and low fractions of semi-volatile particles, to cover the maximum impact of losses of semi-volatiles*
- *Air humidity and temperature (high and low) to cover any conditioning losses of semi-volatiles during the sampling process*
- *Wind speed (high and low) to cover any dependency of inlet performance due to deviations from ideal behaviour as dictated by mechanical design, or deviations from the designated sampling flow rate."*

Figure 18: Text from GDE, page 58 (EC 2010)

A key part of this study has been quantifying what typical conditions are for the UK and developing a statistical protocol for establishing whether measurements made are representative of these conditions. Furthermore, high and low thresholds for semi-volatile PM, air humidity, temperature and wind speed have been quantified.

2. Methodology for assessing typical conditions

This section aims to develop and test a methodology for assessing whether test sites used are representative for typical conditions for which equivalence will be claimed in the UK. As such it refers to the section of the GDE text in Figure 18. It is included to avoid instruments passing equivalence tests in conditions which are unrepresentative of where they will be deployed. However, the guidance does not include a methodology for comparing data gathered during an equivalence test and typical conditions.

2.1 Statistical techniques

One method for demonstrating whether sites used were representative of UK conditions is to perform a comparison between the measurements in the reference dataset assimilated in section 1 and those used to demonstrate equivalence. In this way, any potential dataset could be compared to the established UK reference dataset with pass/fail criteria.

Many statistical techniques exist for comparing two groups of data and identifying whether one differs from the other. The most commonly used is the t-test which can be used to compare datasets which are normally distributed. However, air pollution data is typically non-parametric due to occasional episodes of high concentrations. Data can either be transformed (e.g. a log transformation) and analysed using the t-test or analysed using a non-parametric test such as the Mann-Whitney test.

Statistical tests are accompanied by a significance level (α), this is the probability of incorrectly rejecting the null hypothesis. In this case the null hypothesis would be that there was no difference between the two datasets. It is a "management tool" dependent on the objectives of the study. Traditionally 5% (0.05) is used as a value of α, but there is no reason why other values should not be used. Suppose that an expensive cleanup process will be mandated if the null hypothesis of "no contamination" is rejected, for example. The α-level for this test might be set very small (such as 1%) in order to minimize the chance of needless cleanup costs (Helsel and Hirsch 2002). This example is not dissimilar to the financial implications of retesting equipment. The p-value is calculated by the statistical test and is the probability of obtaining the computed test statistic, or one even less likely, when the null hypothesis is true. Therefore when the p-value is less than the decision criteria (the α-level), the null hypothesis is rejected. When the p-value is greater than α, the null hypothesis is accepted and no difference could be identified between the datasets.

To examine whether this methodology (comparing the reference dataset to the test dataset) was a viable way forward, the Mann-Whitney test was used could be used two compare the reference dataset with two different types of field trials datasets. The statistical formula for the Mann-Whitney test is given in Appendix III.

2.1.1. Equivalence field trials data

Two sets of equivalence field data were available:

- Equivalence field trails already undertaken in the UK and Europe
- Periods within the UK PM_{10} reference dataset that meet the GDE criteria for field trials tests

The equivalence field trials data have been generated from a range of activities in Europe over the last 10 years including the CEN pan-European $PM_{2.5}$ trails, equivalence tests in the UK (both 2004-6, 2007 and 2008), equivalence tests in Austria, equivalence trials in Germany and the latest MCERTS trials in the UK and Germany.

Periods within the UK PM_{10} reference dataset that meet the GDE criteria for field trials tests were identified by selecting 40 day periods from within the established UK reference dataset which are representative of equivalence tests (i.e. having at least 20 % of daily mean PM_{10} concentrations above the Upper Assessment Threshold (UAT)); this was termed the UAT reference dataset.

The Mann-Whitney test showed that nearly all of the equivalence field trials datasets and those in the UAT reference dataset where significantly different from the UK reference dataset based on a significance level (α) of 1%. This is because the GDE statistics include the requirement for 20% of the daily mean measurement to be above the UAT. Equivalence tests are therefore undertaken in locations and time periods when these conditions will be met; the measurements provided by equivalence test may therefore be skewed towards higher concentrations. This is demonstrated in Figure 19 which shows the difference between the UK PM_{10} reference dataset and the UAT reference dataset. No 40 day period from the rural sites had 20 % of daily mean PM_{10} concentrations are greater than the UAT. The mean for the background sites increased from 19.2 µg m^{-3} in the UK PM_{10} reference dataset to 24.0 µg m^{-3} in the UAT reference dataset, the mean for the traffic sites increased from 27.0 µg m^{-3} to 33.0 µg m^{-3} and the mean for the industrial sites increased from 26.2 µg m^{-3} to 27.4 µg m^{-3}. Therefore, because of the requirements in the GDE requirements to have 20% of measurements above the UAT, the test dataset cannot be representative of typical UK conditions as described by the UK PM_{10} reference dataset. This statistical methodology, which compared the two datasets, did not provide a valid way of demonstrating whether datasets were representative of UK conditions.

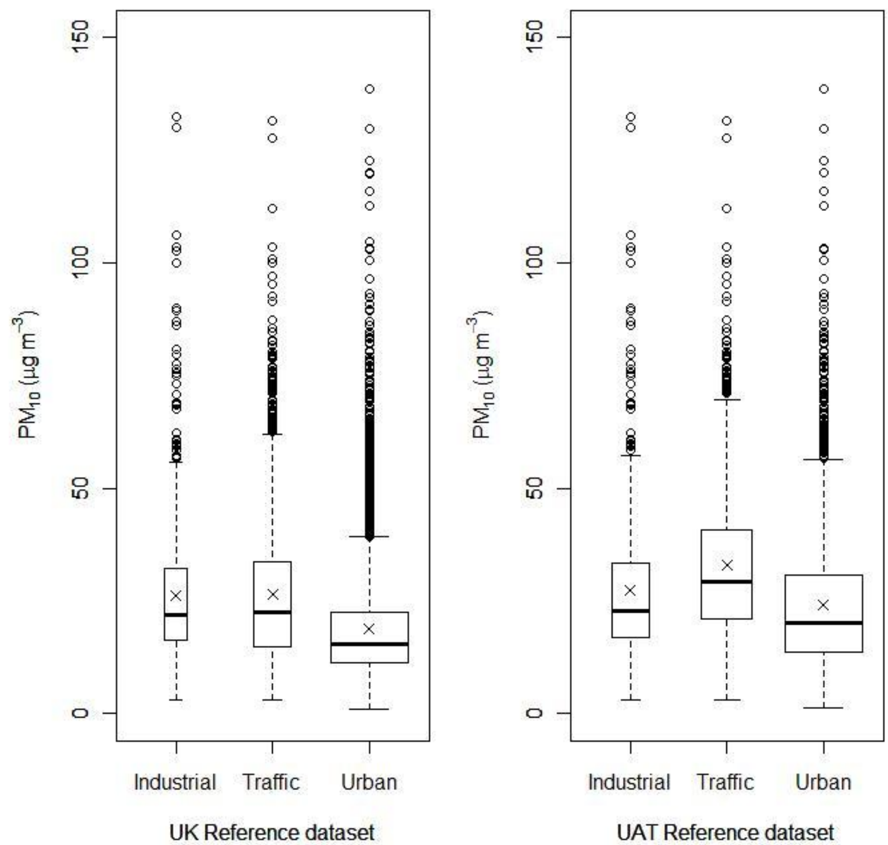

Figure 19: Box and whisker plot of daily mean FDMS PM_{10} measurements from industrial, traffic and background sites in the UK PM_{10} reference and UAT reference datasets

2.1.2. Monitoring site annual mean concentrations

Rather than examining specific datasets used for equivalence, which have been shown to be positively skewed, it was possible to compare data from whole years from individual monitoring sites from around Europe against the UK reference dataset for the corresponding site type using the Mann-Whitney test. Twelve months of data could be considered representative of the monitoring site if it were used for an equivalence field trial and, importantly, free from the positive skew induced by the UAT requirement. If the Mann-Whitney test could not differentiate between the datasets (p value >=0.1), the site could be considered representative of UK conditions. This provided a second possible way forward for comparing datasets using a statistical method.

To establish whether this was a practical methodology, the Mann-Whitney test was used to compare the daily mean PM_{10} concentrations from individual urban background UK monitoring sites in 2008 against the UK reference dataset containing only urban background sites; the results of these tests. The Mann-Whitney test statistic (Z_{rs}) and p value from these tests are shown in Table 10; comparisons with a p value >=0.1 are highlighted. It is clear that not even all UK monitoring sites can be considered representative of the UK using this test.

Table 10: Mann-Whitney test results for individual UK monitoring sites in 2008 against the UK reference dataset

Airbase EOI Site Code	Mann-Whitney test statistic (Z_{rs})	p
GB0962A	-0.03	0.977
GB0658A	-0.57	0.572
GB0646A	-1.27	0.204
GB0739A	-1.41	0.158
GB0731A	1.79	0.073
GB0776A	-2.18	0.029
GB0882A	-2.28	0.023
GB0728A	2.58	0.01
GB0884A	2.69	0.007
GB0568A	-2.7	0.007
GB0613A	2.75	0.006
GB0580A	3.32	0.001
GB0569A	-8.89	0
GB0839A	-4.93	0
GB0597A	-3.71	0
GB0777A	-7.85	0
GB0687A	-8.2	0
GB0615A	5.66	0
GB0598A	3.86	0
GB0730A	-10.16	0

This initially anomalous result can be explained by examining the Mann-Whitney statistical formula in Appendix III. The standard deviation (σ_{wt}) will be very small for large datasets such as the UK reference dataset and the 12 months of data from each of the monitoring sites used in these tests; this will tend the Mann-Whitney test statistic (Z_{rs}) to be large and therefore p to be small. An alternative way of illustrating this effect is demonstrated in Figure 20, which shows the means and confidence intervals of the UK PM_{10} reference dataset for background sites and each background site in the UK PM_{10} reference dataset separately. It is clear that the confidence intervals of many sites do not overlap with the UK reference dataset for background sites. Therefore, because of the small standard deviation of ranks in the Mann-Whitney test for the large datasets compared, different datasets could be distinguished easily. Therefore, this statistical methodology, which compared the two large datasets, did not provide a valid way of demonstrating whether sites used were representative of UK conditions.

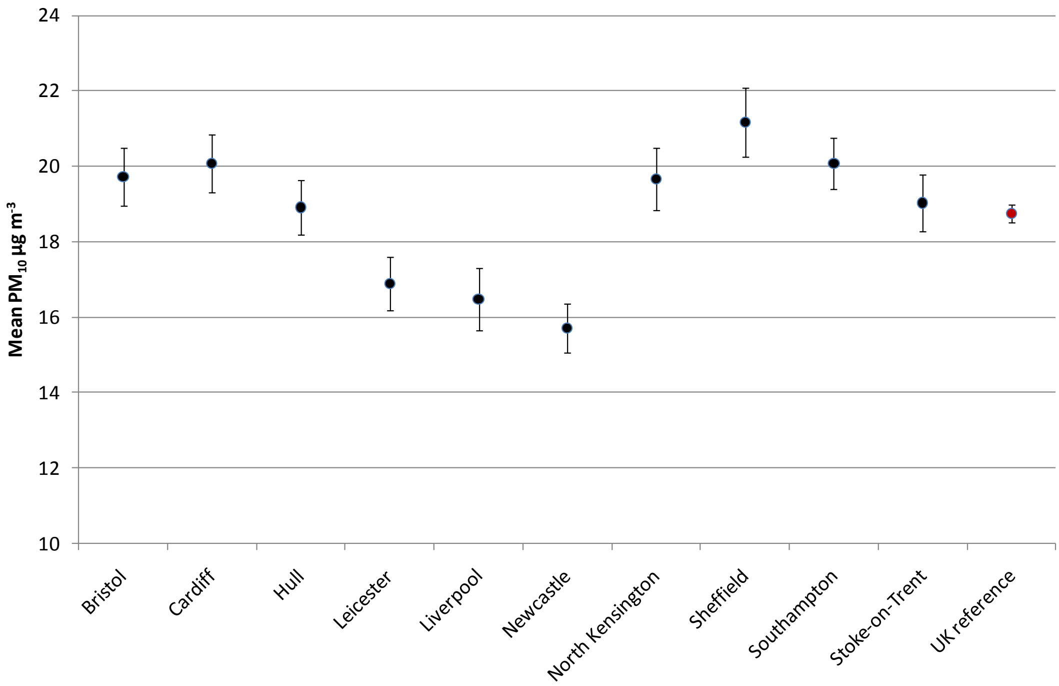

Figure 20: PM_{10} means and confidence intervals of UK background monitoring sites

2.2 Comparison of UK PM_{10} concentrations with European PM_{10} concentrations

As a statistical methodology could not be derived to compare field test datasets or field test locations with the UK reference dataset, a comparison of UK PM_{10} concentration with European PM_{10} concentrations was undertaken to highlight areas of Europe most likely to be representative of typical UK conditions. To enable this, a range of mean concentrations for each site type was calculated, this not only allowed similar areas of Europe to be highlighted but also provided a range of concentrations against which field test locations can be assessed. The long term mean from prospective field test location should fall within the range of means experienced within the UK for that site type.

As discussed, the PM_{10} dataset is not normally distributed. This results in the arithmetic mean being positively skewed due to episodes of high concentrations. Instead the geometric mean is used here, this summary statistic is an appropriate measure for air pollution concentrations that tend to follow a log normal distribution (Frank, Anderson et al. 2011). The geometric mean (GM) is defined in Appendix III.

A geometric annual mean PM_{10} concentration for each site in the UK and Europe was calculated for 2007, 2008 and 2009 where data capture was greater than 75%. Suburban background and urban background sites have been grouped together as background. All sites in the UK were used, rather than being restricted to those chosen for the UK reference dataset to give a more representative range of concentrations. This could be done as issues which would affect the dataset when viewed as a whole, such as changes in the number of sites and distribution of site types, are not of concern when each site and year is included separately. In the UK, the number of rural and industrial sites which used FDMS instruments was very limited (only 2 rural sites and 1 industrial site); the instrument type was therefore expanded to include VCM corrected TEOM measurements. In Europe, only sites where FDMS and gravimetric instruments were known to be used were included as these provided the best direct comparison to UK network measurements and the uncertainties surrounding correction factors for TEOM and BAM instruments would have limited the conclusions which could be drawn. For some stations, the measurement definition in the Airbase database is unclear, for instance the French PM_{10} measurement method is defined as oscillating microbalance rather than TEOM or FDMS and has therefore been omitted from this analysis.

The number and range of geometric annual mean concentrations at UK sites at each site type and the number of sites in Europe which are within this range, above and below this range are shown in Table 11. These results demonstrate that around 60 - 95% of European sites fall within the range of concentrations in the UK, depending on site types.

Table 11: Range of geometric annual mean reference equivalent PM_{10} concentrations experienced at UK site types and the number of European sites which fall below, within and above this range

Site Type	UK PM_{10} Range			Number of European sites		
	n	Minimum (μg m^{-3})	Maximum (μg m^{-3})	Below Range	Within Range	Above Range
Background	52	11.9	25.7	6	263	145
Roadside	14	10.9	42.3	0	206	7
Rural	7	4.3	18.1	0	107	32
Industrial	7	13.8	24.6	0	37	18

The geographical distribution of these sites around Europe is shown in Figure 21 and Figure 22. The distribution in these maps reflects both the concentrations of PM_{10} in Europe and the member states which undertook monitoring using FDMS and gravimetric techniques in the 3 year period. Despite the constraint on measurement technology some patterns are distinguishable.

The background monitoring stations in Poland, Romania and Bulgaria tend (although not all the time) to measure higher concentrations that experienced in the UK. This is also true of the northern part of Italy around the Po Valley. Rural monitoring stations in these locations also measure higher concentrations that experienced in the UK. Some of the background sites in Ireland and Sweden experience concentrations below those of the UK.

The range of concentrations experienced at roadside locations in the UK encompasses most of those in Europe except a few sites in Italy, Romania and Bulgaria. The concentrations found at these sites are more closely related to the strength of the traffic emission source than the regional PM climate. The same is true of the industrial sites.

Although the geographical information from a comparison with European sites is somewhat limited, this analysis does highlight areas of Europe which should be considered to be outside the range of typical conditions for which equivalence will be claimed in the UK. Furthermore, it provides a range of geometric mean concentrations against which a long-term mean from a field test site can be compared against. This range of geometric means from the UK should be updated in future years to improve the geographical and temporal coverage of this description of UK PM_{10} conditions. The test site should only be considered representative for typical conditions in the UK if the long-term geometric mean (preferably annual) falls within the UK range of geometric means for that site type. This may happen at locations other than those indicated.

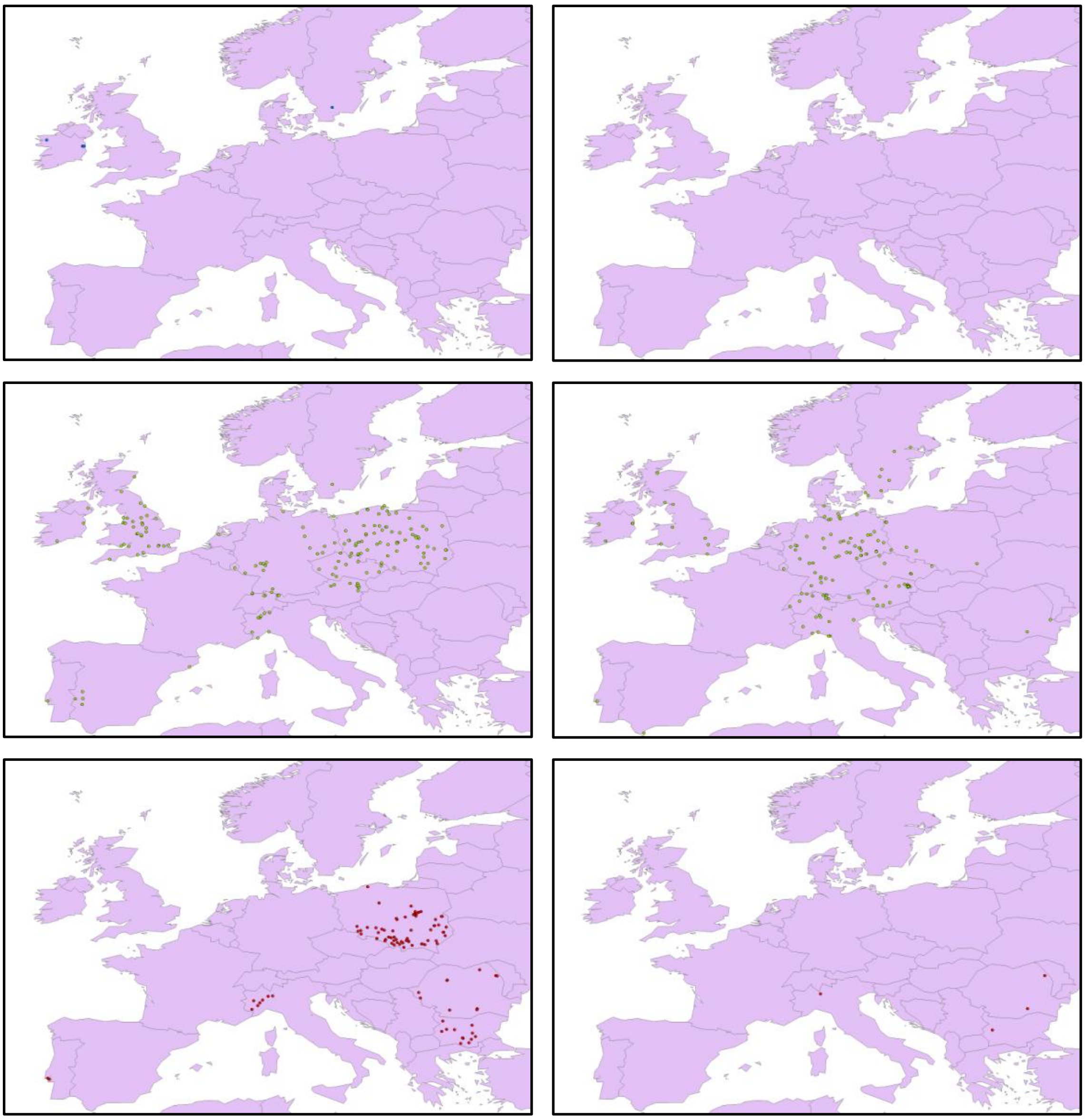

Figure 21: Background (left) and roadside (right) sites in Europe which are below (top) within (middle) and above (bottom) the range of geometric annual mean PM_{10} concentrations experienced in the UK in 2007, 2008 and 2009

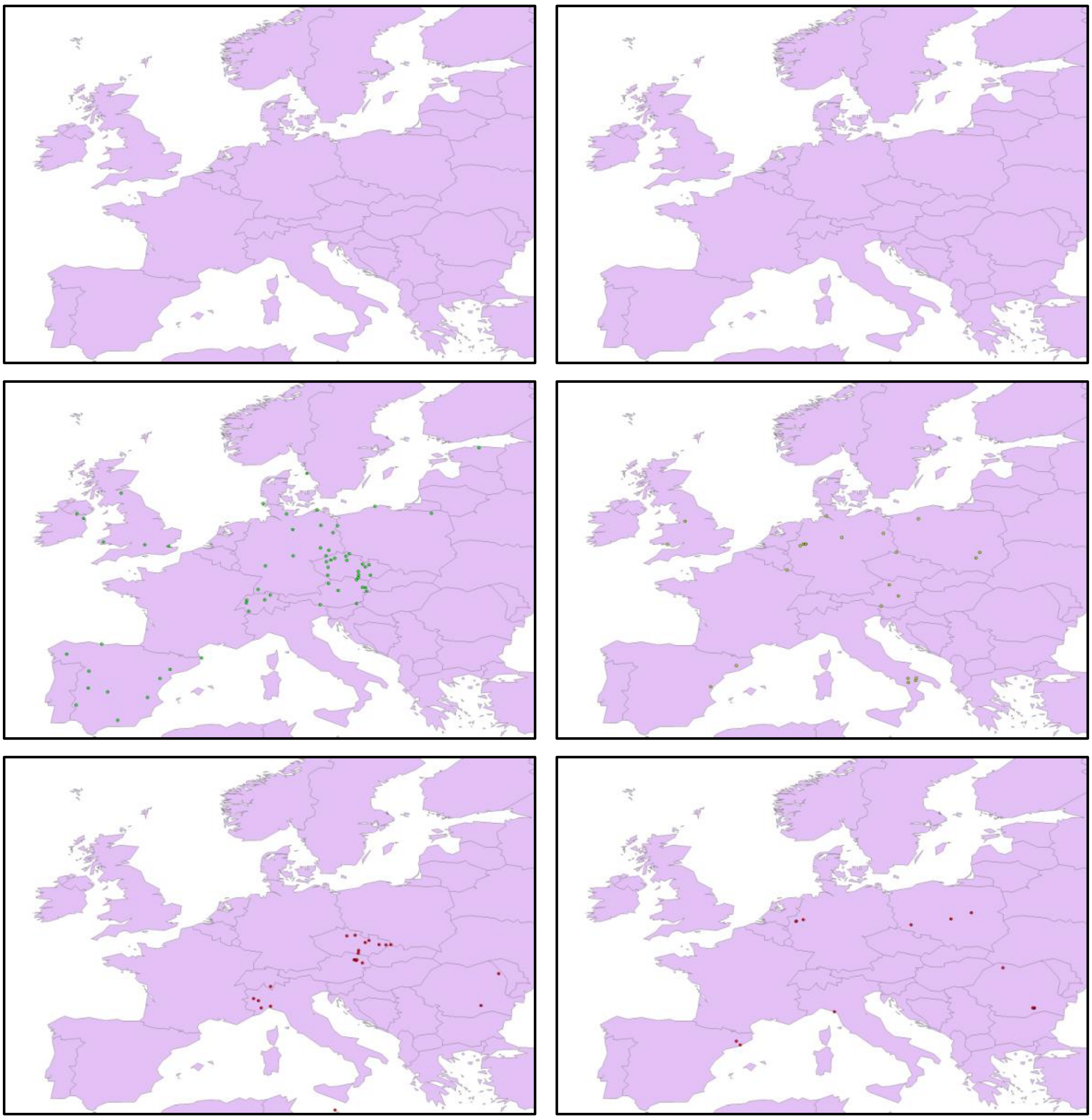

Figure 22: Rural (left) and industrial (right) sites in Europe which are below (top) within (middle) and above (bottom) the range of geometric annual mean PM_{10} concentrations experienced in the UK in 2007, 2008 and 2009

3. High and low thresholds of semi-volatile PM and meteorological conditions

As shown in Figure 18, the GDE states that particular emphasis should be paid to high and low fractions of semi-volatile particles as well as high and low wind speed, ambient temperature and air humidity. The PM and meteorological reference datasets have been analysed to establish potential high and low thresholds. Consideration has been given to the level at which the thresholds should be set to provide a metrological challenge.

3.1 Semi-volatile PM

As discussed in section 3, semi-volatile PM is the term used to describe components of PM which partition into the vapour phase during or after sampling. These components include ammonium nitrate, ammonium chloride, a range of organic compounds and water. This component can be measured at site, using the FDMS, or indirectly as $PM_{2.5}$ ammonium nitrate as it has shown an excellent correlation has been demonstrated in several studies. Alternatively, it could be measured regionally using either of these metrics at a site within 130km; this is the geographical range of the Volatile Correction Model (Green et al. 2009).

Setting a 'high' threshold of semi volatile concentrations which equivalence test should meet needs to consider firstly, concentrations at which the loss of semi-volatiles would significantly affect the measurement. Of course, any semi-volatile PM loss would adversely affect the measurements, however, a threshold level needs to be set at which the loss is significant. This loss also needs to be considered alongside any potential loss from the reference measurement. The loss of this component has been widely reported from samplers (Chow, Watson et al. 2005) and recently commented upon in relation to current equivalence trials by Harrison et al. (2010). To detect a loss of semi volatile PM when compared to the reference method, the loss of semi-volatile PM really needs to be distinguishable from the uncertainty in the measurement. The expanded relative uncertainty of the reference method at the daily mean limit value (50 $\mu g\ m^{-3}$) was calculated as 3.85 $\mu g\ m^{-3}$ (7.7 %) (CEN 2011). Therefore, the high threshold should be greater than 3.85 $\mu g\ m^{-3}$.

Consideration also has to be given to the measurements experienced in the UK when setting both high and low thresholds as these thresholds need to be easily achievable within a test period (although still metrologically challenging). In section 3 the concentration of semi-volatile PM, as measured by the FDMS reference channel at a number of sites around the UK between 2007 and 2010 was summarised. This dataset was used to calculate potential high and low thresholds in the UK using a range of percentiles; these are shown in Table 12.

Clearly, a dataset with a large number of high semi-volatile PM measurements would provide the greatest emphasis on any potential loss of this component but this is an unreasonable expectation. The number of measurements required to provide 'particular emphasis' needs to be large enough to be detectable and influence the equivalence statistics without excluding too many conditions which could provide datasets which conform to the 20 % of measurements above the UAT criteria.

Table 12: Percentiles of semi-volatile measurements in the UAT reference dataset

Statistic	Semi-volatile PM_{10} concentration (µg m^{-3}) in reference dataset
95th percentile	8.1
90th percentile	6.3
75th percentile	3.9
Median	2.1
25th percentile	1.0
10th percentile	0.1
5th percentile	0.3

Losing all of this semi-volatile PM only just exceeds the PM_{10} expanded uncertainty at the limit value; such a loss may not be distinguishable from the uncertainty within the measurement. The 90th percentile is 6.3 µg m^{-3}; the loss of this concentration of semi-volatile material is 163% of the expanded uncertainty and should therefore be detectable under most circumstances. At this 90th percentile 4 of the 40 days would be expected to provide semi-volatile PM concentrations above 6.3 µg m^{-3} by chance. As discussed, the equivalence field trials data are skewed towards higher concentrations and in practice high semi-volatile PM concentrations will also be more prevalent in these datasets. Advice on choosing sampling periods in the UK which are likely to exceed this threshold is given in section 5.

A low threshold for semi-volatile PM only needs to provide a contrast to the high concentrations of semi-volatile PM. The median (2.1 µg m^{-3}) was therefore chosen as the low threshold.

In the absence of these measurements, an as discussed in section 3, $PM_{2.5}$ nitrate concentrations could be used as a surrogate of semi-volatile PM as this has shown a good agreement with FDMS reference channel (Hering, Fine et al. 2004; Green, Fuller et al. 2009).

3.2 High and low meteorological conditions

The statistics in section 4 allow us to quantify what is high and low as referred to in the GDE for wind speed, ambient temperature and air humidity. The meteorological measurements are considered and the feasibility of an equivalence trial achieving the threshold levels set.

Table 13 shows the 1st and 3rd quartiles of the dataset described in section 4. As quartiles, these values represent the 25th and 75th percentiles; on average 25% of measurements will therefore be below the low threshold and 25% of measurements above the high threshold.

Table 13: 25th and 75th percentiles for meteorological conditions measured at Heathrow

	Wind speed						Ambient temperature	Dew Point
	Threshold value (m/s)						Threshold value (°C)	Threshold value (°C)
Height	10m		5m		2.5m			
	Urban	Rural	Urban	Rural	Urban	Rural		
25th Percentile	2.9	6.0	0.7	5.1	0.3	4.2	6.6	3.7
75th Percentile	5.2	12.4	1.2	10.6	0.6	8.8	13.6	10.6

3.2.1. Wind speed

The GDE recommends that the sample inlets should be tested in conditions which "cover any dependency of inlet performance due to deviations from ideal behaviour as dictated by mechanical design, or deviations from the designated sampling flow rate". Deviations from the reference PM_{10} or $PM_{2.5}$ size selection efficiency curve are tested by the US EPA in a wind tunnel at a range of wind speeds (0.5, 2.2 and 6.6 m/s) (VanOsdell 1991).

The wind speed in the reference dataset was measured on a 10 m mast in predominantly rural locations around the UK; London Heathrow was the only urban measurement location. As the wind speed is affected by surface roughness conditions the dataset has been split into urban and rural sites. At rural sites the measured daily mean wind speed varied between 0 and 42 m s^{-1}. At London Heathrow the measured daily mean wind speed varied between 0.9 and 12 m s^{-1}.

The wind speed experienced at the sample inlet height may be much lower depending on location and obstructions due to trees, building etc. In urban environments this is likely to be the case due to the number of immediate and surrounding obstructions, while the wind speed at the inlet in a rural location is likely to be higher. This variation between urban and rural locations is reflected in the different equations and data shown in section 4. To test whether these reductions in wind speed are relevant in urban areas, it is useful to compare them to example datasets in London. Figure 23 shows a box plot of the London Heathrow data adjusted to 5m alongside the Bexley Belvedere site, where the anemometer is positioned at 5m. It also shows shows a box plot of the London Heathrow data adjusted to 2.5m alongside Barnet – Finchley, where the anemometer is position at 2.5m. This good agreement in range and distribution demonstrates that the mathematical correction is an effective way of processing wind speed measurements made at different heights.

Setting a wind speed threshold which stringently tests the sample inlet would necessitate a sampling campaign in an exposed rural environment. This is very likely to have low PM_{10} concentrations and therefore not reach the required 20% of measurements above the UAT; other trials would therefore have to provide many more measurements above the UAT to counteract this. Furthermore, any differences in mass caused by deviations from ideal size separation of sample flow rate would be difficult to detect. This seems an unnecessarily strict requirement.

Instead wind speed thresholds which are representative of UK conditions at different heights in rural or urban environments are proposed. These thresholds, shown in Table 14, are designed to be representative of UK conditions rather than metrologically challenging.

An assessment of the performance of the inlet would need to be made by referring to wind tunnel tests if they are available.

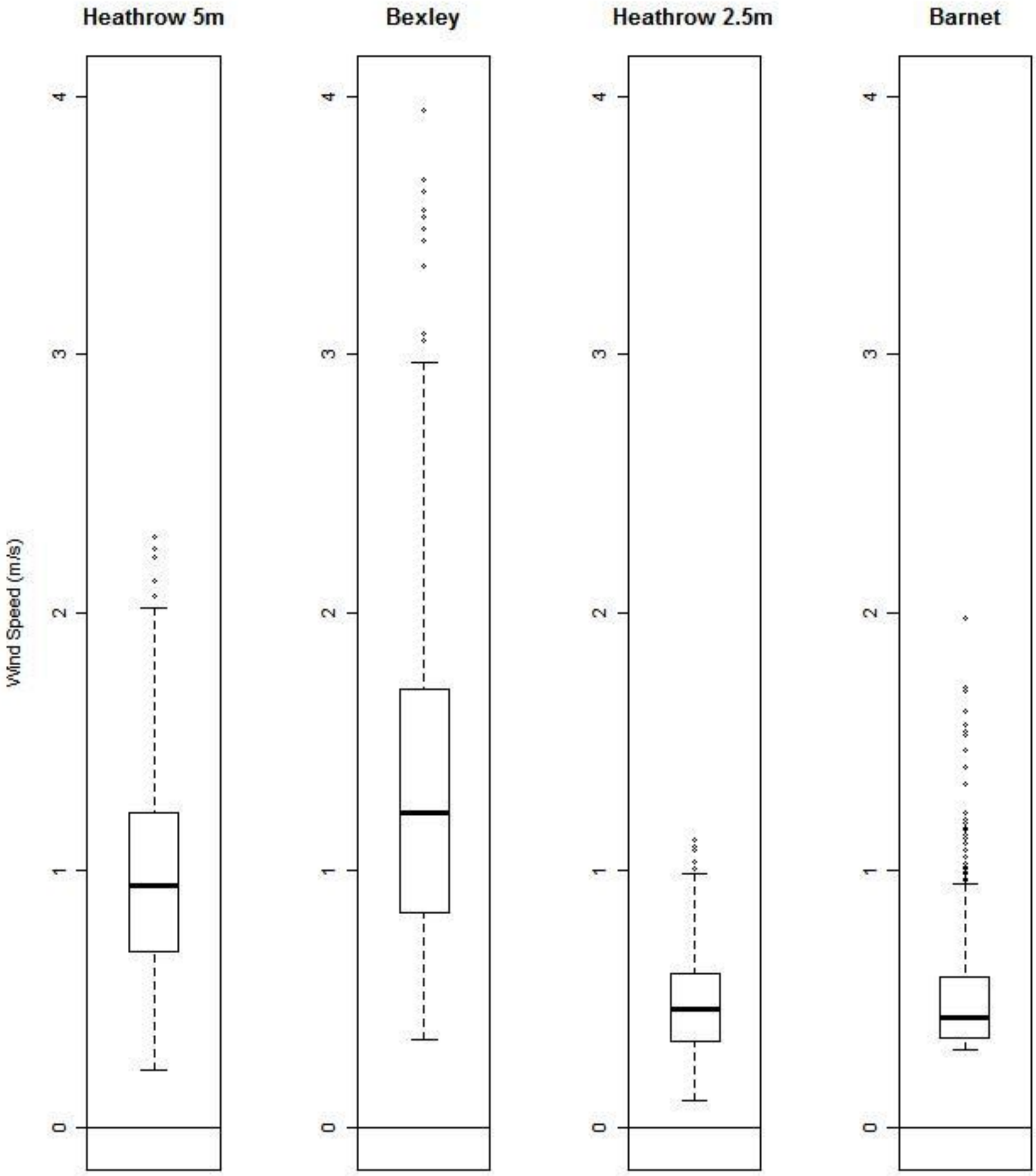

Figure 23: London Heathrow wind speed measurements from 2009 adjusted to 5m and 2.5 m alongside those made at Bexley-Belvedere and Barnet- Fimchley

3.2.2. Ambient temperature

An upper temperature threshold of 13.6 °C is proposed. At first this appears low, however this (as well as the other daily means) obscure hourly variations. In the case of ambient temperatures peak hourly temperatures can have a significant effect on the loss of semi-volatile PM as shown by Chow et al. (2005) and with respect to the recent equivalence trials by Harrison et al. (2010) who indicated that peak daily temperatures in excess of 25 °C led to deviations between the FDMS and the reference method. Examining the temperature measurements on an hourly basis shows that peak hourly temperatures reached 31 °C when the daily mean temperature was between 16 and 17 °C. An upper temperature threshold of 13.6 °C should therefore be considered challenging enough for all systems.

3.2.3. Ambient dew point

Thresholds for ambient dew point have been determined by considering the performance of the Nafion dryers typically installed in FDMS instruments. Figure 24 shows the relationship between daily mean ambient dew point and the sample dew point on the FDMS at North Kensington during 2008. The dashed lines represent the proposed low and high thresholds. At high ambient dew points, the dryer reduces the dew point to between 0 and -2 °C; this can be seen in Figure 24. Inefficiencies in dryer performance at these dew points may lead to water being retained by the PM and water condensing in on eth purge filter, which is held at 4°C. The high threshold lies in this range.

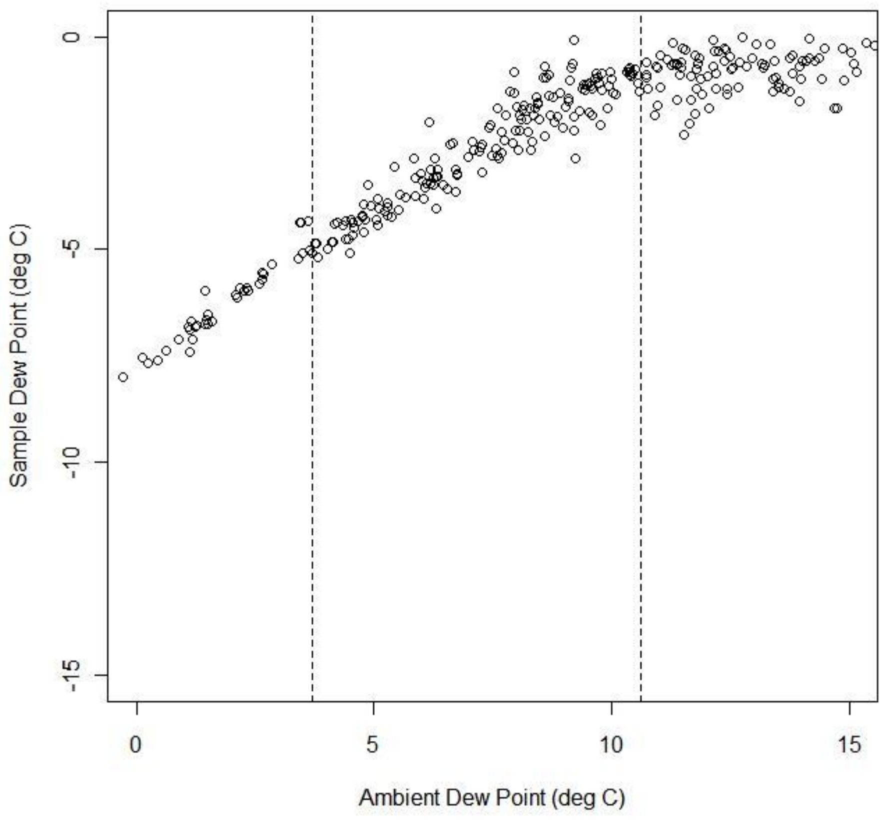

Figure 24: Relationship between daily mean ambient dew point and (left) sample dew point for an FDMS instrument

3.2.4. Proposed thresholds

The minimum number of daily means above the high threshold and below the low threshold needs to be established. It is suggested that 10% of values need to be above the high threshold or below the low threshold in at least one of the four tests to impact on the regression statistics. By chance 25% of measurements should be above the high threshold or below the low threshold, setting a lower percentage provide a balance between achievability within the test period and having enough measurements outside the required thresholds to influence the statistics required for the GDE.

Table 14: Low and high thresholds for meteorological conditions

	Wind speed						Ambient temperature	Dew Point
	Threshold value (m/s)						Threshold value (°C)	Threshold value (°C)
Height	10m		5m		2.5m			
	Urban	Rural	Urban	Rural	Urban	Rural		
low	2.9	6.0	0.7	5.1	0.3	4.2	6.6	3.7
high	5.2	12.4	1.2	10.6	0.6	8.8	13.6	10.6

4. Comparison of UK PM_{10} concentrations with accepted equivalence field trials

The measurements from several equivalence trials have already been accepted by Defra as being representative of typical UK conditions, notably the equivalence trials between 2004 and 2006 in the UK and the MECERTs currently being undertaken in the UK and Germany. The long term mean from each test site and the meteorological measurements from each test dataset compared to the range / threshold proposed in section2 and section 3 are shown in the following sections as a demonstration of the methodology proposed.

The table structure in the following sections provides a proforma for either manufacturers or the competent authority to check that their field trial data is representative of typical UK conditions. The shaded area (geometric mean PM_{10}) must be passed for each site to be considered representative of typical UK conditions. One pass in each of the other categories is required for the field trial data to be considered to have been undertaken in different climatic seasons to represent the different concentrations of semi volatile PM and a range of meteorological conditions as recommended by the GDE.

4.1 UK equivalence field trials 2004-2006

The geometric mean concentrations for each site lay within the range of UK.

The high and low thresholds for semi-volatile PM were met at all locations.

The high and low thresholds for ambient temperature were met at all locations except East Kilbride.

Comprehensive meteorological measurements (notably wind speed and ambient dew point) were not available for these field trials. However, given that they were undertaken in the UK at four locations, over two years the meteorological measurements are likely to meet the relatively lose 25th percentile thresholds. Further meteorological data to validate this assumption would be helpful.

These field trials should therefore be considered representative of typical UK conditions and have been performed in different climatic seasons to represent the different concentrations of semi volatile PM and a range of meteorological conditions.

Table 15: Comparison of 2004-2006 UK equivalence trials datasets with proposed PM_{10} geometric mean ranges and semi-volatile PM and meteorological parameter thresholds

Site	Type	Period	Test	Threshold / Range		Value	Pass
				Value	n		
Teddington	Background	16/11/04-30/06/05	Geometric mean PM_{10}	11.9 – 25.7 ($\mu g\ m^{-3}$)	224	19.4 ($\mu g\ m^{-3}$)	Y
			Semi-volatile PM	Count <=2.1 ($\mu g\ m^{-3}$)	11	141	Y
			Semi-volatile PM	Count >=6.3 ($\mu g\ m^{-3}$)	11	32	Y
			Wind speed		22	No data	
			Wind speed		22	No data	
			Ambient Temperature	Count <=6.6 (°C)	22	68	Y
			Ambient Temperature	Count >=13.6 (°C)	22	66	Y
			Ambient Dew Point	Count <=3.7 (°C)	22	No data	-
			Ambient Dew Point	Count >=10.6 (°C)	22	No data	-
Birmingham	Background	01/12/04-29/06/05	Geometric mean PM_{10}	11.9 – 25.7 ($\mu g\ m^{-3}$)	164	16.6 ($\mu g\ m^{-3}$)	Y
			Semi-volatile PM	Count <=2.1 ($\mu g\ m^{-3}$)	8	117	Y
			Semi-volatile PM	Count >=6.3 ($\mu g\ m^{-3}$)	8	28	Y
			Wind speed		16	No data	-
			Wind speed		16	No data	-
			Ambient Temperature	Count <=6.6 (°C)	16	77	Y
			Ambient Temperature	Count >=13.6 (°C)	16	53	Y
			Ambient Dew Point	Count <=3.7 (°C)	16	No data	-
			Ambient Dew Point	Count >=10.6 (°C)	16	No data	-
Bristol	Background	13/08/05-13/12/05	Geometric mean PM_{10}	10.9 – 42.3 ($\mu g\ m^{-3}$)	155	20.5 ($\mu g\ m^{-3}$)	Y
			Semi-volatile PM	Count <=2.1 ($\mu g\ m^{-3}$)	8	68	Y
			Semi-volatile PM	Count >=6.3 ($\mu g\ m^{-3}$)	8	31	Y
			Wind speed		16	No data	-
			Wind speed		16	No data	-
			Ambient Temperature	Count <=6.6 (°C)	16	38	Y
			Ambient Temperature	Count >=13.6 (°C)	16	76	Y
			Ambient Dew Point	Count <=3.7 (°C)	16	No data	-
			Ambient Dew Point	Count >=10.6 (°C)	16	No data	-
East Kilbride	Rural	10/08/05-19/12/05	Geometric mean PM_{10}	4.3 – 18.1 ($\mu g\ m^{-3}$)	144	8.9 ($\mu g\ m^{-3}$)	Y
			Semi-volatile PM	Count <=2.1 ($\mu g\ m^{-3}$)	7	8	Y
			Semi-volatile PM	Count >=6.3 ($\mu g\ m^{-3}$)	7	101	Y
			Wind speed		14	No data	-
			Wind speed		14	No data	-
			Ambient Temperature	Count <=6.6 (°C)	14	48	Y
			Ambient Temperature	Count >=13.6 (°C)	14	26	N
			Ambient Dew Point	Count <=3.7 (°C)	14	No data	-
			Ambient Dew Point	Count >=10.6 (°C)	14	No data	-

4.2 MCERTS equivalence field trials 2008-2010

Geometric mean PM_{10} concentrations lay within the range of typical UK conditions at each site.

The high and low thresholds for semi-volatile PM were met at Cologne (winter) and Teddington (winter). Only the low threshold for semi-volatile PM was met at Bornheim (summer) and Teddington (summer). This reflects the partitioning of the semi-volatile PM into the gaseous phase at higher temperatures. Nevertheless, both high and low thresholds were met at least one of the trials and the field trials therefore represented both high and low fractions of this component of PM.

The low wind speed threshold was met at all field trial locations, however, the high threshold was not met at Bornheim. This result may therefore reflectthe positioning of the wind speed sensor or the local building layout. As discussed, wind flows are very site specific and individual sites will also have different area densities and canopy heights. In heavily urbanised areas (greater than 30% area density) skimming effects across the top of the urban canopy may result in very low wind speeds.

The low ambient temperature threshold was met at all sites except at Teddington in the summer. The high ambient temperature threshold was met during the summer campaigns but not the winter campaigns.

The low dew point temperature threshold was met at all sites. The high dew point temperature threshold was met during the winter campaigns.

These field trials should therefore be considered representative of typical UK conditions and have been performed in different climatic seasons to represent the different concentrations of semi volatile PM and a range of meteorological conditions.

Table 16: Comparison of MCERTS equivalence trials datasets with proposed PM_{10} geometric mean ranges and semi-volatile PM and meteorological parameter thresholds

Site	Type	Period	Test	Threshold / Range		Value	Pass
				Value	n		
Cologne	Background	07/12/08-13/04/09	Geometric mean PM_{10}	11.9 – 25.7 (µg m^{-3})	79	23.1 (µg m^{-3})	Y
			Semi-volatile PM	Count <=2.1 (µg m^{-3})	4	26	Y
			Semi-volatile PM	Count >=6.3 (µg m^{-3})	4	41	Y
			Wind speed (5m Urban)	Count <=0.7 (ms^{-1})	8	34	Y
			Wind speed (5m Urban)	Count >=1.2 (ms^{-1})	8	71	Y
			Ambient Temperature	Count <=6.6 (°C)	8	100	Y
			Ambient Temperature	Count >=13.6 (°C)	8	7	N
			Ambient Dew Point	Count <=3.7 (°C)	8	107	Y
			Ambient Dew Point	Count >=10.6 (°C)	8	0	N
Bornheim	Roadside	16/08/09-22/10/09	Geometric mean PM_{10}	10.9 – 42.3 (µg m^{-3})	57	20.3 (µg m^{-3})	Y
			Semi-volatile PM	Count <=2.1 (µg m^{-3})	3	49	Y
			Semi-volatile PM	Count >=6.3 (µg m^{-3})	3	1	N
			Wind speed (5m Urban)	Count <=0.7 (ms^{-1})	6	56	Y
			Wind speed (5m Urban)	Count >=1.2 (ms^{-1})	6	5	N
			Ambient Temperature	Count <=6.6 (°C)	6	4	N
			Ambient Temperature	Count >=13.6 (°C)	6	45	Y
			Ambient Dew Point	Count <=3.7 (°C)	6	8	Y
			Ambient Dew Point	Count >=10.6 (°C)	6	27	Y
Teddington	Background	09/12/09-04/03/10	Geometric mean PM_{10}	11.9 – 25.7 (µg m^{-3})	86	19.5 (µg m^{-3})	Y
			Semi-volatile PM	Count <=2.1 (µg m^{-3})	4	52	Y
			Semi-volatile PM	Count >=6.3 (µg m^{-3})	4	6	Y
			Wind speed (5m Urban)	Count <=0.7 (ms^{-1})	8	54	Y
			Wind speed (5m Urban)	Count >=1.2 (ms^{-1})	8	14	N
			Ambient Temperature	Count <=6.6 (°C)	8	83	Y
			Ambient Temperature	Count >=13.6 (°C)	8	0	N
			Ambient Dew Point	Count <=3.7 (°C)	8	69	Y
			Ambient Dew Point	Count >=10.6 (°C)	8	0	N
Teddington	Background	27/04/10-01/07/10	Geometric mean PM_{10}	11.9 – 25.7 (µg m^{-3})	61	13.9 (µg m^{-3})	Y
			Semi-volatile PM	Count <=2.1 (µg m^{-3})	3	42	Y
			Semi-volatile PM	Count >=6.3 (µg m^{-3})	3	0	N
			Wind speed (5m Urban)	Count <=0.7 (ms^{-1})	6	36	Y
			Wind speed (5m Urban)	Count >=1.2 (ms^{-1})	6	15	N
			Ambient Temperature	Count <=6.6 (°C)	6	0	N
			Ambient Temperature	Count >=13.6 (°C)	6	65	Y
			Ambient Dew Point	Count <=3.7 (°C)	6	9	Y
			Ambient Dew Point	Count >=10.6 (°C)	6	22	Y

5. Location and time of year for planning an equivalence trial

It is important to provide information for equipment manufacturers when planning a trial so that they can choose the optimum location and time period to conduct the trial; the outputs from this study can be used to influence these choices. The data used here provides this information for the UK, in other countries is likely to vary.

5.1 Time of year

5.1.1. PM10

Due to the seasonal variability of PM_{10}, the time of year that the trial is undertaken was expected to be important. Firstly, the time of year when there are 20% of measurements greater than the UAT needs to be considered. The reference dataset has been analysed to show the percentage of measurements in each month which are greater than the UAT (28 µg m^{-3}); the results are shown (split by site type) in Figure 25. At the traffic sites, all months except July and August, have 20% of measurements greater than the UAT. At background sites only February, April, October and December have 20% of measurements greater than the UAT. At the industrial site all months have 20% of measurements greater than the UAT. At Rural sites no months have 20% of measurements greater than the UAT. This has major implications for equivalence tests, especially at background and rural sites.

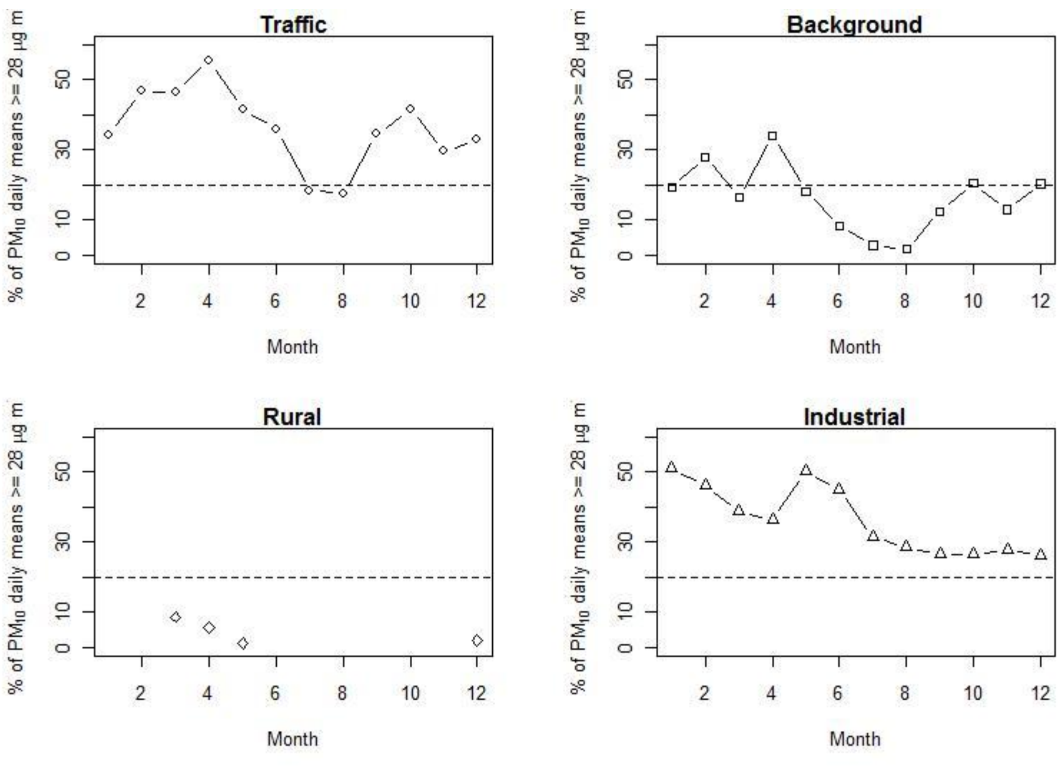

Figure 25: Percentage of FDMS PM_{10} measurements in the reference dataset greater or equal to the UAT (28 µg m^{-3}) grouped by month for each site type. Dashed line shows 20%.

5.2 Semi-volatile PM

Due to the seasonal variability of semi-volatile PM, the time of year that the trial is undertaken was expected to be important. In section 2.1, a high threshold of 6.3 µg m^{-3} was suggested as a challenging but achievable high threshold at which an effect on the measurements could be detected. The reference dataset has been analysed to show the percentage of measurements in each month which are greater than this threshold (6.3 µg m^{-3}); the results are shown (split by site type) in Figure 25. At the traffic and background sites, all months except June, July and August, have 5% of measurements greater than the threshold. At the industrial site only August has 5% of measurements lower than the threshold. At Rural sites March and April had 5% of measurements greater than the threshold. This shows that equivalence trials should not be undertaken in the summer months (June –August) if they wish to measure high and low fractions of semi-volatile PM.

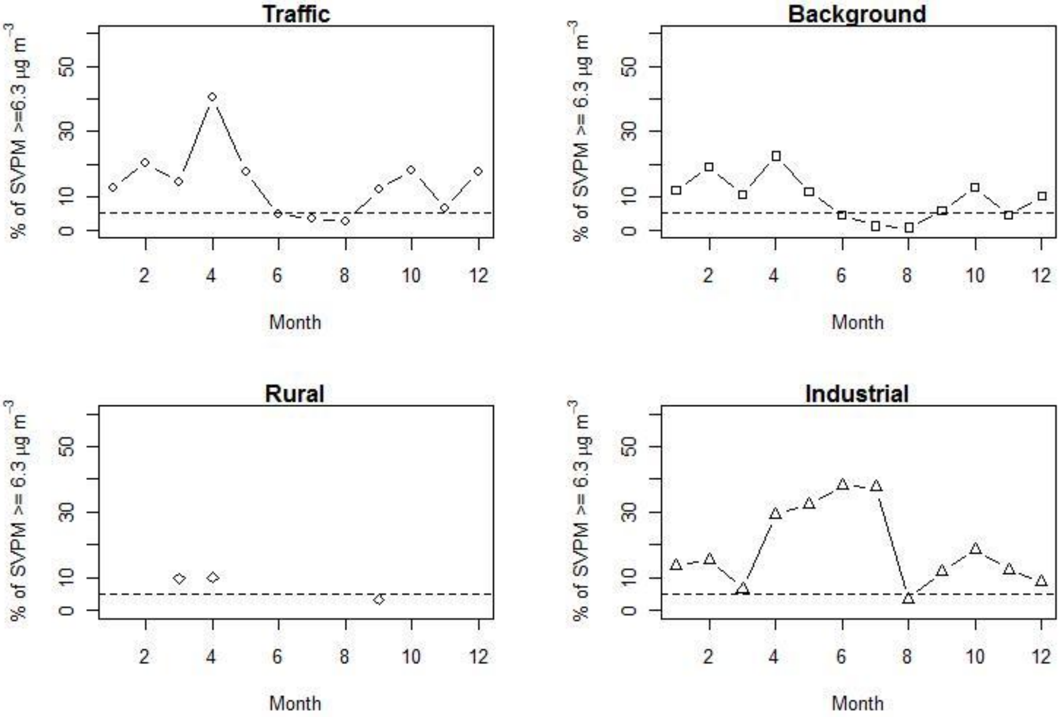

Figure 26: Percentage of semi-volatile PM measurements in the reference dataset greater or equal to the high threshold (6.3 µg m^{-3}) grouped by month for each site type. Dashed line shows 5%.

5.3 Meteorological conditions

The ability of any 40 day period to represent the high and / or low conditions referred to in the GDE depends on the seasonality of the meteorological parameter and the season / month that the test is undertaken. For instance, a winter test would not be expected to be representative of high temperature conditions.

The reference dataset has been analysed to show the percentage of measurements in each month which are greater than the high and low thresholds shown in Table 14; the results are shown in Figure 27, Figure 28 and Figure 29. A dashed line representing 10% has been drawn on each graph as a suggested minimum percentage of daily mean measurements which should be above / below the appropriate threshold.

As seen in Figure 10, there is some seasonal variation shown in the wind speed plots; summer months experience the lowest peak wind speeds and the high wind speed threshold is not achieved at 10m during the summer. The temperature plots in Figure 29 clearly reflect the seasonality of temperature seen in Figure 11. The high temperature threshold would only be achievable between May and October. The low temperature threshold would only be achievable between November and April. The ambient dew point plots in Figure 29 have a similar seasonal pattern to ambient temperature. The high ambient dew point threshold would only be achievable between May and October. The low ambient dew point threshold would only be achievable between November and April.

Both the high temperature and high dew point thresholds are at odds with the high semi-volatile threshold and it is likely that that all of these could only be achieved during the change between spring and summer or the change between summer and autumn. This would be extremely difficult to plan and would be subject to the vagaries of the weather. It is therefore suggested that the semi-volatile PM high threshold is not applicable during a summer trial.

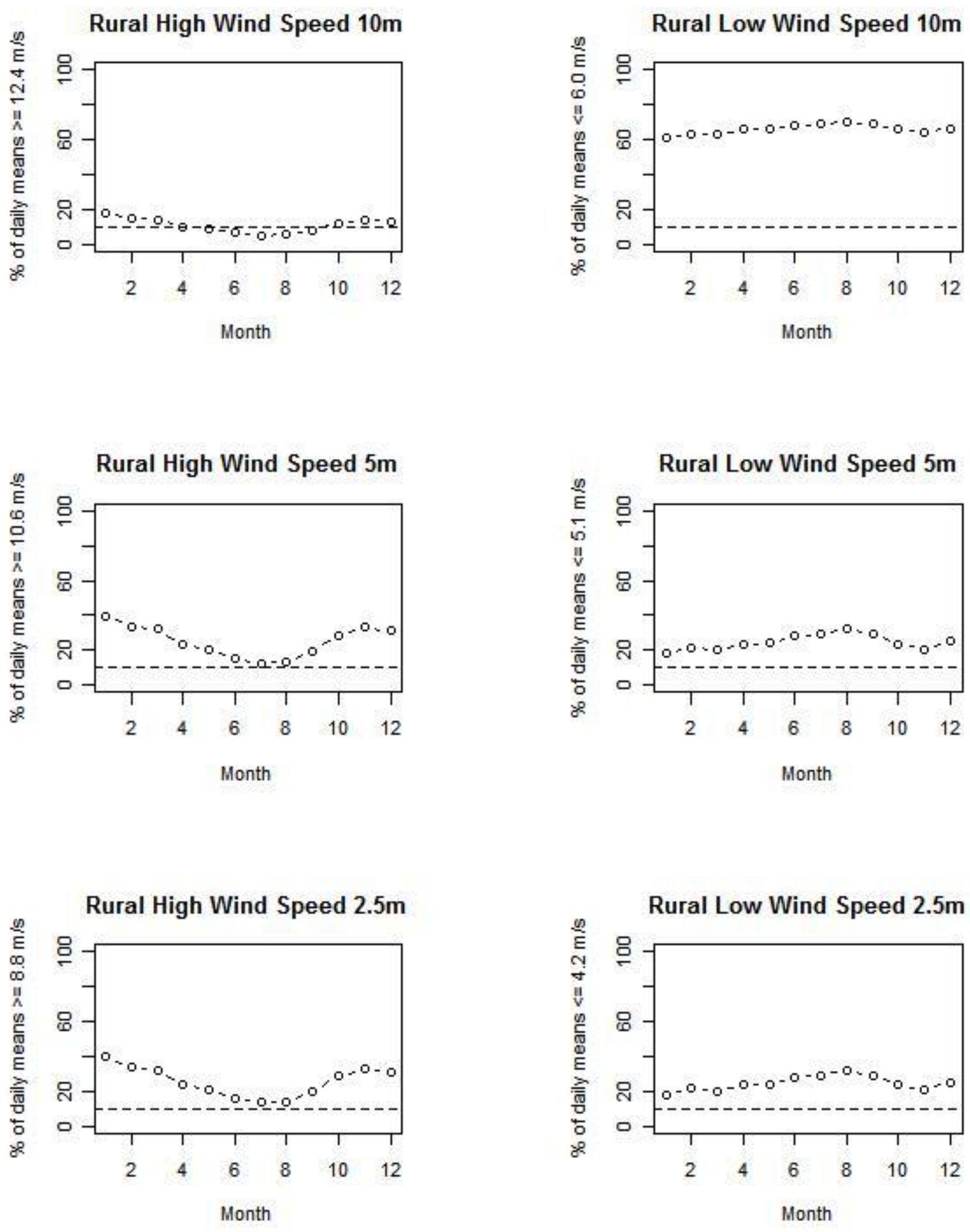

Figure 27: Percentage of measurements in each month above or below the rural wind speed thresholds. Dashed line shows 10%.

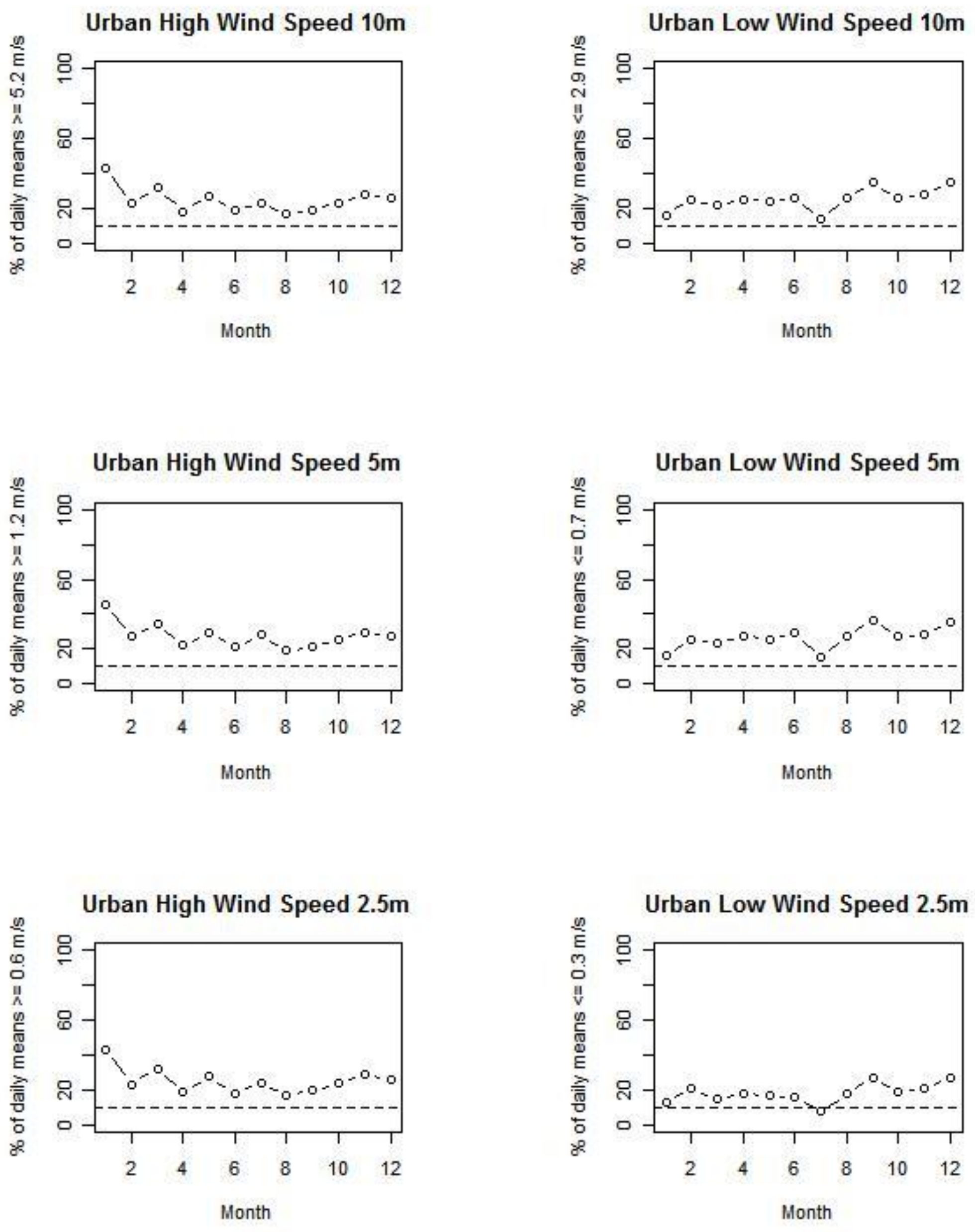

Figure 28: Percentage of measurements in each month above or below the urban wind speed thresholds. Dashed line shows 10%.

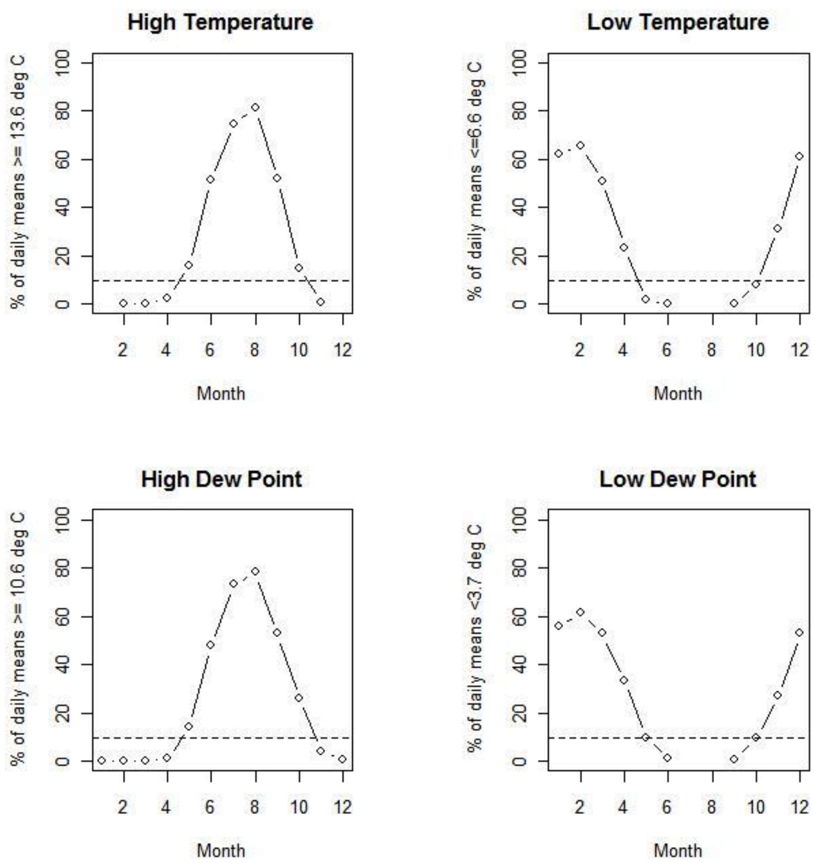

Figure 29: Percentage of measurements in each month above or below the ambient temperature and dew point thresholds. Dashed line shows 10%.

6. Impact of PM composition and meteorology on different instrumentation

Both PM composition and meteorology can affect how individual instruments respond when compared to the reference method. For instance, it is widely acknowledged that sampler systems are prone to the loss of semi-volatile PM due to ambient heating of the sample post collection (Chang, Sioutas et al. 2000; Chow, Engelbrecht et al. 2002; Eatough, Long et al. 2003; Chow, Watson et al. 2005). It is therefore important that instruments are tested in conditions which challenge these susceptibilities.

Many of these challenges are already inherent in the prescribed tests and thresholds which pertain to these conditions (semi-volatile PM, wind speed, ambient temperature and ambient dew point) have been proposed in this report. As discussed, some of these thresholds are mutually exclusive such as the high ambient temperature and high semi-volatile thresholds. It is therefore important that instruments which have, for instance a susceptibility to the loss of semi-volatile PM, are tested in conditions in the UK which challenge this susceptibility rather than in the summer.

6.1 All instruments

All instruments are subject to the loss of semi-volatile PM to some extent (not least the reference method). We would expect instruments with heated inlets, either 'smart' or otherwise, to be vulnerable to the loss of semi-volatile PM. Similarly, samplers which are prone to exposing the filter to elevated temperatures during and after sampling could be expected to lose semi-volatile PM. ***It is therefore important that all instruments are tested in conditions above the high semi-volatile PM threshold.***

6.2 Instruments with dryers

At high ambient humidity the dryer may not remove the water effectively from sample stream as shown in Figure 30. ***Instruments which use dryers should be tested in conditions above the high dew point threshold.***

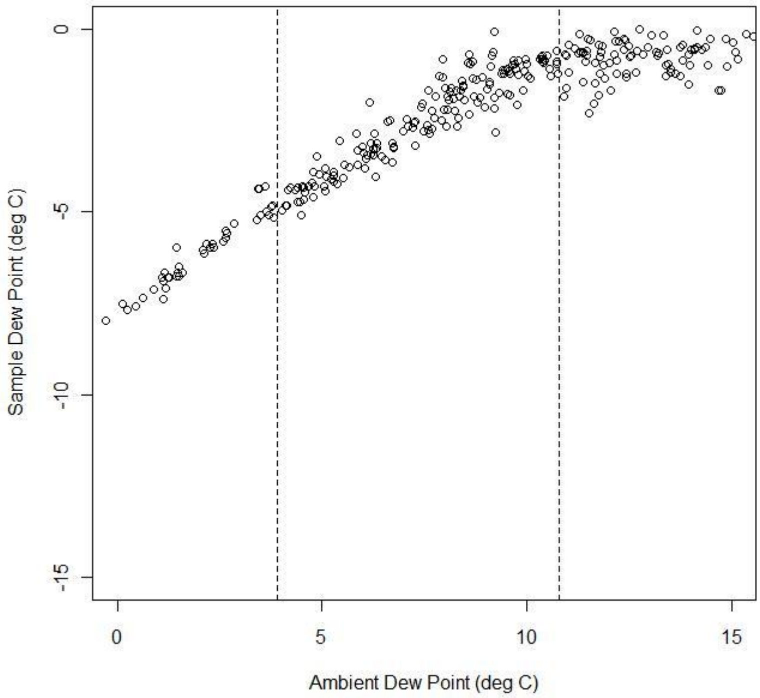

Figure 30: Relationship between daily mean ambient dew point and (left) sample dew point for an FDMS instrument

6.3 Optical particle sizers

Optical particle sizers, which depend on particle diameter to calculate a mass concentration, may not deal effectively with changes in atmospheric humidity. If an instrument does not control changes in particle size due to humidity, in a similar way to instruments with dryers, it will be prone to overestimate the mass concentration. This is composition dependent, hygroscopic components such as ammonium sulphate and ammonium nitrate will be more prone to this effect (Seinfeld and Pandis 1998). This has been shown experimentally in the US by Malm et al (2001); a summary of their findings is shown in Figure 31. ***Optical particle sizers should therefore be tested in conditions above the high dew point threshold to reflect periods of high relative humidity.***

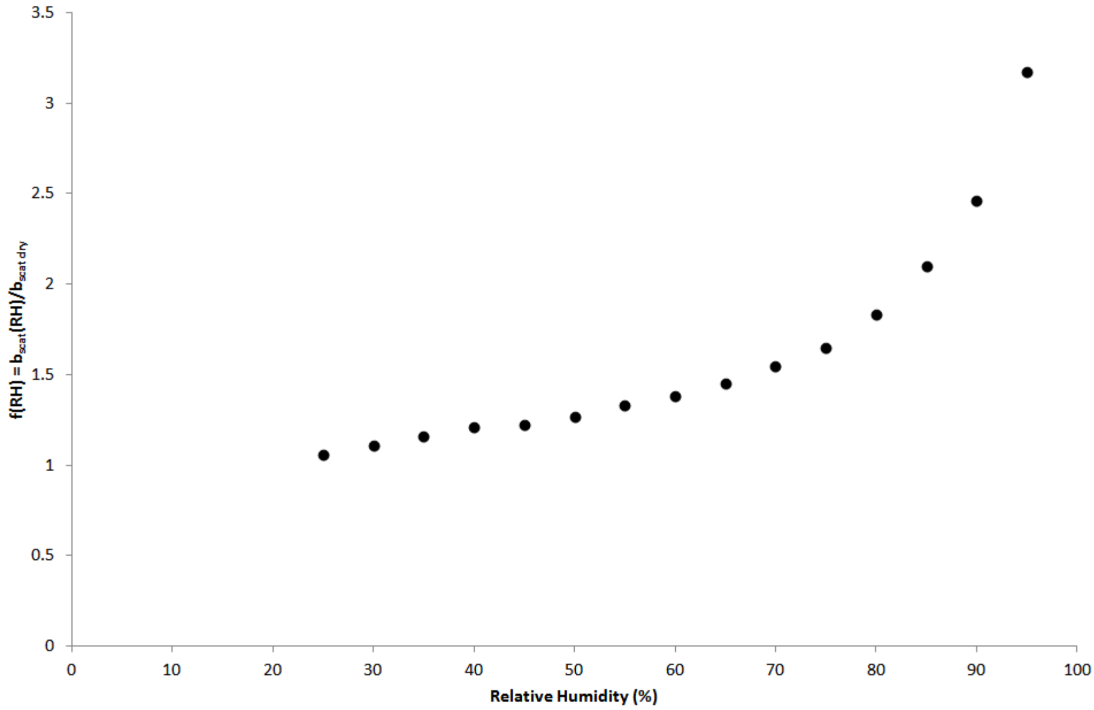

Figure 31: Relationship between light scattering intensity ($f(RH)=b_{scat}(RH)/b_{scat\_dry}$) from

6.4 Sampler systems

It is widely acknowledged that sampler systems are prone to the loss of semi-volatile PM due to ambient heating of the sample post collection (Chow, Watson et al. 2005) this has also been reported recently in relation to the current equivalence trials by Harrison (2010). ***Sampler systems should therefore be tested in conditions above the high ambient temperature threshold.***

7. Estimation of $PM_{2.5}$ Annual Geometric Mean Ranges

A range of $PM_{2.5}$ geometric annual mean concentrations is required for the UK so that manufacturers can assess locations prior to any field tests. However, the available data for $PM_{2.5}$ is limited as widespread measurement only started in 2008, although data from some sites is available from 2006 onwards; this is shown in Figure 32.

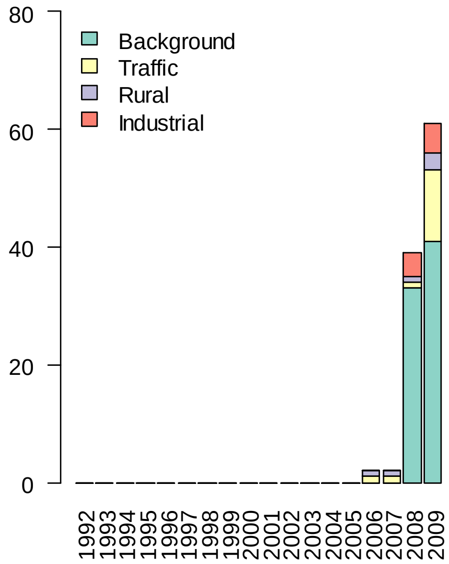

Figure 32: Number of FDMS $PM_{2.5}$ sites split by each site type

This limited number of sites (especially for traffic (n=1), rural (n=2) and industrial (n=1)) implies that the range of geometric annual means would not be representative of UK conditions and is supported in the formation of the reference datasets in section 2. Nevertheless, the range of available $PM_{2.5}$ geometric annual means has been calculated from all available data and is shown in Table 11 alongside the range of PM_{10} geometric annual means. Although $PM_{2.5}$ would be expected to have a more limited geometric annual mean range as it has fewer sources, the small ranges for traffic, rural and industrial sites are clearly narrower than would be expected.

To provide a more accurate estimate of the range of $PM_{2.5}$ geometric annual means, the relationship between the PM_{10} and $PM_{2.5}$ geometric annual means for the same sites and years was established. The PM_{10} geometric mean is plotted against the $PM_{2.5}$ geometric mean in Figure 35. This figure shows that there are three distinct groups of sites, the background and traffic sites show some agreement however, the rural have much lower concentrations and the industrial site has a markedly different PM_{10}:$PM_{2.5}$ ratio. At the industrial sites, this relationship is likely to be very source and site specific and may differ from other site types. The limited number of rural sites here produced lower PM_{10}:$PM_{2.5}$ ratios than reported in the literature (Putaud, Van Dingenen et al.). Therefore, as no clear regression line could be drawn through these different site types, the mean ratio (0.70 σ=0.08) of the urban background sites was used as the best descriptor of PM_{10}:$PM_{2.5}$ ratios as it was representative of a large number of sites and years. It is acknowledged that this factor includes significant uncertainty, previous studies have failed to establish PM_{10}:$PM_{2.5}$ ratios over large areas (Putaud, Van Dingenen et al.), however until more data is available to establish a representative $PM_{2.5}$ geometric annual mean range then this provides the most robust solution. The PM_{10} geometric annual mean minima and maxima for each site type have therefore been multiplied by this factor to provide an estimated range; this is shown in Table 17. It is worth noting that the estimated range for urban background sites is similar but not as large as that provided by the direct measurements.

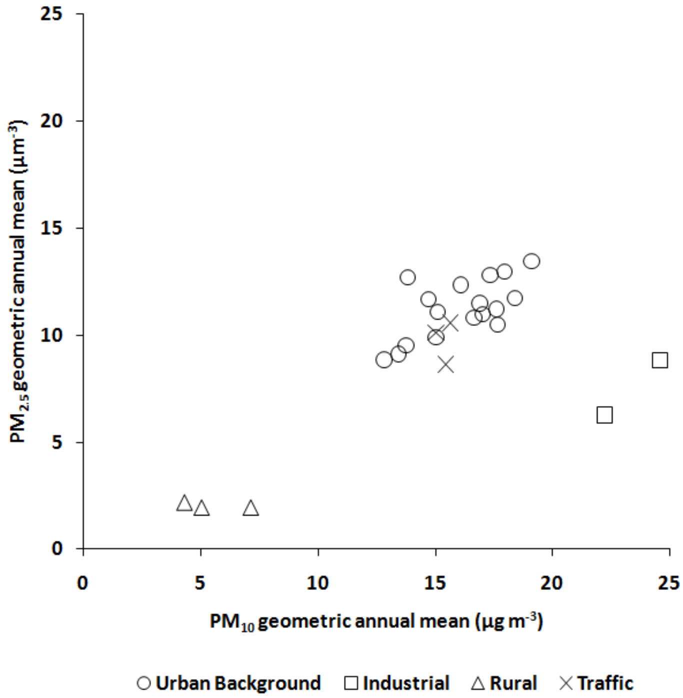

Figure 33: Relationship between geometric annual mean PM_{10} and $PM_{2.5}$

Table 17: Range of PM_{10} and $PM_{2.5}$ geometric annual mean concentrations experienced at UK site types and the range of geometric annual mean $PM_{2.5}$ estimated from the relationship between PM_{10} and $_{PM2.5}$ at urban background sites

Site Type	Geometric Mean PM_{10} Range (µg m^{-3})	Geometric Mean $PM_{2.5}$ Range (µg m^{-3})	Estimated Geometric Mean $PM_{2.5}$ Range Estimated from Factors (µg m^{-3})
Background (urban or suburban)	11.9 – 25.7	8.8 – 13.4	8.4 - 18.1
Traffic	10.9 – 42.3	8.6 – 10.6	7.7 - 29.7
Rural	4.3 – 18.1	2.0 – 2.2	3.0 - 12.7
Industrial	13.8 – 24.6	6.2 – 8.8	9.7 - 17.3

9. Conclusions

An understanding of the UK (and to some extend the European) PM 'climate' was required to inform the experimental conditions for field tests for declaration of equivalence for PM analysers within the MCERTS framework. This required the production of reference datasets which were representative of UK conditions from the available quality assured data.

Firstly, a methodology for producing representative reference datasets for the UK, and potentially, other locations was developed. This can now be used to update the datasets when new measurements become available or the monitoring network changes. The production of these reference datasets highlighted several deficiencies in the available data to represent the PM climate over the last 10-20 years. Chief amongst these was the change in measurement methodology from TEOM to FDMS which limits the start of current time series of PM_{10} measurements to 2007. There was also a lack of measurements from traffic locations, which limited the use of this dataset. Both these issues will reduce in prominence as more measurements and measurement locations are include in the reference dataset; the reference dataset will then also better reflect the inter-annual variability in PM concentrations. Furthermore, as more $PM_{2.5}$ measurements become available the reference dataset for this fraction will increase and begin to represent inter-annual variability (as will the reference dataset for the coarse fraction). The lack of a geographical spread of quality assured meteorological measurements available for this project has limited the conclusions which can be drawn from this dataset; this needs to be addressed.

Nevertheless, the reference datasets produced provide the best available assessment of PM climate in the UK. These datasets have been used to establish trends and seasonality of the PM and meteorological metrics. They have also been used to quantify upper and lower thresholds against which equivalence datasets can be assessed. In the case of wind speed the measurements have been scaled to account for the height at which measurements are made in different environments. For each of the parameters in the table below a threshold and a percentage of daily means either above the high threshold or below the low threshold is set. It is proposed that these thresholds should be reached by the requisite number of daily means in at least one field test.

Threshold	Semi-volatile PM (or $PM_{2.5}$ nitrate) ($\mu g\ m^{-3}$)		Wind speed (m/s)							Ambient Temperature (°C)		Ambient Dew Point (°C)	
	Threshold	%	Threshold						%	Threshold	%	Threshold	%
			10m		5m		2.5m						
			Urban	Rural	Urban	Rural	Urban	Rural					
Low	3.2	5	2.9	6.0	0.7	5.1	0.3	4.2	10	6.6	10	3.7	10
High	6.3	5	5.2	12.4	1.2	10.6	0.6	8.8	10	13.6	10	10.6	10

Table 18: Low and high thresholds for semi volatile PM and meteorological conditions

An assessment of the available literature on PM_{10} concentrations in Europe showed significant heterogeneity. It was hoped that this would provide an indication of other regions of Europe whose equivalence tests would be applicable to the UK. Europe was broadly grouped into three regions (north western, central and southern) by some authors but the variation in concentrations within these groups suggested that equivalence trials would need to be assessed on a case-by-case basis.

Attempts to provide a statistical methodology using a non-parametric statistical test which would allow potential equivalence field trial data to be compared to the UK reference dataset proved unsuccessful. This was due the positive skew introduced by the GDE requirement to have 20% of measurements above the upper assessment threshold and the small confidence intervals on the large datasets used. However, a range of PM_{10} geometric annual mean concentrations experienced at each site type in the UK was calculated. This provides a concentration range against which measurements from sites where equivalence field trials have been (or will be) undertaken can be compared against. The long term (preferably annual) geometric mean PM_{10} concentration should lie within the minimum and maximum range shown in the table below. This range of PM_{10} geometric annual means and PM_{10}:$PM_{2.5}$ ratio at urban background sites was used to estimate a range of $PM_{2.5}$ geometric annual means; both these ranges are shown in Table 19.

Table 19: Range of PM_{10} and $PM_{2.5}$ geometric annual mean concentrations experienced at UK site types and the range of geometric annual mean $PM_{2.5}$ estimated from the relationship between PM_{10} and $PM_{2.5}$ at urban background sites

Site Type	Geometric Mean PM_{10} Range (µg m^{-3})	Geometric Mean $PM_{2.5}$ Range (µg m^{-3})	Estimated Geometric Mean $PM_{2.5}$ Range Estimated from Factors (µg m^{-3})
Background (urban or suburban)	11.9 – 25.7	8.8 – 13.4	8.4 - 18.1
Traffic	10.9 – 42.3	8.6 – 10.6	7.7 - 29.7
Rural	4.3 – 18.1	2.0 – 2.2	3.0 - 12.7
Industrial	13.8 – 24.6	6.2 – 8.8	9.7 - 17.3

A comparison against European measurements showed that 60% of European sites lay within the UK range of background PM_{10} geometric mean concentrations; the majority of exceptions were in the more highly polluted areas of Eastern Europe and the Po Valley in Italy.

Measurements from equivalence field trials already undertaken in the UK and Germany were compared to the ranges and thresholds proposed. They were found, excepting a lack of available data in some cases, to be representative of typical UK conditions. The field trials were also found to have been undertaken in different climatic seasons to represent the different concentrations of semi volatile PM and a range of meteorological conditions as recommended by the GDE. A proforma suitable for manufacturers or the competent authority to use as a check list was proposed.

The results of this report have several implications for the acceptance of available equivalence trial data and the planning of new equivalence trials. One of the most significant problems will be achieving the 20% of measurements greater than the UAT at background locations. On average this is only achievable between December and April in the UK and is very unlikely to be achieved in the summer months. Any summer testing would need to be undertaken at a more traffic oriented site; even at these sites (marginally) less than 20% of daily means were greater than the UAT.

When the reference dataset was compared to the high and low thresholds for semi-volatile PM, ambient temperature, air humidity and wind speed proposed key features of the seasonality of PM concentration and composition as well as meteorological parameters to be identified. This will allow equivalence tests to be targeted at key times of the year and maximise the chances of instrument manufacturers achieving the prescribed thresholds. It will also allow existing equivalence trial datasets to be assessed to find out whether they are representative of the high and low conditions prescribed in the GDE. The analysis highlighted the incompatibility of some of the high and low thresholds. For instance, the high ambient temperature and high semi-volatile PM thresholds; because high temperatures lead to the partitioning of semi-volatile PM into the gas phase. Certain thresholds should therefore not be applied rigidly during the same trials. However, it remains important that instruments are tested in conditions which are above and below the thresholds at some point; although it doesn't have to be during the same trial. It also remains important to test instruments in conditions which challenge their measurements methodology. In particular, semi-volatile PM, which is one of the most difficult components to measure and may increase in the future.

Appendix I - Reference dataset formation

9.1 TEOM PM_{10}

The number of sites measuring PM_{10} using a TEOM in 1992 was limited to 18 sites on the Statutory and Enhanced Urban Networks. Limiting to these sites would not maximise the use of the data available, also, some sites have closed in the intervening period. The network expanded rapidly between 1994 and 1997. As the TEOM instruments were upgraded to FDMS instruments the number of available sites dropped. Although the data available reduced in 2008, the data capture over the preceding years was enough to sustain it above 75%.

The sites in the TEOM PM_{10} reference dataset are shown in Table 20. The distribution of site types shown in Table 21 demonstrates that the reference dataset has a very similar make up to the TEOM PM_{10} sites as they were during 2007 – the point at which they started being replaced with FDMS instruments.

The geographical distribution of sites shown in Figure 35 provides a fairly good coverage of the UK. The sites tend to be concentrated in England, there is a relative lack of coverage in Scotland (only Glasgow Centre and Glasgow Kerbside). Adding site in this region would require a lowering of the data capture threshold, there was not significant justification for this.

Table 20: TEOM PM_{10} sites used in reference dataset

Site Name	Type	Data Capture (%)
STOKE-ON-TRENT CENTRE	Background	77
CARDIFF CENTRE	Background	78
BRADFORD CENTRE	Background	80
BIRMINGHAM CENTRE	Background	81
SOUTHAMPTON CENTRE	Background	81
PORT TALBOT	Industrial	81
LEICESTER CENTRE	Background	82
LONDON ELTHAM	Background	83
NEWCASTLE CENTRE	Background	83
REDCAR	Background	83
MANCHESTER PICCADILLY	Background	83
NOTTINGHAM CENTRE	Background	83
SHEFFIELD CENTRE	Background	84
NARBERTH	Rural	85
LONDON A3 ROADSIDE	Traffic	85
NORWICH CENTRE	Background	85
WOLVERHAMPTON CENTRE	Background	86
LONDON HILLINGDON	Background	87
LONDON BRENT	Background	87
HARWELL	Rural	88
LONDON BLOOMSBURY	Background	89
LONDON BEXLEY	Background	90
BOLTON	Background	90
ROCHESTER STOKE	Rural	91
LEAMINGTON SPA	Background	92
HARINGEY ROADSIDE	Traffic	92
LONDON MARYLEBONE ROAD	Traffic	94

MIDDLESBROUGH	Industrial	94
DERRY	Background	94
BELFAST CENTRE	Background	95
SALFORD ECCLES	Industrial	95
GLASGOW KERBSIDE	Traffic	95
BURY ROADSIDE	Traffic	95
THURROCK	Background	95
CAMDEN KERBSIDE	Traffic	96
GLASGOW CENTRE	Background	96
LEEDS CENTRE	Background	96
LOUGH NAVAR	Rural	99
LONDON N. KENSINGTON	Background	99

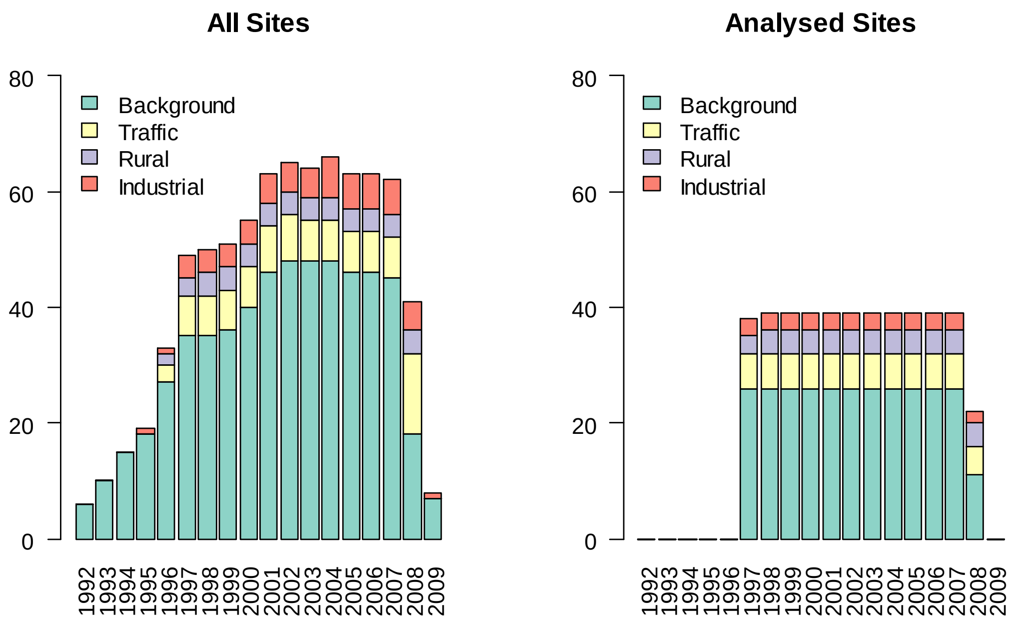

Figure 34: Number of TEOM PM_{10} sites split by each site type. All sites (left), sites with >75% data capture (right)

Table 21: Distribution of TEOM PM_{10} sites according to site type in reference dataset and for all available sites in 2007

Type	Reference		2007	
	Sites	%	Sites	%
Background	26	67	46	71
Traffic	6	15	7	11
Rural	4	10	6	9
Industrial	3	8	6	9
Total	39		65	

Figure 35: Geographical distribution of TEOM PM_{10} reference sites

9.2 FDMS PM_{10}

Some FDMS measurements were available from 2003 onwards, however, the widespread installation of FDMS instruments began in 2007.

The sites in the FDMS PM_{10} reference dataset are shown in Table 22. The distribution of site types shown in Table 23 demonstrates that the reference dataset has a similar make up to the FDMS PM_{10} sites as they were during 2009 – the latest year available. There are slightly less traffic sites and more background sites, reflecting the priority given to background sites in the Defra upgrade programme. However, this was felt to be an accurate enough reflection of the current FDMS network.

The geographical spread shown in Figure 37 lacked sites in London and the south east. Furthermore, only one roadside site was available. The south east of the UK experiences the highest concentrations of semi-volatile PM due to its proximity to continental Europe; additional sites in this area were judged to be important. Sites could be added in this area from the LAQN without compromising the data capture threshold of 75%. Two sites from the LAQN were therefore included in the reference dataset: North Kensington (background) as an AURN site which had an FDMS operating prior to affiliation and Tower Hamlets (traffic) as a traffic site with a high data capture rate.

Table 22: FDMS PM_{10} sites used in reference dataset

Site Name	Type	Data Capture (%)
NORTH KENSINGTON	Background	76
TOWER HAMLETS ROADSIDE	Traffic	95
SHEFFIELD CENTRE	Background	75
PORT TALBOT MARGAM	Industrial	77
LEICESTER CENTRE	Background	78
STOKE-ON-TRENT CENTRE	Background	82
AUCHENCORTH MOSS PM10 PM25	Rural	82
CARDIFF CENTRE	Background	83
NEWCASTLE CENTRE	Background	84
HULL FREETOWN	Background	87
LIVERPOOL SPEKE	Background	87
SOUTHAMPTON CENTRE	Background	88
SWANSEA ROADSIDE	Traffic	92
BRISTOL ST PAUL'S	Background	93

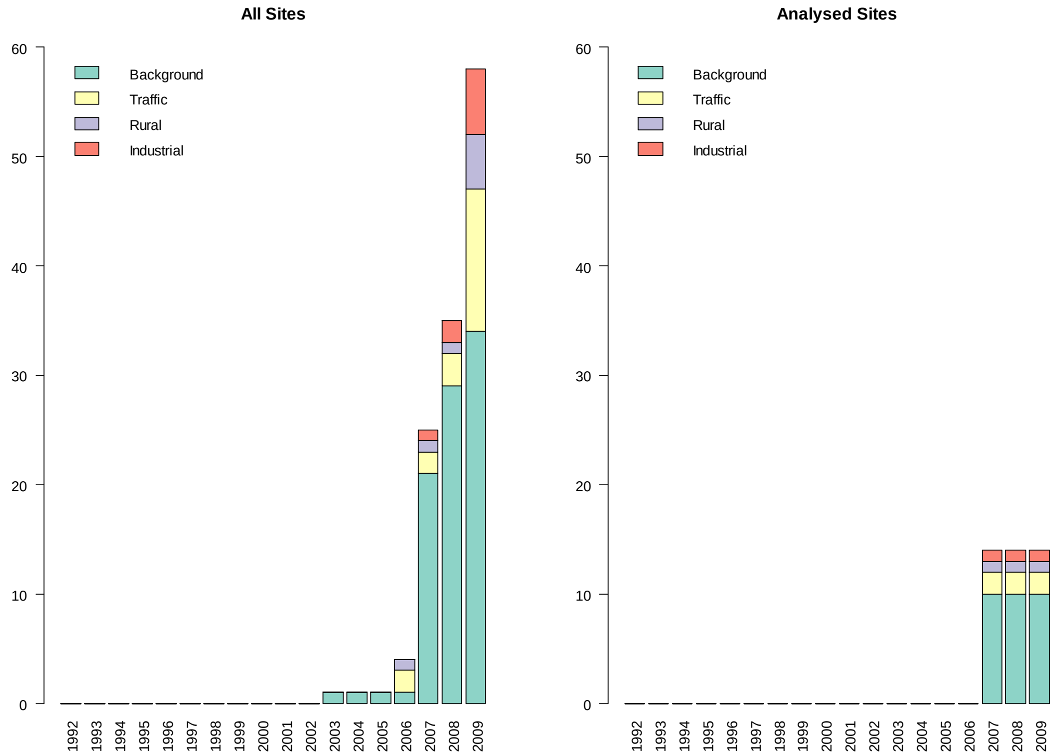

Figure 36: Number of FDMS PM_{10} sites split by each site type. All sites (left), sites with >75% data capture (right)

Table 23: Distribution of FDMS PM_{10} sites according to site type in reference dataset and for all available sites in 2009

Type	Reference		2009	
	Sites	%	Sites	%
Background	10	71	34	59
Traffic	2	14	13	22
Rural	1	7	5	9
Industrial	1	7	6	10
Total	14		58	

Figure 37: Geographical distribution of FDMS PM_{10} reference sites

9.3 TEOM $PM_{2.5}$

There were clearly far fewer TEOM $PM_{2.5}$ measurements available from the AURN than there were for PM_{10}. Four sites operated long term from 1999 to 2008 when they were replaced by FDMS instruments.

The sites in the TEOM $PM_{2.5}$ reference dataset are shown in Table 24. The distribution of site types shown in Table 24 demonstrates that the reference dataset has a similar make up to the TEOM $PM_{2.5}$ sites as they were during 2008 – the point at which they started being replaced with FDMS instruments.

The geographical distribution shown in Figure 39 was centred on the south of the UK, with two sites in London, one in Oxfordshire and one n Kent. There was little scope for extending the geographical distribution without recourse to individual local authority datasets and a reduction in the data capture threshold.

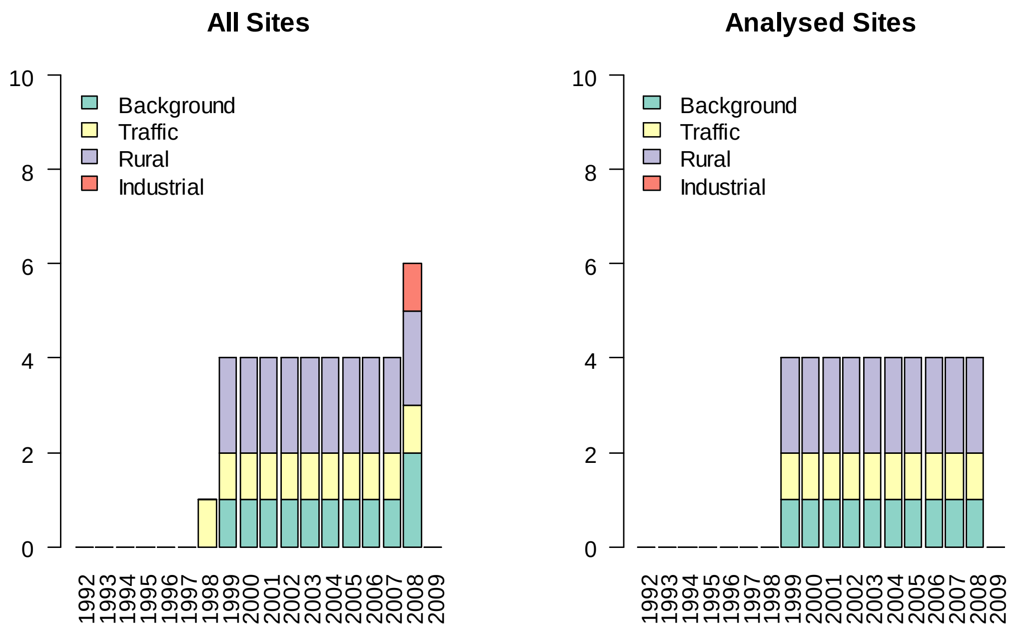

Figure 38: Number of TEOM $PM_{2.5}$ sites split by each site type. All sites (left), sites with >75% data capture (right)

Table 24: TEOM $PM_{2.5}$ sites used in reference dataset

Site Name	Type	Data Capture (%)
LONDON MARYLEBONE ROAD	Traffic	79
ROCHESTER STOKE	Rural	80
HARWELL	Rural	81
LONDON BLOOMSBURY	Background	84

Table 25: Distribution of TEOM $PM_{2.5}$ sites according to site type in reference dataset and for all available sites in 2009

Type	Reference		2008	
	Sites	%	Sites	%
Background	1	25	2	33
Traffic	1	25	1	17
Rural	2	50	2	33
Industrial	0	0	1	17
Total	4		6	

Figure 39: Geographical distribution of TEOM $PM_{2.5}$ reference sites

9.4 FDMS $PM_{2.5}$

The widespread installation of FDMS $PM_{2.5}$ instruments began during 2008. The 75% data capture threshold meant that the optimum site coverage was achieved in 2009; this single year is used as the reference dataset. This clearly limits any conclusions which can be drawn regarding seasonal variation. Nothing can be deduced regarding the inter-annual variability in these measurements.

The sites in the FDMS $PM_{2.5}$ reference dataset are shown in Table 27. The site distribution for the reference dataset shown in Table 26 is consequently the same as the distribution in 2009.

The geographical distribution of the sites shown in Figure 41 is very good.

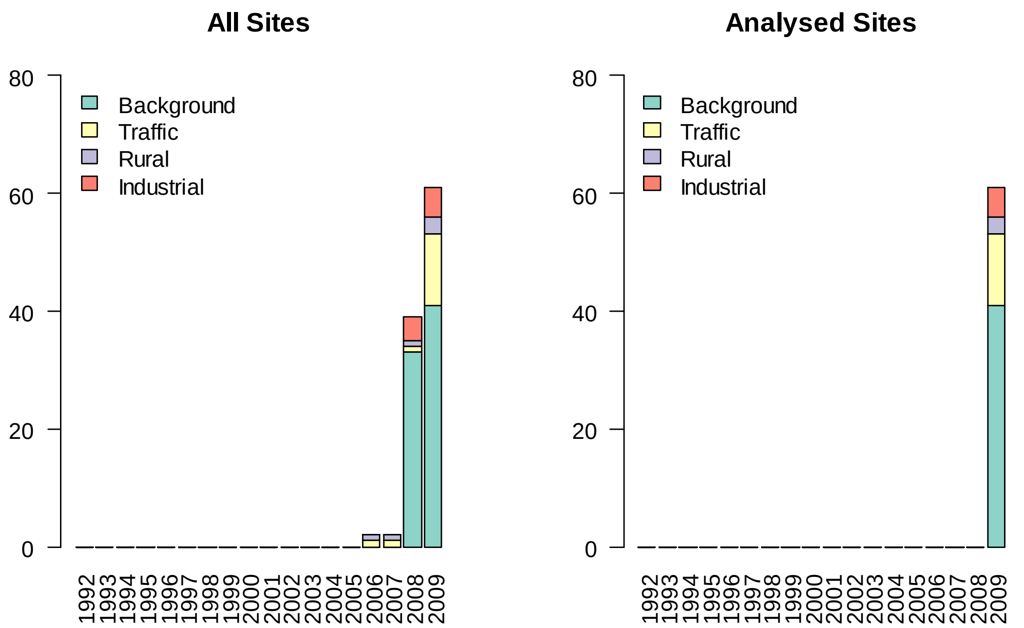

Figure 40: Number of FDMS $PM_{2.5}$ sites split by each site type. All sites (left), sites with >75% data capture (right)

Table 26: Distribution of FDMS $PM_{2.5}$ sites according to site type in reference dataset and for all available sites in 2009

Type	Reference		2009	
	Sites	%	Sites	%
Background	41	67	41	67
Traffic	12	20	12	20
Rural	3	5	3	5
Industrial	5	8	5	8
Total	61		61	

Table 27: FDMS $PM_{2.5}$ sites used in reference dataset

Site Name	Type	Data Capture (%)
CARLISLE ROADSIDE	Traffic	76
WIRRAL TRANMERE	Background	78
WIGAN CENTRE	Background	80
MANCHESTER PICCADILLY	Background	80
LONDON HARROW STANMORE	Background	81
BLACKPOOL MARTON	Background	82
SHEFFIELD CENTRE	Background	83
BELFAST CENTRE	Background	85
SANDY ROADSIDE	Traffic	86
COVENTRY MEMORIAL PARK	Background	87
NOTTINGHAM CENTRE	Background	87
LONDON BEXLEY	Background	88
LONDON BLOOMSBURY	Background	89
PORTSMOUTH	Background	89
LIVERPOOL SPEKE	Background	89
HULL FREETOWN	Background	90
SOUTHEND-ON-SEA	Background	90
BRISTOL ST PAUL'S	Background	91
BIRMINGHAM TYBURN	Background	92
CHESTERFIELD	Background	92
LEEDS CENTRE	Background	93
NEWCASTLE CENTRE	Background	94
OXFORD ST EBBES	Background	94
EDINBURGH ST LEONARDS	Background	94
GRANGEMOUTH	Industrial	94
CARDIFF CENTRE	Background	95
LONDON N. KENSINGTON	Background	95
LEAMINGTON SPA	Background	95
SALFORD ECCLES	Industrial	96
LONDON ELTHAM	Background	96
SOUTHAMPTON CENTRE	Background	96
PORT TALBOT MARGAM	Industrial	96
WARRINGTON	Background	96
AUCHENCORTH MOSS PM10 PM25	Rural	97
STOKE-ON-TRENT CENTRE	Background	97
LONDON TEDDINGTON	Background	98
GLASGOW CENTRE	Background	98
YORK BOOTHAM	Background	98
READING NEW TOWN	Background	98
NEWPORT	Background	99

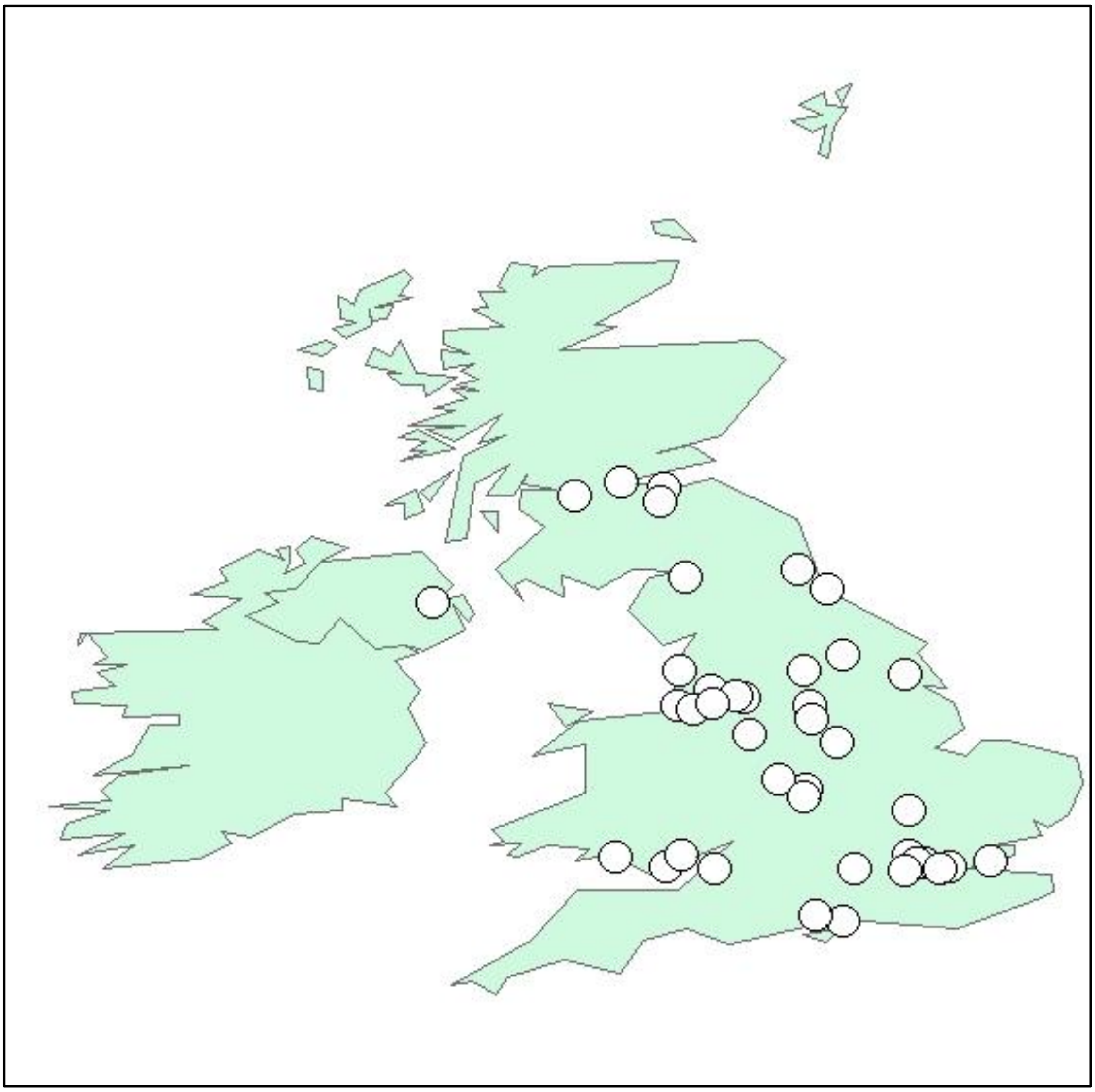

Figure 41: Geographical distribution of FDMS $PM_{2.5}$ reference sites

9.5 FDMS PM_{coarse}

The data capture target is more challenging for PM_{coarse} measurements as both PM_{10} and $PM_{2.5}$ measurements need to be present to create a valid PM_{coarse} measurement. Only four sites had a data capture greater than 75% (Newport, Chesterfield, London Bloomsbury and Port Talbot Margam). To increase geographical coverage the data capture target has been reduced to 56.25% (75% x75%); this has the effect of adding Marylebone Road to the list of sites.

The sites in the FDMS PM_{coarse} reference dataset are shown in Table 28.The distribution of site types is somewhat different to the network as it was in 2009, however, there are limited sites to remove from the dataset and no further sites available in the UK to include.

The geographical distribution shown in Figure 43 was centred on England. There was little scope for extending the geographical distribution without lowering the data capture rate still further.

Table 28: FDMS PM_{coarse} sites used in reference dataset

Site Name	Type	Data Capture (%)
LONDON MARYLEBONE ROAD	Traffic	61
NEWPORT	Background	79
CHESTERFIELD	Background	86
LONDON BLOOMSBURY	Background	88
PORT TALBOT MARGAM	Industrial	94

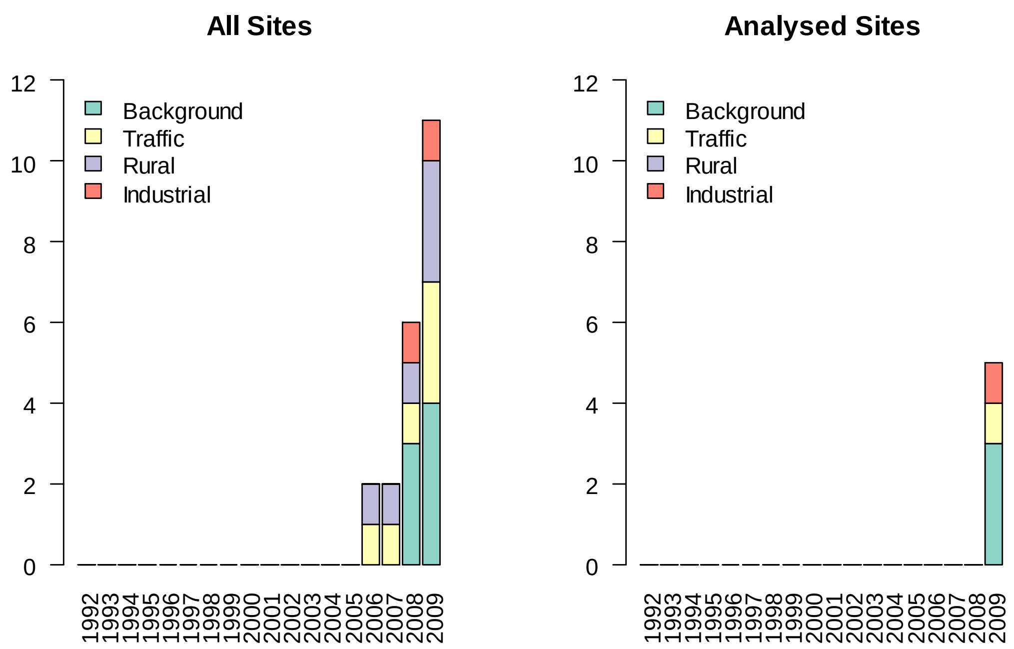

Figure 42: Number of FDMS PM_{coarse} sites split by each site type. All sites (left), sites with >75% data capture (right)

Table 29: Distribution of FDMS PM_{coarse} sites according to site type in reference dataset and for all available sites in 2009

Type	Reference		2009	
	Sites	%	Sites	%
Background	3	60	4	36
Traffic	1	20	3	27
Rural	1	20	3	27
Industrial	0	0	1	9
Total	5		11	

Figure 43: Geographical distribution of FDMS PM_{coarse} reference sites

9.6 Semi-volatile PM

For the purposes of this analysis we have defined semi-volatile PM as that measured in the reference mode of the FDMS PM_{10} instrument. Some FDMS measurements were available from 2003 onwards, however, the widespread installation of FDMS instruments began in 2007.

The sites the semi-volatile PM reference dataset are shown in Table 30. The distribution of site types shown in Table 31 demonstrates that the reference dataset has a similar make up to the FDMS PM_{10} sites as they were during 2009 – the latest year available. There are slightly less traffic sites and more background sites, reflecting the priority given to background sites in the Defra upgrade programme. However, this was felt to be an accurate enough reflection of the current FDMS network.

The geographical spread shown in Figure 37 lacked sites in London and the south east. Furthermore, only one roadside site was available. The south east of the UK experiences the highest concentrations of semi-volatile PM due to its proximity to continental Europe; additional sites in this area were judged to be important. Sites could be added in this area from the LAQN without compromising the data capture threshold of 75%. Two sites from the LAQN were therefore included in the reference dataset: North Kensington (background) as an AURN site which had an FDMS operating prior to affiliation and Tower Hamlets (traffic) as a traffic site with a high data capture rate.

Table 30: Semi-volatile PM sites used in reference dataset

Site Name	Type	Data Capture (%)
NORTH KENSINGTON	Background	76
TOWER HAMLETS ROADSIDE	Traffic	95
SHEFFIELD CENTRE	Background	75
PORT TALBOT MARGAM	Industrial	77
LEICESTER CENTRE	Background	78
STOKE-ON-TRENT CENTRE	Background	82
AUCHENCORTH MOSS PM10 PM25	Rural	82
CARDIFF CENTRE	Background	83
NEWCASTLE CENTRE	Background	84
HULL FREETOWN	Background	87
LIVERPOOL SPEKE	Background	87
SOUTHAMPTON CENTRE	Background	88
SWANSEA ROADSIDE	Traffic	92
BRISTOL ST PAUL'S	Background	93

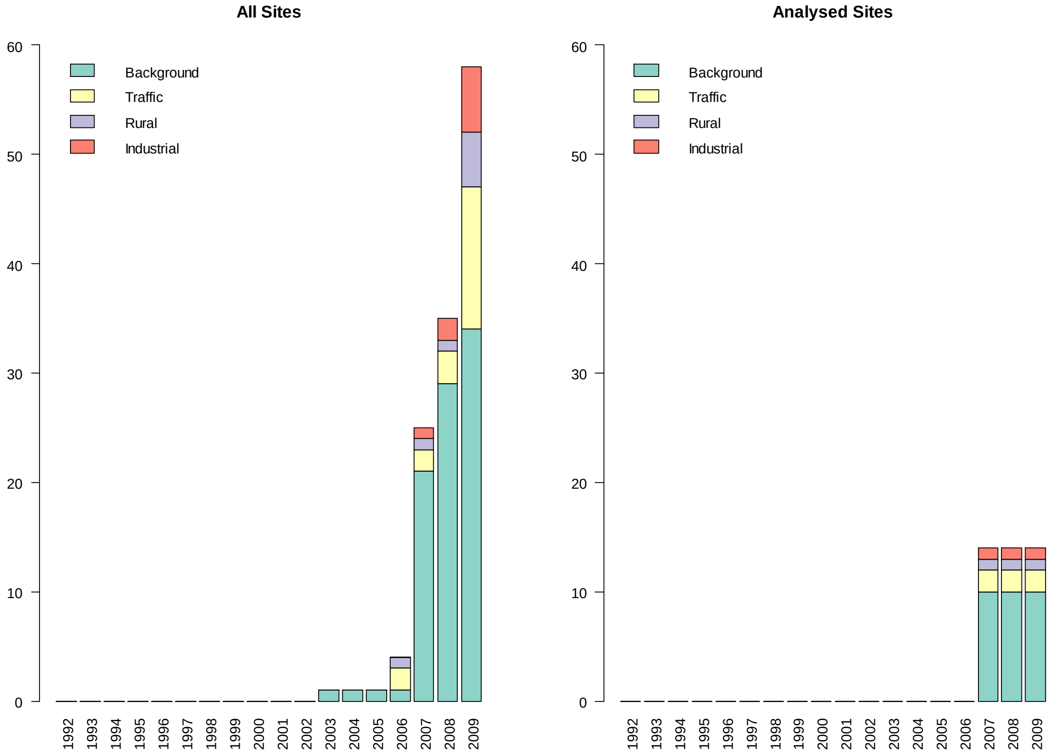

Figure 44: Number of semi-volatile PM sites split by each site type. All sites (left), sites with >75% data capture (right)

Table 31: Distribution of semi-volatile PM sites according to site type in reference dataset and for all available sites in 2009

Type	Reference		2009	
	Sites	%	Sites	%
Background	10	71	34	59
Traffic	2	14	13	22
Rural	1	7	5	9
Industrial	1	7	6	10
Total	14		58	

Figure 45: Geographical distribution of semi-volatile PM reference sites

9.7 $PM_{2.5}$ Nitrate

$PM_{2.5}$ nitrate measurements are presented here as an alternative to the semi-volatile PM measurements as supplied by the FDMS reference channel. These were available in the UK using the R&P 8400 nitrate monitor between 2003 and 2009. These have shown a good agreement with the FDMS reference channel (Hering, Fine et al. 2004; Green, Fuller et al. 2009).

Although three sites (Harwell, Marylebone Road and later North Kensington) measured $PM_{2.5}$ nitrate, only Marylebone Road had a data capture greater than 75% for a long period (2004-2009). This clearly leaves a dataset which is very limited in the site type and geographical representation. Furthermore, it does not provide a dataset which could confirm the comparability of $PM_{2.5}$ nitrate and FDMS reference measurements. An examination of the data capture from the instruments for the 2007-2009 period (the same as the semi-volatile reference dataset) showed a minimum data capture of 49 % from North Kensington. A relaxation of the data capture threshold was considered worthwhile to address these factors.

The sites the $PM_{2.5}$ nitrate reference dataset are shown in Table 32. The distribution of site types shown in Table 33 this demonstrates that most site types are represented but are limited by the availability of measurements. The small number of sites means that geographical representation is limited to southern England.

Table 32: $PM_{2.5}$ nitrate sites used in reference dataset

Site Name	Type	Data Capture (%)
Harwell - Nitrate	Rural	70
North Kensington - Nitrate	Background	49
Marylebone Road - Nitrate	Traffic	81

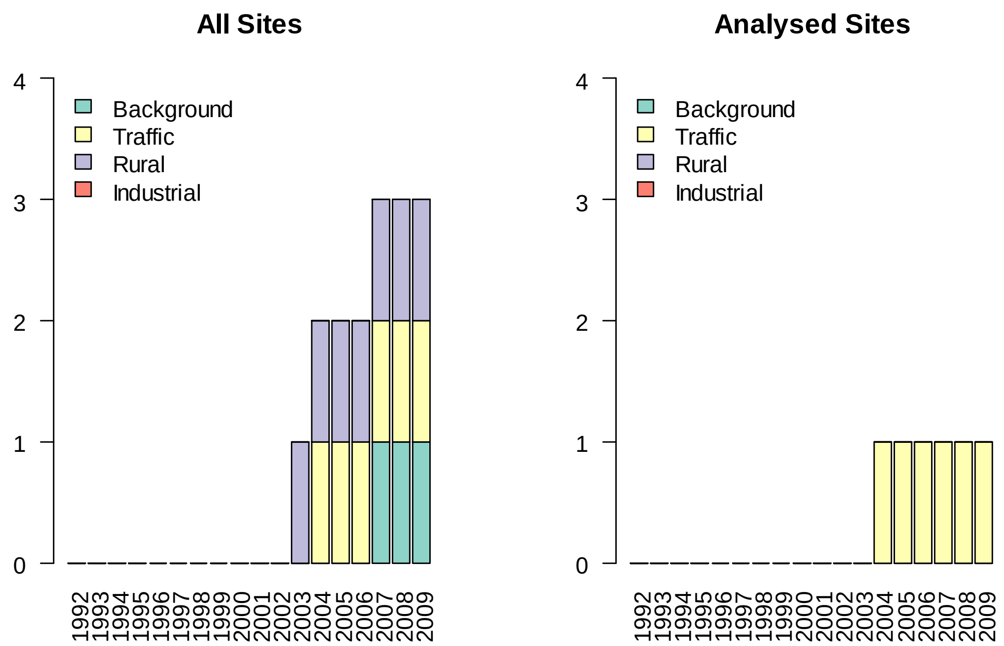

Figure 46: Number of $PM_{2.5}$ nitrate sites split by each site type. All sites (left), sites with >75% data capture (right)

Table 33: Distribution of $PM_{2.5}$ nitrate sites according to site type in reference dataset

Type	Reference		2009	
	Sites	%	Sites	%
Background	1	33	1	33
Traffic	1	33	1	33
Rural	1	33	1	33
Industrial	0	0	0	0
Total	3		3	

Figure 47: Geographical distribution of $PM_{2.5}$ nitrate reference sites

Appendix II - UK PM Climate Concentrations

Concentration ranges have been summarised using box and whisker plots, the key statistics are also tabulated. Each pollutant is differentiated by year to highlight any inter-annual variation or trends in these statistics and by site type. A summary of all years is used to quantify the concentration range of each pollutant.

9.8 TEOM PM_{10}

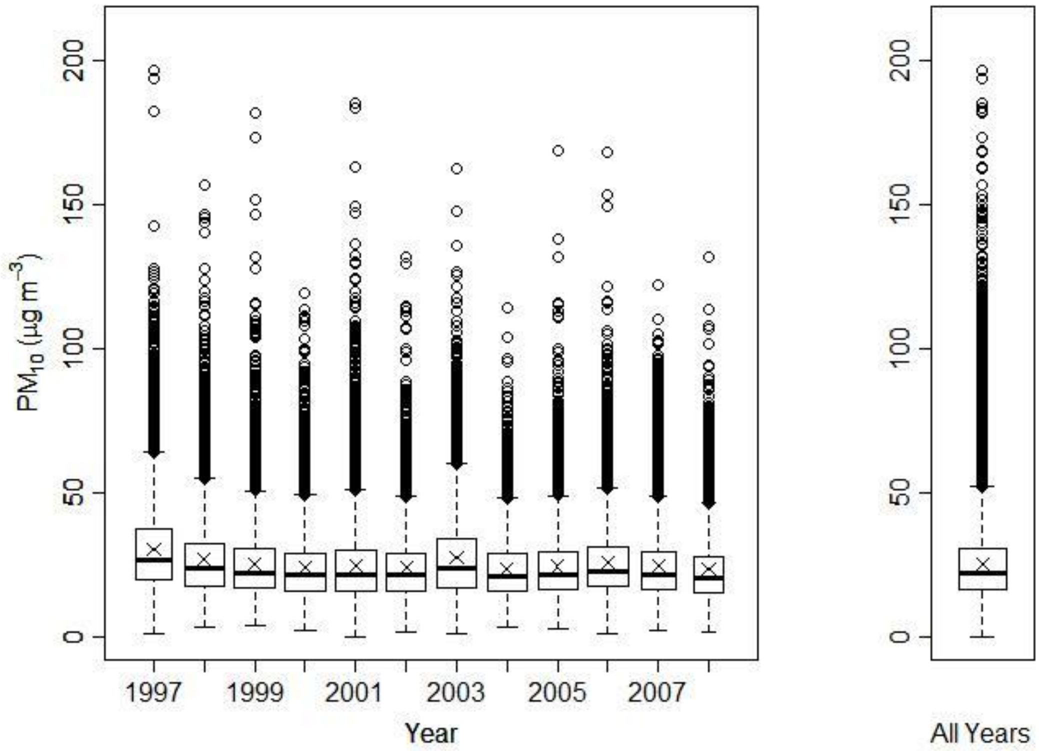

Figure 48: Box and whisker plot of TEOM PM_{10} measurements from 1997 to 2008 inclusive split by year and a summary of all years.

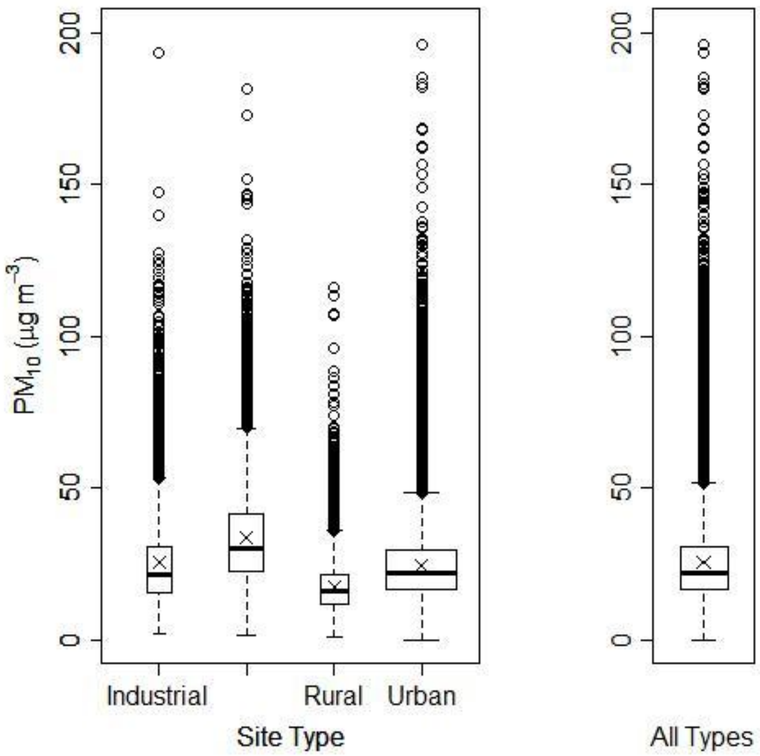

Figure 49: Box and whisker plot of TEOM PM_{10} measurements from 1997 to 2008 inclusive split by site type and a summary of all types.

Table 34: Statistical summary of UK TEOM PM_{10} concentrations from 1997 to 2006 inclusive

Year	Mean	Median	1st Quartile	3rd Quartile	Whisker min	Whisker max	Min	Max
1997	30.4	26.5	19.6	37.4	1.1	64.2	1.1	196.1
1998	26.7	23.5	17.6	32.4	3.2	54.7	3.2	156.5
1999	25.1	22.2	16.7	30.3	4	50.7	4	181.3
2000	23.9	21.2	15.8	29	2	49	2	119.2
2001	24.7	21.6	15.9	29.9	0	50.9	0	185.2
2002	23.9	21.3	16	29	1.3	48.6	1.3	131.5
2003	27.2	23.5	16.7	34.1	0.9	60.2	0.9	162.3
2004	23.5	20.9	15.8	28.8	3	48.2	3	113.7
2005	24.2	21.5	16.2	29.3	2.6	48.9	2.6	168.4
2006	25.8	22.7	17.3	31	1.1	51.5	1.1	167.9
2007	24.4	21.5	16.2	29.2	1.9	48.8	1.9	121.7
2008	23.6	20.5	15.4	27.9	1.8	46.6	1.8	131.7
Industrial	25.3	21.4	15.7	30.8	1.8	53.5	1.8	193.7
Roadside	33.5	30.1	22.6	41.5	1.3	69.9	1.3	181.3
Rural	17.6	15.9	11.7	21.4	1.1	35.9	1.1	115.9
Urban	24.4	21.8	16.6	29.3	0	48.3	0	196.1
All	25.3	22.1	16.5	30.6	0	51.9	0	196.1

9.8.1. FDMS PM10

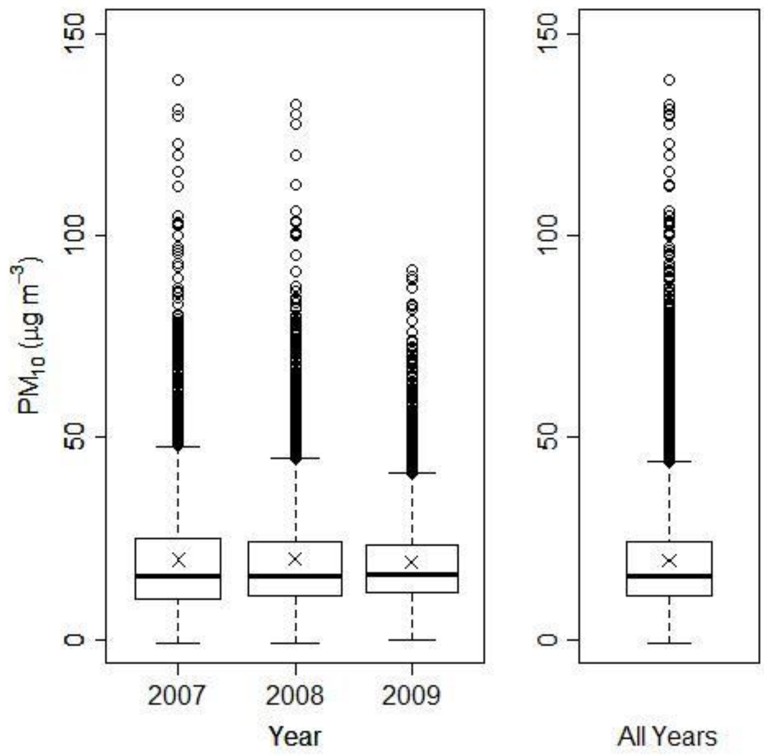

Figure 50: Box and whisker plot of FDMS PM_{10} measurements from 2007 to 2009 inclusive and a summary of all years.

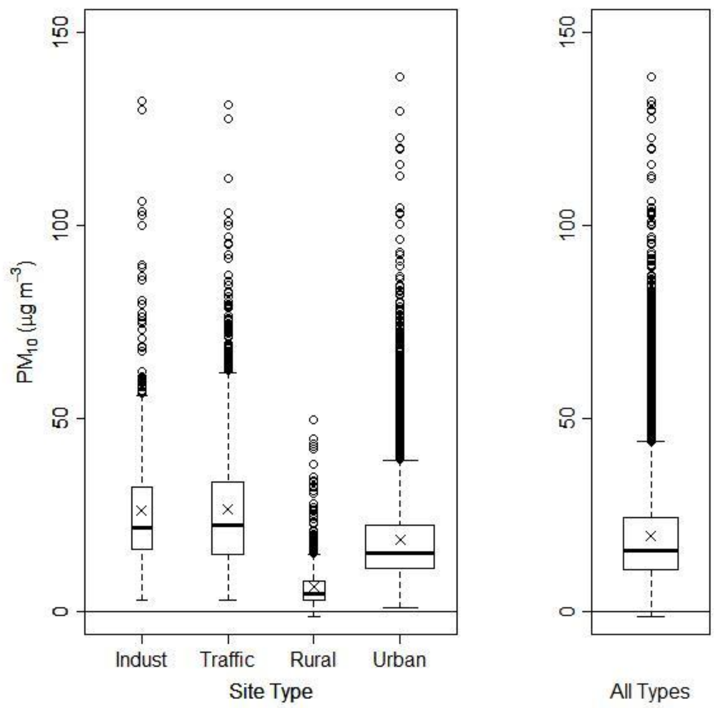

Figure 51: Box and whisker plot of FDMS PM_{10} measurements from 2007 to 2009 inclusive split by site type and a summary of all types.

Table 35: Statistical summary of UK FDMS PM_{10} concentrations from 2007 to 2009 inclusive

Year	Mean	Median	1st Quartile	3rd Quartile	Whisker min	Whisker max	Min	Max
2007	19.7	15.6	10	25.2	-1.1	48	-1.1	138.6
2008	19.8	15.7	10.8	24.4	-0.8	44.8	-0.8	132.3
2009	19.3	16.2	11.8	23.6	0	41.2	0	91.5
Industrial	26.2	21.9	16.2	32.2	3	56.3	3	132.3
Roadside	26.5	22.4	14.7	33.7	3.1	62	3.1	131.4
Rural	6.5	4.7	3	7.9	-1.1	15.3	-1.1	49.8
Urban	18.8	15.3	11.2	22.5	1	39.4	1	138.6
All	19.8	15.7	10.5	24.8	-1.1	46.2	-1.1	138.6

9.9 TEOM $PM_{2.5}$

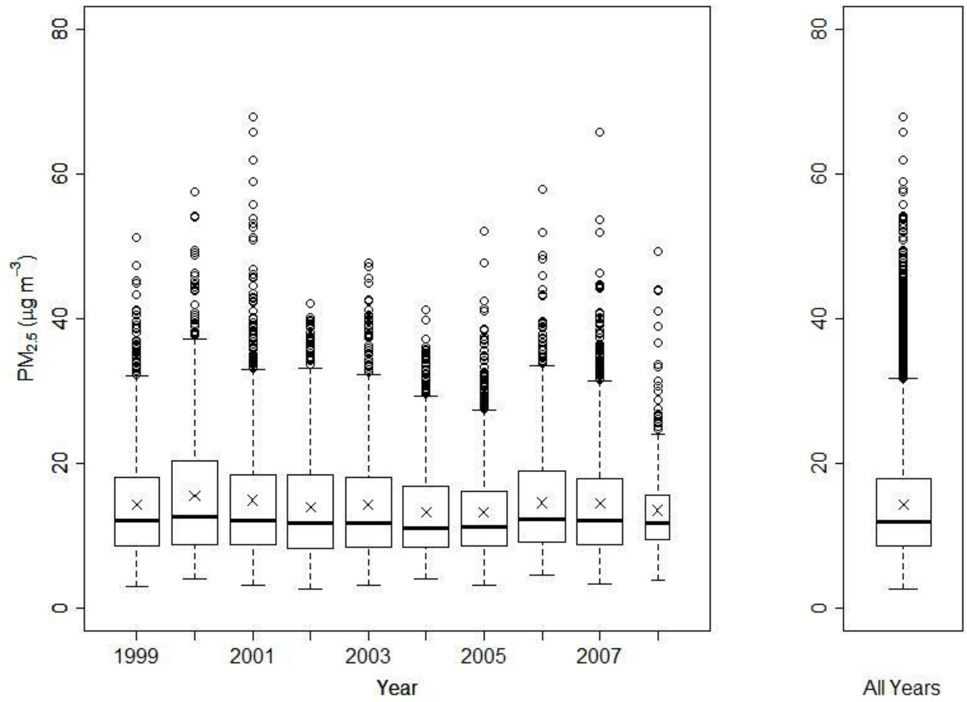

Figure 52: Box and whisker plot of TEOM $PM_{2.5}$ measurements from 1999 to 2008 split by month

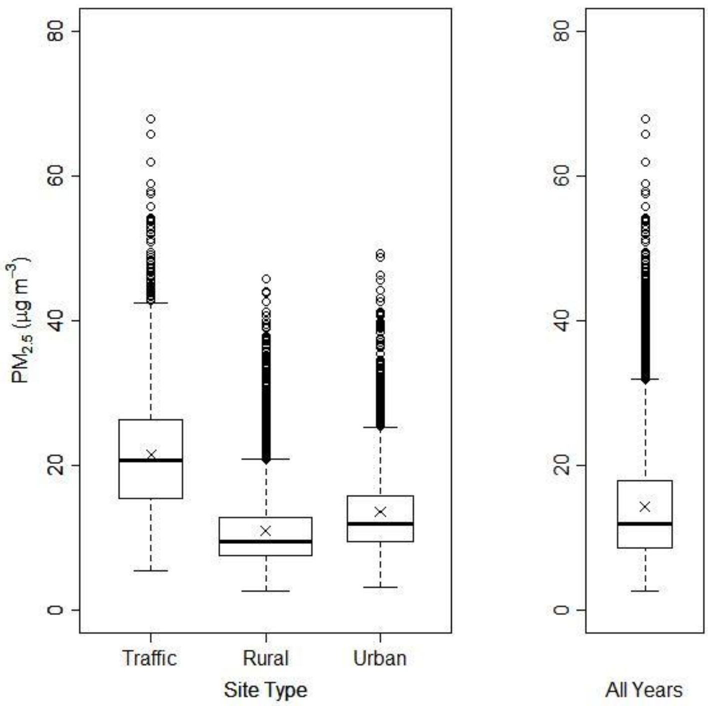

Figure 53: Box and whisker plot of TEOM $PM_{2.5}$ measurements from 1999 to 2008 inclusive and a summary of all years.

Table 36: Statistical summary of UK TEOM $PM_{2.5}$ measurements from 1999 to 2008 inclusive

Year	Mean	Median	1st Quartile	3rd Quartile	Whisker min	Whisker max	Min	Max
1999	14.3	12.2	8.6	18	3	32.2	3	51.3
2000	15.5	12.8	8.8	20.4	4.1	37.8	4.1	57.6
2001	15	12.1	8.8	18.5	3.3	33.2	3.3	68
2002	14	11.8	8.3	18.4	2.7	33.7	2.7	42.1
2003	14.3	11.9	8.5	18.1	3.1	32.5	3.1	47.8
2004	13.3	11.1	8.5	16.9	4	29.5	4	41.3
2005	13.3	11.3	8.6	16.2	3.2	27.5	3.2	52.1
2006	14.6	12.3	9.2	19	4.6	33.6	4.6	57.9
2007	14.5	12.1	8.9	17.9	3.4	31.5	3.4	65.9
2008	13.6	11.9	9.6	15.6	3.9	24.7	3.9	49.4
Roadside	21.6	20.8	15.5	26.4	5.5	42.8	5.5	68
Rural	11	9.5	7.5	12.9	2.7	21	2.7	45.8
Urban	13.6	12	9.6	15.9	3.1	25.4	3.1	49.4
All	14.3	12	8.7	18	2.7	31.8	2.7	68

9.10 FDMS PM2.5

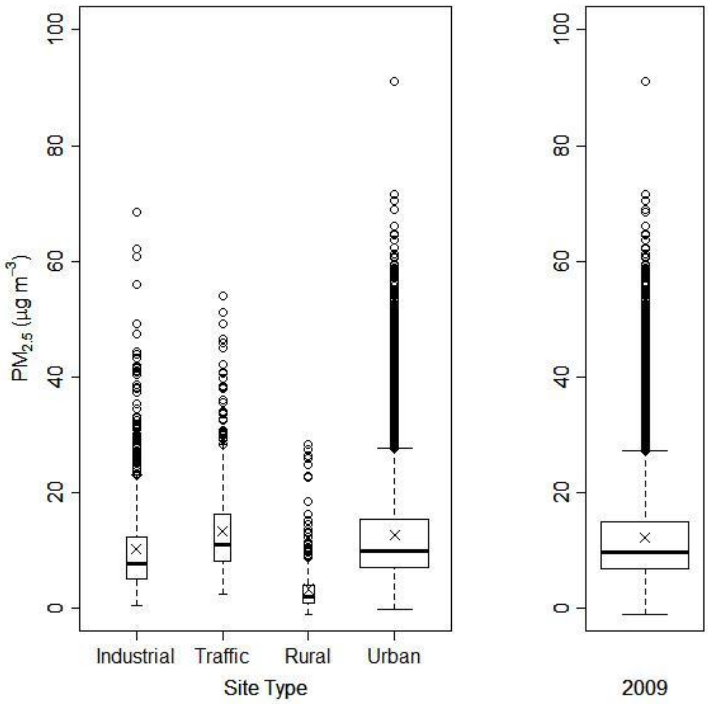

Figure 54: Box and whisker plot of FDMS $PM_{2.5}$ measurements for 2009 inclusive split by site type and a summary of all types (2009).

Table 37: Statistical summary of UK FDMS $PM_{2.5}$ concentrations

Year	Mean	Median	1st Quartile	3rd Quartile	Whisker min	Whisker max	Min	Max
2009	11.8	9.2	6.3	14.6	-1	26.9	-1	91.1
Industrial	10.2	7.8	5.1	12.3	0.5	23.1	0.5	68.5
Roadside	13.4	11	8.1	16.3	2.5	28.5	2.5	54
Rural	3.3	2	0.9	4	-1	8.8	-1	28.4
Urban	12.7	10	7.1	15.3	-0.2	27.6	-0.2	91.1
All Years	11.8	9.2	6.3	14.6	-1	26.9	-1	91.1

9.11 FDMS PM_{coarse}

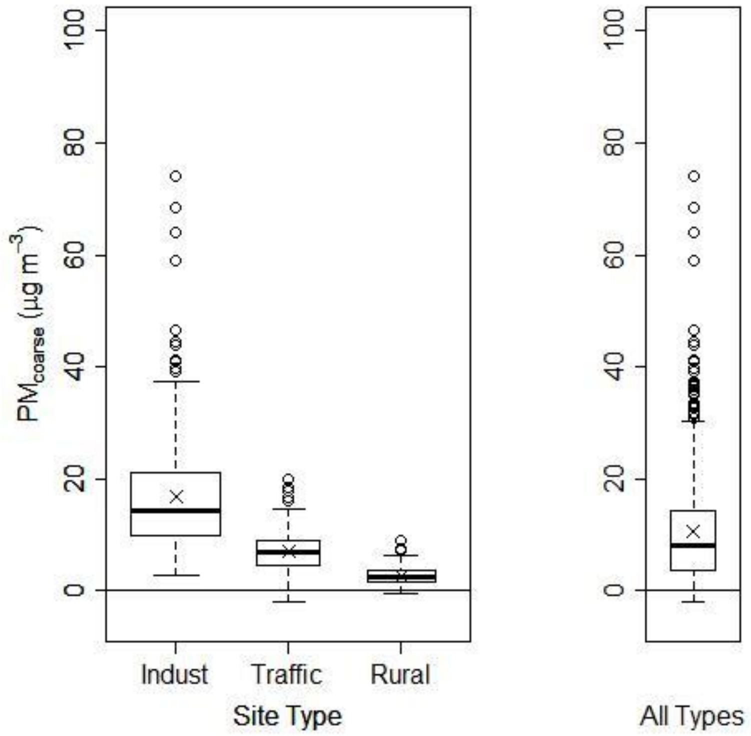

Figure 55: Box and whisker plot of FDMS PM_{coarse} measurements for 2009 inclusive split by site type and a summary of all types (2009).

Table 38: Statistical summary of UK FDMS PM_{coarse} concentrations

Year	Mean	Median	1st Quartile	3rd Quartile	Whisker min	Whisker max	Min	Max
2009	10.6	8.1	3.6	14.4	-1.8	30.7	-1.8	74.1
Industrial	16.8	14.3	10	21.2	2.7	38.1	2.7	74.1
Traffic	8.1	7.1	5.3	10.3	0	17.6	-5.1	21.1
Background	5.2	4.6	2.1	8	-3.6	16.8	-3.6	18.6
All Years	10.6	8.1	3.6	14.4	-1.8	30.7	-1.8	74.1

9.12 Semi-volatile PM

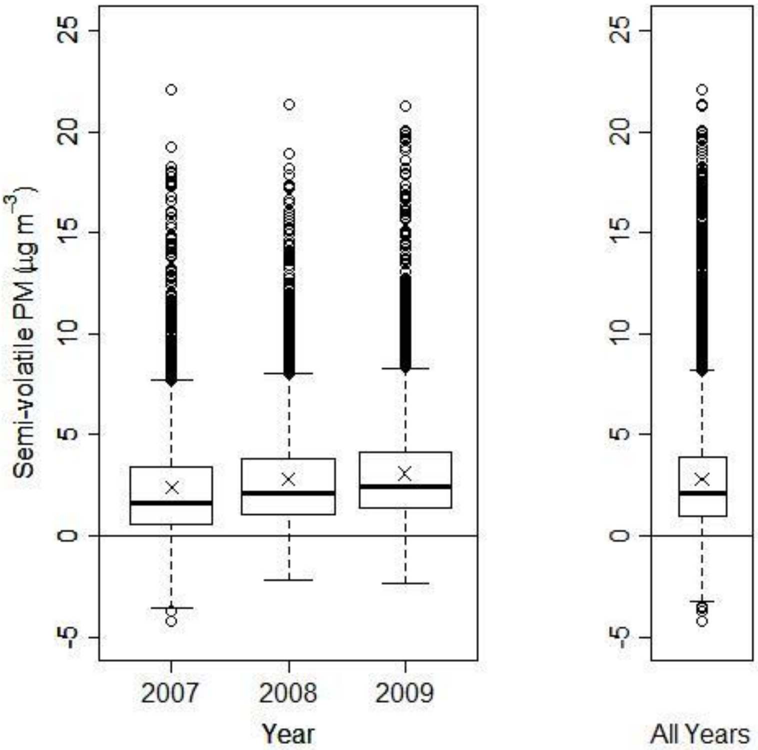

Figure 56: Box and whisker plot of semi-volatile PM concentrations from 2007 to 2009 inclusive and a summary of all years

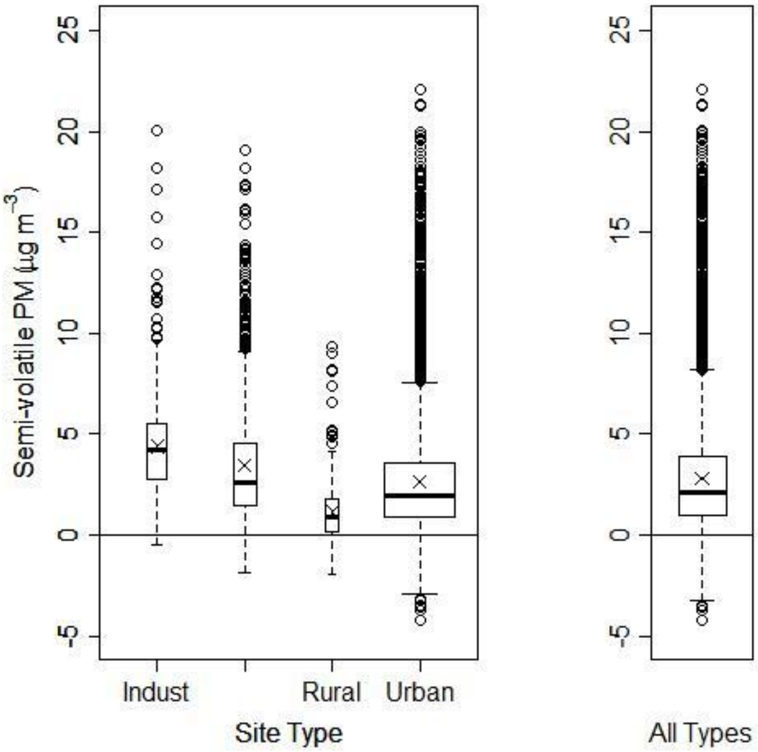

Figure 57: Box and whisker plot of semi-volatile PM concentrations from 2007 to 2009 inclusive split by site type and a summary of all types.

Table 39: Statistical summary of semi-volatile PM concentrations from 2007 to 2009 inclusive

Year	Mean	Median	1st Quartile	3rd Quartile			Min	Max
2007	2.4	1.6	0.6	3.4	-3.7	7.7	-4.2	22.1
2008	2.8	2.1	1	3.8	-2.2	8	-2.2	21.3
2009	3.1	2.4	1.4	4.2	-2.4	8.4	-2.4	21.3
Industrial	4.4	4.2	2.8	5.5	-0.5	9.7	-0.5	20.1
Roadside	3.5	2.6	1.5	4.6	-1.9	9.2	-1.9	19
Rural	1.1	1	0.2	1.8	-1.9	4.2	-1.9	9.3
Urban	2.6	2	0.9	3.6	NULL	7.6	-4.2	22.1
All	2.8	2.1	1	3.9	-3.3	8.2	-4.2	22.1

9.13 PM$_{2.5}$ Nitrate

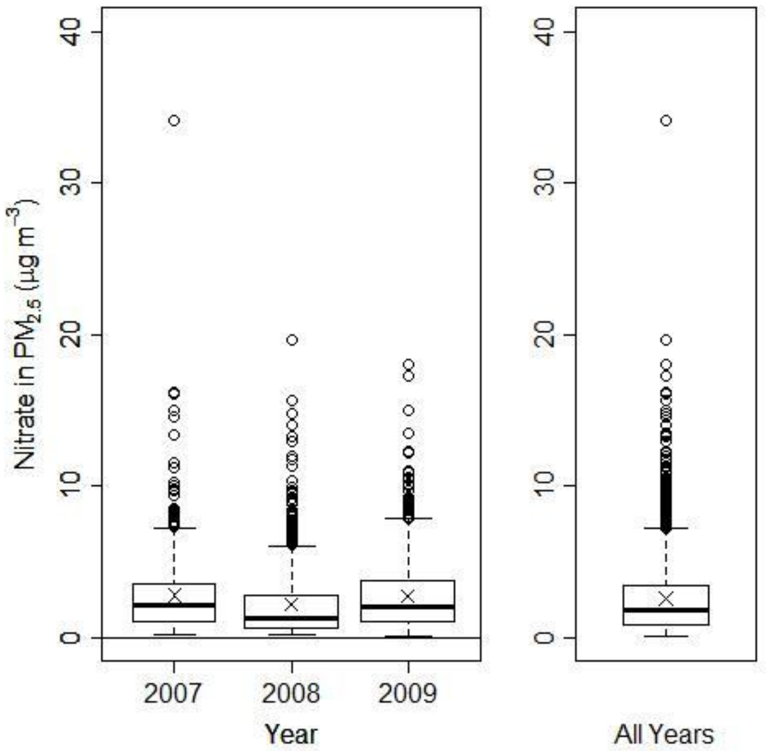

Figure 58: Box and whisker plot of PM$_{2.5}$ nitrate measurements from 2007 to 2009 inclusive and a summary of all years.

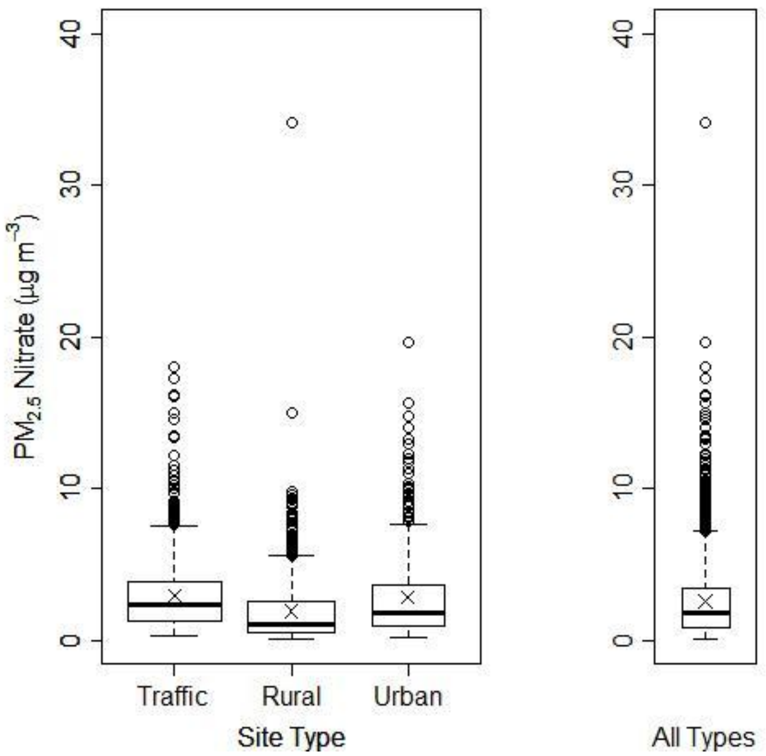

Figure 59: Box and whisker plot of $PM_{2.5}$ nitrate measurements from 2007 to 2009 inclusive split by site type and a summary of all types.

Table 40: Statistical summary of $PM_{2.5}$ nitrate concentrations from 2007 to 2009 inclusive

Year	Mean	Median	1st Quartile	3rd Quartile	Whisker min	Whisker max	Min	Max
2007	2.8	2.2	1.1	3.6	0.2	7.3	0.2	34.1
2008	2.2	1.3	0.7	2.8	0.2	6	0.2	19.7
2009	2.8	2	1	3.7	0.1	7.8	0.1	18
Roadside	3	2.3	1.3	3.8	0.3	7.6	0.3	18
Rural	1.9	1.1	0.5	2.6	0.1	5.6	0.1	34.1
Urban	2.8	1.8	0.9	3.7	0.2	7.8	0.2	19.7
All	2.6	1.9	0.8	3.4	0.1	7.2	0.1	34.1

Appendix III – Statistical Methods

9.14 Mann-Whitney Test

The Mann-Whitney the two-sided, nonparametric rank sum test which tests for whether one group tends to produce larger observations than the second group. Indeed, it can determine whether the two groups come from the same population (same median and other percentiles). It achieves this by ranking the data (smallest observation has rank=1, largest has rank=N) to compute the joint ranks R_k. Data with the same value (tied data) are given the same average rank, the ranks from the smaller sample are then summed to provide the rank sum statistic (W_{rs}). Groups with the same distribution of data will produce identical rank sums. For small datasets the exact test is used and W_{rs} is compared to standard statistical tables to provide a p-value. For large datasets a large sample approximation is used as the distribution of the tests of the test statistic (Z_{rs}) is produced after a continuity correction.

$$Z_{rs} = \begin{cases} \dfrac{W_{rs} - \frac{1}{2} - m_W}{\sigma_{Wt}} & if\ W_{rs} > m_W \\ 0 & if = m_W \\ \dfrac{W_{rs} + \frac{1}{2} - m_W}{\sigma_{Wt}} & if\ W_{rs} > m_W \end{cases}$$

Where:

$W_{rs} =$ sum of ranks for the group having the smaller sample size $= \sum \mathrm{R_i}$

$i = 1, n$ $(use\ either\ group\ when\ sample\ sizes\ are\ equal: n = m)$

$m_W = mean\ rank$

$\sigma_{Wt} = standard\ deviation\ of\ ranks\ with\ a\ correction\ for\ ties$

$$= \sqrt{\frac{nm}{N(N-1)} \sum_{k=1}^{N} R_{k^2} - \frac{nm(N+1)^2}{4(N-1)}}\ where\ N = n + m$$

It has as its null hypothesis: Prob [x > y] = 0.5. In the case of a 2-sided test such as this the alternative hypothesis is: Prob [x > y] ≠ 0.5

9.15 Geometric Mean

The geometric mean (GM) is defined as:

$$\left(\prod_{i=1}^{n} x_i\right)^{1/n} = \sqrt[n]{x_1 . x_2 .... x_n} == \exp\left[\frac{1}{n} \sum_{i=1}^{n} \ln x_i\right]$$

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