

Measurements of Particulate Matter Volatility

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

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Table of Contents

1	INTRODUCTION	9
2	METHOD	11
2.1	Monitoring Locations	11
2.2	Monitoring Methods	11
2.3	Quality Assurance	15
2.4	Data Pre-processing.....	17
2.5	Measuring Agreement	19
3	RESULTS	21
3.1	Marylebone Road Nitrate Measurements	21
3.2	Comparison of Nitrate Measurements to FDMS Measurements at Marylebone Road.	22
3.3	Comparison Between PM ₁₀ Measurements	25
3.4	Assessing of the differences in volatile PM concentration in London using measurements from the six FDMS instruments.	37
4	CONCLUSIONS	41
5	ACKNOWLEDGEMENTS	43
6	SITE LOCATIONS	45
7	REFERENCES	49

List of Figures

Figure 1: Monitoring site locations.....	11
Figure 2: FDMS co-location study at Marylebone Road.....	12
Figure 3: FDMS base measurement mode (left) and purge measurement mode (right) configurations, source (Rupprecht & Patashnick Co., I., 2003).....	13
Figure 4: Partisol 2025 PM ₁₀ at Marylebone Road.....	13
Figure 5: Ambient and temperature at the filter alongside the difference between them from the Partisol 2025 at Marylebone Road during 2004.....	14
Figure 6: R&P Nitrate 8400N alongside co-located FDMS instruments at Marylebone Road....	15
Figure 7: Aqueous calibration of R&P 8400N from 12 th May 2004	17
Figure 8: Aqueous calibration results for the R&P 8400N February to December 2004.....	17
Figure 9: Relationship between TEOM and reference method at Marylebone Road during 2004 with and without inbuilt TEOM correction factor.....	18
Figure 10: US EPA STP and ambient temperature and pressure correction for TEOM measurements from Marylebone Road during 2003	19
Figure 11: Time series graph of R&P 8400N hourly mean nitrate measurements made at Marylebone Road during 2004	22
Figure 12: Time series of R&P 8400N daily mean nitrate measurements and daily mean FDMS purge cycle measurements made at Marylebone Road during 2004	23
Figure 13: Correlation between daily mean ammonium nitrate in PM _{2.5} and the daily mean FDMS purge measurement made at Marylebone Road during 2004.....	23
Figure 14: Diurnal variation of ammonium nitrate and the FDMS purge measurement from Marylebone Road during 2004	24
Figure 15: Hourly mean ammonium nitrate and FDMS purge measurement concentrations between 3 rd and 5 th August 2004 at Marylebone Road.....	24
Figure 16: Limits of agreement analysis of daily mean Partisol and FDMS measurements at Marylebone Road	28
Figure 17: Limits of agreement analysis of daily mean Partisol and FDMS measurements at North Kensington	29
Figure 18: Limits of agreement analysis of daily mean TEOM and FDMS base measurements at Marylebone Road	30
Figure 19: Limits of agreement analysis of daily mean TEOM and FDMS base measurements at North Kensington.....	30
Figure 20: Limits of agreement analysis of daily mean TEOM and FDMS base measurements at Belvedere.....	31
Figure 21: Limits of agreement analysis of daily mean TEOM and FDMS base measurements at Thames Road North.....	31

Figure 22: Limits of agreement analysis of daily mean Partisol and TEOM measurements at Marylebone Road	32
Figure 23: Limits of agreement analysis of daily mean Partisol and TEOM measurements at North Kensington	33
Figure 24: Correlation between Partisol Daily Mean minus TEOM Daily mean and FDMS purge concentration measurements made at Marylebone Road during 2004	34
Figure 25: Correlation between Partisol Daily Mean minus TEOM Daily mean and FDMS purge concentration measurements made at North Kensington during 2004	35
Figure 26: Correlation between Partisol Daily Mean minus TEOM Daily mean and FDMS Purge concentration measurements made on common days at Marylebone Road and North Kensington during 2004	36
Figure 27: Difference between the Partisol and TEOM measurements as a time series alongside the FDMS purge measurements at Marylebone Road during 2004	36
Figure 28: Time series plot of FDMS purge measurements made in the LAQN during 2004	38
Figure 29: Time series plot of FDMS purge measurement variation from a network mean during 2004	39
Figure 30: Marylebone Road site picture and location	45
Figure 31: North Kensington site picture and location.....	45
Figure 32: Millennium Village site picture and location.....	46
Figure 33: Westthorne Avenue site picture and location	46
Figure 34: Belvedere site picture and location	46
Figure 35: Thames Road North site picture and location	47

List of Tables

Table 1: Summary of measurements available from FDMS equipped sites ordered west to east by location.....	21
Table 2: Summary of R&P8400N hourly nitrate measurements made at Marylebone Road during 2004	21
Table 3: RMA regression analysis of time-shifted hourly FDMS purge and ammonium nitrate measurements.....	25
Table 4: Regression Analysis Results from Marylebone Road PM ₁₀ Instruments during 2004 ..	26
Table 5: Regression Analysis Results from North Kensington PM ₁₀ Instruments during 2004...	27
Table 6: Mean concentrations of the FDMS purge measurements during 2004	38
Table 7: Standard deviations of the difference between FDMS purge measurement and a network mean.....	39

1 INTRODUCTION

The composition of particulate matter (PM) is very diverse with respect to its physical and chemical properties. In the atmosphere the composition of PM changes through a host of processes including coagulation, condensation, chemistry, water uptake, rainout, sedimentation, dry deposition and transport (Jacobson, M. Z., 2002). Many different aspects of PM, physical or chemical, can be measured using a variety of methods. However, most measurements are concerned with the assessment of the mass of a fraction of PM defined by its size e.g. PM₁₀ or PM_{2.5}.

This study concerns the measurements of PM made using the Filter Dynamic Measurement System (FDMS) in the London Air Quality Network (LAQN) during 2004. In particular the measurement of volatile PM, which is facilitated by the FDMS filter purge measurement cycle. Further details of this measurement methodology can be found in section 2.2.1.

For the purposes of this study volatile PM is defined as the mass lost from the instrument sample collection filter during (or after) sampling, although it is recognised that the volatile fraction of PM in the atmosphere is dynamic and complex.

The accurate assessment of PM mass is frequently compromised by the loss of the volatile fraction of PM. This problem is common to most types of PM mass measurement methods, including the Tapered Element Oscillating Microbalance (TEOM). This instrument is widely used on the Automatic Urban and Rural Network (AURN) and LAQN. Its elevated sampling temperature results in it measuring a lower mass concentration than the reference method due to the loss of volatile PM (Allen, G. *et al.*, 1997; Salter, L. F. *et al.*, 1999; Green, D. *et al.*, 2001; Charron, A. *et al.*, 2003). However, measurements equivalent to those made using the reference method are required for the assessment of the National and European Air Quality Standards (1999/30/EC). This situation is complicated by the requirement to supply up-to-date information to the public, which is only possible using an automatic instrument such as the TEOM. The public information requirements have prevented a change in the monitoring methodology and led to the derivation of a correction factor, which is then applied to the measurements made using the TEOM so that they equate to the reference method.

It is hypothesised that, firstly, the FDMS purge measurement can be used as a surrogate for measurements of ammonium nitrate. This has been described for similar measurement methodologies (Hering, S. *et al.*, 2004). Secondly, as ammonium nitrate accounts for a large percentage of the difference between the TEOM and the Partisol (Allen, G. *et al.*, 1997), the FDMS purge measurement can be used to correct for this difference.

The following tasks were undertaken in this study to test these hypotheses:

1. Ratification and reporting of the ammonium nitrate measurements made at Marylebone Road using the R&P 8400N automatic nitrate monitor.
2. Investigation of the relationship between ammonium nitrate and the FDMS purge measurements made at Marylebone Road
3. Investigation of the relationship between the different PM measurements made at Marylebone Road and North Kensington. Specifically the potential of the FDMS purge measurement to approximate the difference between the TEOM and the Partisol.
4. To assess the variations in the concentrations of volatile PM by examining the FDMS purge measurements from the LAQN sites.

This work was undertaken for the Department for Environment, Food and Rural Affairs (DEFRA), the Scottish Executive, the Welsh Assembly Government and the DoE in Northern Ireland, hereafter referred to as DEFRA.

2 METHOD

This section outlines the monitoring locations, the methods used, the treatment of data and provides a summary of the data analysis techniques used.

2.1 Monitoring Locations

The monitoring locations are shown in Figure 1, further details of the monitoring locations are given in section 6.

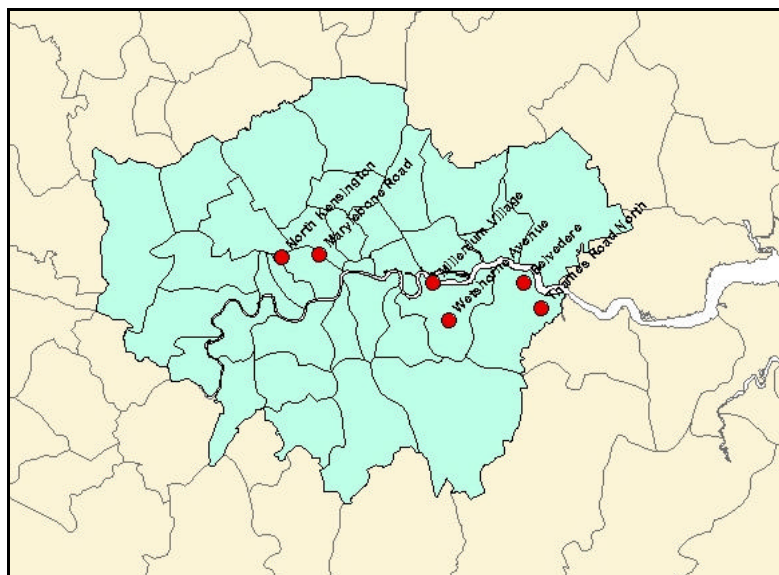


Figure 1: Monitoring site locations

2.2 Monitoring Methods

PM₁₀ measurements were undertaken using three different measurement methodologies in this study. Additionally, the R&P 8400N was used to measure the mass of nitrate in PM_{2.5}. Each measurement method and any associated laboratory analysis are described briefly here.

2.2.1 TEOM 1400

The TEOM is a real time particulate mass monitor; its mass measurement method relies on the microbalance. This consists of a hollow glass tapered tube, clamped at one end free to oscillate at the other. An exchangeable filter is placed on the free end. This tube is maintained in constant oscillation through an electronic feedback system, adding sufficient energy to the system to overcome losses. The frequency of oscillation is measured and recorded by a microprocessor at two second intervals.

The TEOM was operated in its standard configuration. Air was drawn air through An R&P PM₁₀ sampling inlet at 16.7 lmin⁻¹. The flow was then split using an isokinetic flow splitter into a main flow of 3 lmin⁻¹, which passed through the microbalance, and an auxiliary flow of 13.7 lmin⁻¹. The filter and the air stream were heated to 50°C to reduce the interferences from particle bound water and to minimise thermal expansion of the tapered element which may affect the oscillating frequency (Chung, A. *et al.*, 2001). This has the widely reviewed disadvantage of driving off semi-volatile material such as ammonium nitrate and organic aerosols (Allen, G. *et al.*, 1997; Salter, L. F. *et al.*, 1999; Soutar, A. *et al.*, 1999; Cyrus, J. *et al.*, 2001; Green, D. *et al.*, 2001; Charron, A. *et al.*, 2003). However, the TEOM received US EPA certification as an equivalent method for PM₁₀ monitoring (Patashnick, H. *et al.*, 1991).

2.2.2 Filter Dynamic Measurement System 8500

The FDMS aims to measure the mass concentration of airborne PM and quantify the mass changes of the filter due to evaporative and condensation processes that will affect the measurements. This system is based on TEOM technology, using the same microbalance. The instrument at Marylebone Road is shown in Figure 2 during a co-location study.



Figure 2: FDMS co-location study at Marylebone Road

The FDMS sampled air through an R&P PM₁₀ inlet, and then used a dryer to remove water from the sample; this allowed the mass to be measured at 30°C rather than 50°C. After passing through the dryer measurement was alternated between two modes (base and purge), switching between them every six minutes, the different configurations of these modes are shown in Figure 3. The change in mass on the filter was measured by the microbalance during both modes.

1. Base Measurement

The change in mass of the filter was measured by the microbalance after size selection and passing through the dryer. This provided a mass concentration of PM₁₀.

2. Purge Measurement

A purge filter, chilled to 4 °C, removed particulate matter and low molecular weight organic compounds from the sample stream. This purged air was passed through the microbalance filter and the change in mass of filter measured. This provided in a mass concentration due to evaporative and condensation processes on the filter.

A total PM concentration was calculated as:

$$\text{FDMS mass measurement} = \text{base measurement} - \text{purge measurement}$$

During the purge measurement mode, the mass lost due to the evaporation of volatile PM tended to exceed the mass gained due to any condensation of gaseous material onto the filter. This resulted in a predominately negative purge measurement and therefore increased the FDMS mass measurement above the base measurement.

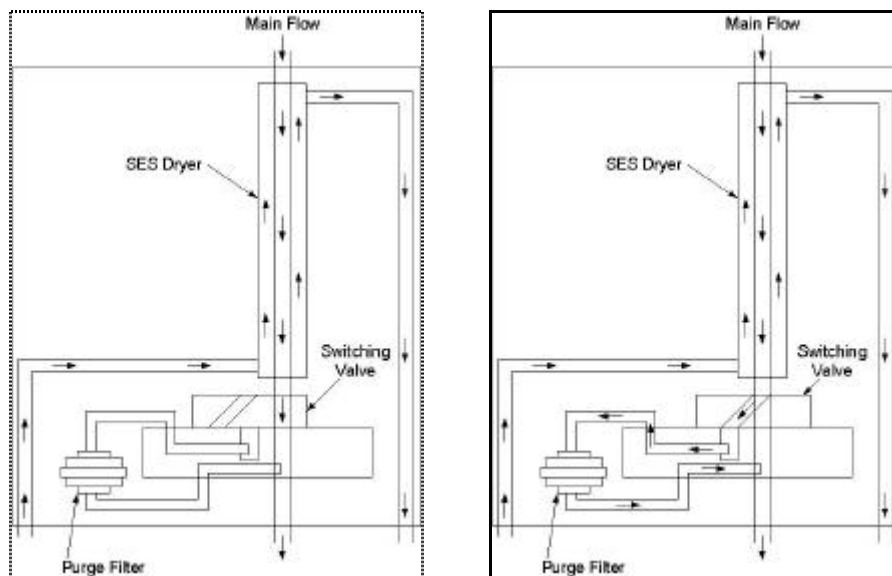


Figure 3: FDMS base measurement mode (left) and purge measurement mode (right) configurations, source (Rupprecht & Patashnick Co., I., 2003)

2.2.3 R & P Partisol 2025

The Partisol 2025 is a sampler system. It has received US EPA certification as a PM₁₀ and PM_{2.5} reference sampler and has proved equivalence under the conditions laid down by CEN (CEN, 1998). The PM₁₀ Partisol 2025 at Marylebone Road is shown in Figure 4.



Figure 4: Partisol 2025 PM₁₀ at Marylebone Road

The Partisol 2025 samplers were operated at default settings and in accordance with the DEFRA operation manual (Maggs, R., 1999). The system utilised the same size selection inlets as the TEOM and therefore flow through the sampling inlet was 16.7 lmin⁻¹. This total flow was passed through a 47 mm quartz fibre filter, which was exchanged automatically at midnight each night. The filters, pre and post exposure, were kept in two canisters, to the left and right of the sampling filter respectively. At midnight sampling was stopped briefly while the filter being exposed was pneumatically shuttled to the top of the canister containing exposed filters. At the same time an unexposed filter was pneumatically shifted into the sampling position and sampling was restarted. To minimise the loss of volatile material from the exposed filters air was pumped through the equipment housing in an attempt to maintain the storage temperature within 5°C of ambient temperature. The efficiency of this mechanism is shown in Figure 5, it is clear that on some days the average difference between the storage and ambient temperature exceeds the 5°C target.

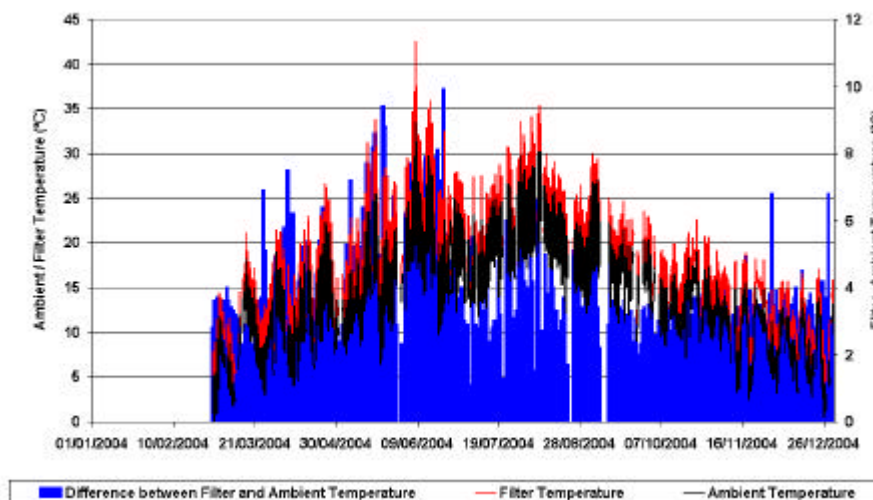


Figure 5: Ambient and temperature at the filter alongside the difference between them from the Partisol 2025 at Marylebone Road during 2004

14 pre-weighed filters were loaded into the instrument every 14 days, in a canister, and unique identifier numbers programmed into the sampler in the order that the filters were to be exposed. The system then operated for 14 days unattended. While the last filter in the Partisol was sampling a new batch of 14 filters were loaded. These filters were collected and the entire canister sent by post to the analysis laboratory: Casella SEAL.

Casella SEAL is an accredited laboratory and analysed the filters (pre and post analysis) in accordance with the criteria laid down by EN12341 (CEN, 1998). Given previous studies demonstrating the equivalence of this instrument and the method used to analyse the filters, the Partisol was considered a reference method, and referred to as such.

The exposure data (flow, sample temperature and meteorological parameters) was downloaded remotely, this was then reconciled with the mass of deposited material measured by the analytical laboratory to provide a mass concentration. This was undertaken by the consultants employed by DEFRA to manage this equipment: Casella Stanger. The mass concentration data was transferred to the ERG SQL database for comparison with other LAQN sites.

2.2.4 R P Nitrate Monitor 8400N

The R&P 8400N is a near real-time particulate nitrate monitor, measuring the inorganic nitrate composition of $PM_{2.5}$. It consists of two instruments: a C3 Pulse Generator and a NO_x Pulse Analyser and is shown alongside the co-located FDMS instruments at Marylebone Road in Figure 6. $PM_{2.5}$ was impacted onto a NiChrome flash strip, which acted as the impaction surface during sample collection. Flashing took place in an N_2 atmosphere and the resulting gas was measured by the Pulse Analyser. The instrument is quoted as having a base line stability of $0.4 \mu m^{-3}$ and a measurement resolution of $0.2 \mu m^{-3}$ (Rupprecht & Patashnick Co., I., 2001).



Figure 6: R&P Nitrate 8400N alongside co-located FDMS instruments at Marylebone Road

The R&P 8400N was operated at default settings, although the cycle time was set to 15 minutes so that it could be directly compared to the TEOM instruments. The sample system had a flow of 5 lmin^{-1} through a rain-capped inlet; this was then split into 1 lmin^{-1} and 4 lmin^{-1} . The higher flow rate acted as a sheath flow, maintaining the lower flow rate and the analysis section of the Pulse Generator close to ambient temperature. This 1 lmin^{-1} flow passed through a $\text{PM}_{2.5}$ sharp cut cyclone to eliminate the coarse particles, an activated charcoal denuder to remove gaseous interferences and a humidifier to maximise collection efficiency by reducing particle bounce. After 15 minutes the collected particles were flash-volatilised in a nitrogen atmosphere by resistive heating of the NiChrome strip. The NO_x Pulse Analyser measured the resulting pulse of NO_x .

The 8400N logged 23 diagnostic and measurement parameters in its cycle data memory. This data was collected on a daily basis using the MONNET data collection system. A member of the ERG Monitoring Team checked the data for faults and continuity with other network sites on a daily basis.

2.3 Quality Assurance

All AURN data was ratified by AEA Technology plc. The LAQN TEOM and FDMS instruments were leak checked and their mass calibration factor was assessed using a pre-weighed filter. All data was ratified in accordance with DEFRA specifications (DEFRA, 2003). The ratification of the R&P 8400N is described in detail in section 2.3.1.

2.3.1 R&P 8400N Data Ratification

No standard procedure exists in the UK for the ratification of the R&P 8400N. The method detailed by Wittig (2004) was therefore used as a basis for ratifying the data from the 8400N. Variations in the response of the NO_x analyser due to changes in the reaction cell pressure are acknowledged but were considered accounted for in the NO_x analyser calibrations.

2.3.1.1 Data Reduction

Some measurements were excluded from the data set produced by the R&P 8400N for the following reasons:

- Site operation, including:
 - Calibration

- Changing consumables such as filters, flash strips and denuders
- Cleaning the rain cap
- Audit
- Service
- Breakdown, including:
 - Dehumidifier breakdown
 - Faulty temperature sensor
 - Flash strip failure
 - Loss of purge gas
 - Power supply failure

2.3.1.2 Variations In NO_x Analyser Response

The response of the NO_x analyser was assessed using a cylinder containing a known amount of NO (5003 ppb until 14th May 2004 and 4730 ppb thereafter) during the instrument nightly audit cycle. Calibration factors derived from this response were applied to all measurements, including blank and calibration responses. Calibration factors were linearly interpolated between calibrations.

2.3.1.3 Instrument Blank Correction

In previous studies in the US (Harrison, D. *et al.*, 2004; Wittig, A. E. *et al.*, 2004) a HEPA filter was used to estimate the instrument blank level, however, no such system was available here. The values from these studies are consistent ($0.235 \pm 0.12 \mu\text{g m}^{-3}$ and $0.18 \pm 0.15 \mu\text{g m}^{-3}$ respectively) and correspond to minimum values in the Marylebone Road data set. An average of these two values ($0.21 \mu\text{g m}^{-3}$) has been used as the instrument blank correction throughout 2004.

2.3.1.4 Average aqueous standard calibrations

Standard potassium nitrate solutions (Aldrich solution ($110\text{ng NO}_3^-/\mu\text{l}$) were pipetted directly onto the NiChrome flash strip according to the manufacturers instructions (Rupprecht & Patashnick Co., I., 2001) to assess the conversion efficiency of the instrument. This necessitated applying three repeat aliquots of solution at a range of volumes to produce a linear calibration range as shown in Figure 7. These calibration measurements were scaled using the results of the NO_x analyser calibrations; the slope provides the conversion efficiency for the instrument. These calibrations proved linear during the first six months of operation ($R^2 \geq 0.95$), the aqueous calibration was consequently reduced to a two-point calibration (de-ionised water and 50 μl) during the final six months of operation.

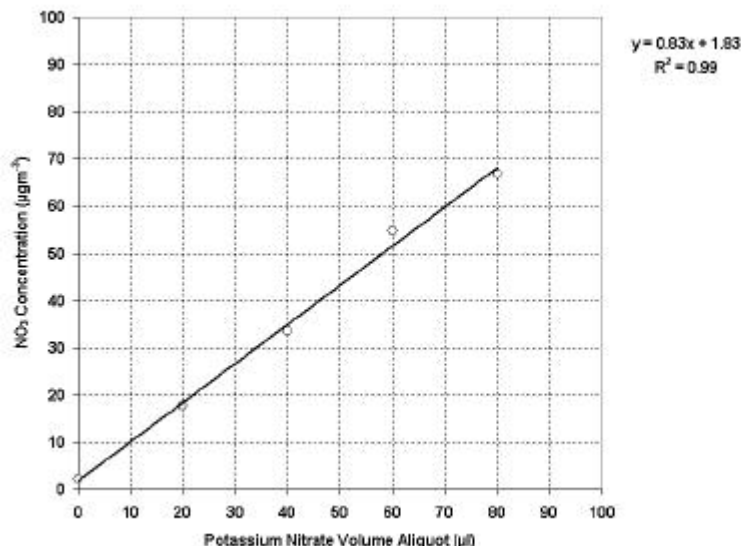


Figure 7: Aqueous calibration of R&P 8400N from 12th May 2004

The slopes of all of the aqueous calibrations are shown in Figure 8, variations in the accuracy of this calibration procedure are expected to be due to the precision of pipetting of the standard solution (Harrison, D. *et al.*, 2004). The conversion efficiency of the instrument is therefore considered to be $90 \pm 20\%$. This is similar to the $90.5 \pm 4\%$ measured by Harrison *et al* (2004) who applied a uniform scaling factor to the entire data set. Wittig *et al* (2004) measured an average converter efficiency of 96% (-38% to +16%) and applied scaling factors averaged over a rolling 30 day period. Given the uncertainties in the pipetting methodology a uniform scaling factor of 1.11 was applied to all the measurements to account for the conversion efficiency.

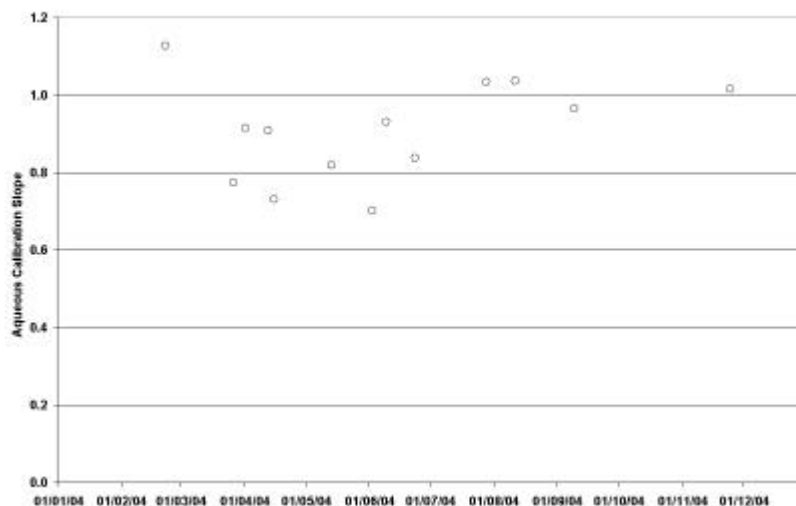


Figure 8: Aqueous calibration results for the R&P 8400N February to December 2004

2.4 Data Pre-processing

To enable a valid comparison between the measurement methods two types of adjustments have been made to the measurements. The first corrects for the inbuilt correction factor in the TEOM. The second corrects for the reporting conditions of the TEOM and FDMS, which default to the US EPA standard of 25 °C and 1 atmosphere pressure. These adjustments are described in sections 2.4.1 and 2.4.2 and will lead to differences between the dataset examined in this report and that disseminated to the public.

2.4.1 The TEOM Inbuilt Correction Factor

The TEOMs in this study operate with the inbuilt correction factor ($\text{TEOM} = 3.0 \mu\text{g m}^{-3} + 1.03 \text{ Raw TEOM}$), consistent with all other TEOM measurements in the UK and Europe. The inbuilt correction factor was included in the TEOM measurement to account for the relative underestimation when compared to the US EPA reference method (Patashnick, H. *et al.*, 1991). The correction factor can confound the comparison between TEOM measurements and those from other instruments and was therefore removed before analysis. This approach has been adopted in previous studies and was found to improve the level of agreement between the different measurement methods (Charron, A. *et al.*, 2003). An example of the effect that removing this inbuilt correction factor has on the comparison between the TEOM and the reference methods at Marylebone Road is shown in Figure 9. The correction factor shifts the intercept by approximately $3 \mu\text{g m}^{-3}$ and increases the gradient of the line of best fit.

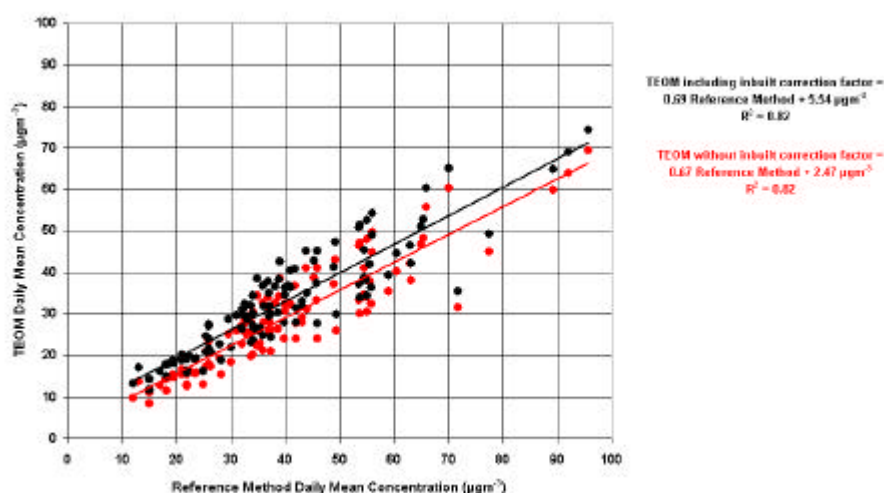


Figure 9: Relationship between TEOM and reference method at Marylebone Road during 2004 with and without inbuilt TEOM correction factor

2.4.2 Reporting to Ambient Temperature and Pressure

The TEOM 1400AB, FDMS and R&P nitrate instruments used active flow control to ensure that the correct volumetric flow was sampled through the instrument using variable mass flow controllers with inputs from ambient pressure and temperature sensors. This ensured that the correct operation of the size selective inlet was achieved in the size selection inlet. Measurements were converted to US EPA STP of 25 °C and 1013 mbar and are routinely publicly disseminated and analysed in this format. However, the reference method measurements (including Partisol 2025) were reported to ambient temperature and pressure (as required by EN12341). To ensure consistency when comparing results between instrumentation, all measurements were converted to a common ambient temperature and pressure using the measurements made by each instrument's ambient pressure and temperature sensors. The effect of this conversion is shown in Figure 10, differences between ambient temperature and the US EPA standard temperature of 25°C drive the discrepancy.

It should be noted that the North Kensington TEOM is a 1400A model, as such it does not benefit from active volumetric control. However, it does correct data to US EPA STP and the data has therefore been treated in the same way as the 1400AB.

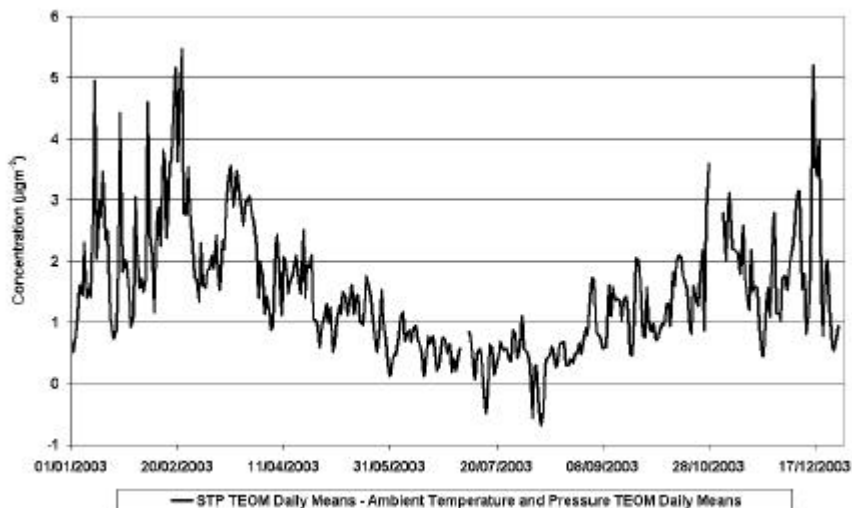


Figure 10: US EPA STP and ambient temperature and pressure correction for TEOM measurements from Marylebone Road during 2003

2.5 Measuring Agreement

In this study two methods of examining the comparability of instrumentation were used, which require some explanation.

2.5.1 Reduced Major Axis (RMA) Regression

Regression analysis was used to demonstrate the relationships between measurements; in particular slopes and intercepts were used to quantify bias between measurements. There is no presumption as to which method is more accurate and therefore no differentiation between the dependent and independent variables. RMA regression analysis has therefore been employed to provide slopes, intercepts and correlation coefficients for these relationships. This analysis accounts for deviations in both x and y variables due to random measurement error (Ayers, G. P., 2000).

2.5.2 Limits of Agreement

Quantifying agreement between the methods is obviously important to this analysis. Many studies use correlation coefficient (R), however, this can be misleading. It does not measure the agreement between instruments, only the strength of the relationship between two variables (Bland, M. J. *et al.*, 1986). This is the case for several reasons:

- True agreement will only occur when the value lies on the line of equality.
- The correlation coefficient takes no account of the scale of the measurement. For instance one measurement could be exactly double the other, having an R value of 1 yet the two measurements would not agree.
- Correlation depends on the range of the sample; a wide range will give a higher R value than a small range.

It is unrealistic to expect one measurement to agree exactly with another. What we want to know is how much one method is likely to differ from another and whether this difference is significant to the interpretation of the measurement. This examination followed several steps:

- Examination of the plot of the measurements against one another for obvious differences.

- Examination of the difference between the methods (X-Y) and the mean difference (d) for obvious relationships between the difference and the mean. If there is a relationship between them a correction can be made by calculating the bias.
- Most of the differences, assuming the distribution is normal, will be within $d \pm 2$ standard deviations (2s). These limits have been termed the 'limits of agreement' (Bland, M. J. *et al.*, 1986). As these limits of agreement are based on 2 standard deviations, approximately 95 % of the measurements will fall within these boundaries and it is therefore a good assessment of the comparability of the instruments.

The limits of agreement described here are neither uncertainty nor precision but contain aspects of both.

3 RESULTS

This study incorporated three types of monitoring equipment at six sites in the LAQN, a map of the site locations was shown in Figure 1, further sites details are in section 6. The start dates of all the relevant measurements made at these sites is shown in Table 1.

Attribute	PM Fraction	Method	North Kensington	Marylebone Road	Millennium Village	Westhorne Avenue	Belvedere	Thames Rd North
Mass	PM ₁₀	FDMS	16/10/03	22/01/04	05/08/04	20/12/04	28/04/04	01/04/04
Mass	PM ₁₀	TEOM	29/03/95	28/05/97			24/01/98	05/04/04
Mass	PM ₁₀	Partisol	28/09/00	03/06/99				
NO ₃ ⁻	PM _{2.5}	R&P 8400N		16/02/04				

Table 1: Summary of measurements available from FDMS equipped sites ordered west to east by location

3.1 Marylebone Road Nitrate Measurements

The first objective of this study was the ratification of the R&P 8400N nitrate measurements made at Marylebone Road. This was carried out as described in section 2.3.1. A time series graph of the daily nitrate concentration is shown in Figure 11, a summary of the measurements made is shown in Table 2. This table also shows the inferred mass of ammonium nitrate, assuming all the nitrate measured is present as it's ammonium salt. These results are calculated from valid hourly means (three fifteen minute means are required to make a valid hourly average). A data capture rate of 77% was achieved, the mean nitrate concentration was 3.0 $\mu\text{g m}^{-3}$; 3.8 $\mu\text{g m}^{-3}$ expressed as ammonium nitrate. The maximum nitrate concentration measured was 17.9 $\mu\text{g m}^{-3}$, 23.1 $\mu\text{g m}^{-3}$ expressed as ammonium nitrate.

Unfortunately, measurements of nitrate are not available from the PM₁₀ sampler operated for DEFRA under a separate contract to allow comparison to allow comparison between continuous and non-continuous methods. Previous comparisons between the R&P 8400N and filter based methods have found that the R&P 8400N underestimates the filter-based method by 17% (Wittig, A. E. *et al.*, 2004).

	Nitrate ($\mu\text{g m}^{-3}$)	Ammonium Nitrate ($\mu\text{g m}^{-3}$) – assuming all NO ₃ is NH ₄ NO ₃
n	5903	-
Data Capture	77%	-
Mean	3.0	3.8
Minimum	0.1	0.1
Maximum	17.9	23.1

Table 2: Summary of R&P8400N hourly nitrate measurements made at Marylebone Road during 2004

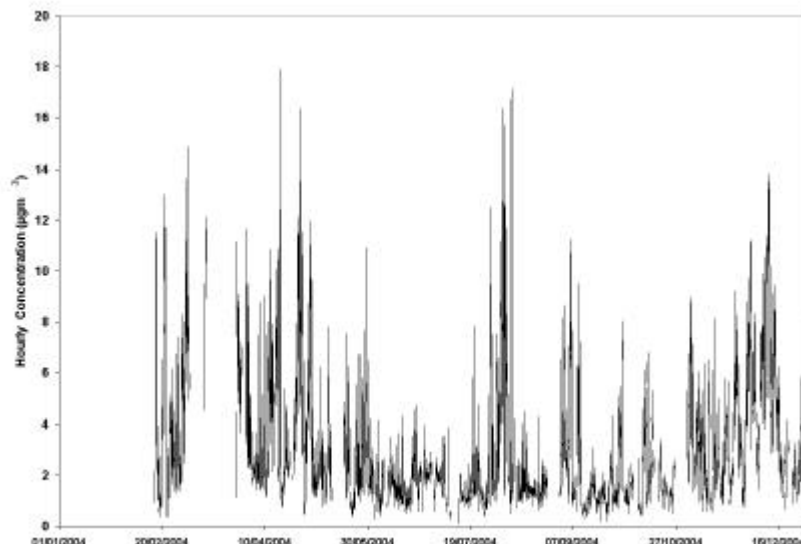
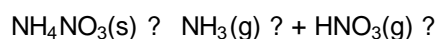


Figure 11: Time series graph of R&P 8400N hourly mean nitrate measurements made at Marylebone Road during 2004

3.2 Comparison of Nitrate Measurements to FDMS Measurements at Marylebone Road

The predecessor to the FDMS, the Differential TEOM, was shown to generate a reasonable assessment of the “true” mass of ambient particulate matter when compared with a Multi-Orifice Uniform-Deposit Impactor (MOUDI) cascade impactor which is not prone to the degree of nitrate loss associated with the reference method (Jaques, P. A. *et al.*, 2004). Further work at the same location found a strong relationship between the mass change during its purge cycle to measurements of nitrate in $PM_{2.5}$ and found that this properly accounts for the levels of vaporisation from the filter (Hering, S. *et al.*, 2004). Additional co-location studies have confirmed that the Differential TEOM measures total $PM_{2.5}$, including semi-volatile particulate matter (Eatough, D. J. *et al.*, 2003; Grover, B. *et al.*, 2004). However, the relationship between nitrate concentration and the FDMS purge measurement (which is similar to the Differential TEOM purge measurement) has not been investigated.

As discussed in section 2.2.1, during the FDMS purge cycle, the purge filter removes particulate matter and low molecular weight organic compounds from the sample stream, allowing air with a zero particulate matter concentration to pass over the filter. The mass changes due to evaporative and condensation processes on the filter are measured as the purge measurement. The dominant process during this cycle is evaporation due to the volatile nature of many of the components of PM (such as ammonium nitrate and organic compounds). The evaporation of ammonium nitrate into nitric acid and ammonia is shown in the equation below. However, positive measurements are also made, indicating that adsorption is occurring during certain conditions.



The FDMS purge measurement, alongside the measurement of the nitrate concentration in $PM_{2.5}$ (expressed as ammonium nitrate) from Marylebone Road, is shown in Figure 12. The relationship between these two measurements is clear from this chart; the purge measurement is negative as it indicates mass lost from the filter. The strength of the relationship is further demonstrated as a correlation in Figure 13, the results of the RMA regression are shown on the chart. The slope of -1.01 and the intercept of 0.09 show that there was a linear relationship between these two metrics, the R value of -0.89 also demonstrated that this relationship was very strong.

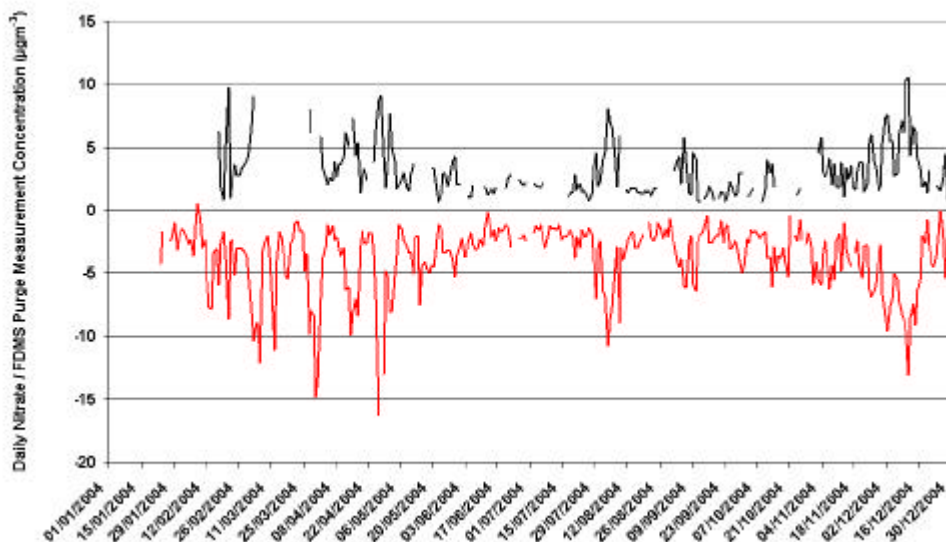


Figure 12: Time series of R&P 8400N daily mean nitrate measurements and daily mean FDMS purge cycle measurements made at Marylebone Road during 2004

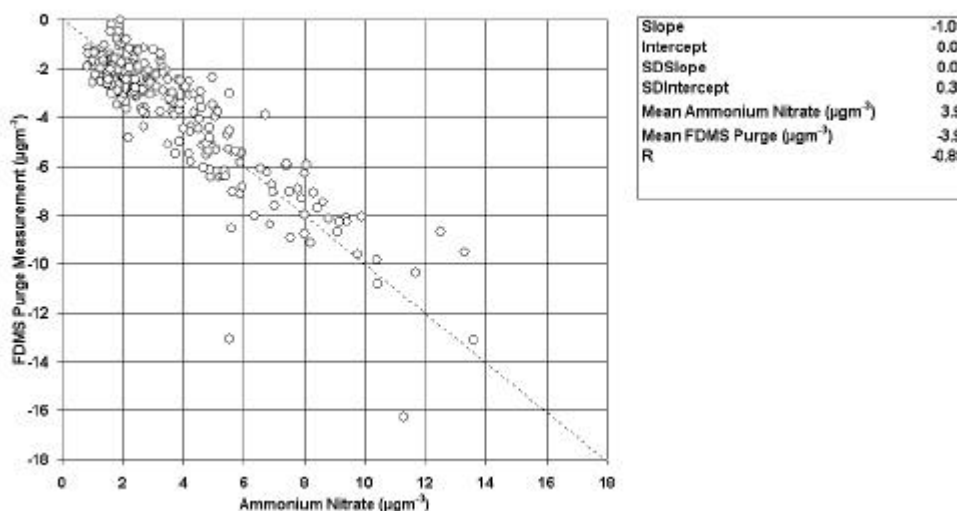


Figure 13: Correlation between daily mean ammonium nitrate in PM_{2.5} and the daily mean FDMS purge measurement made at Marylebone Road during 2004

It would therefore appear that the FDMS instrument purge measurement was approximating the mass of ammonium nitrate in PM_{2.5}. If this were the case then it would imply that there was little volatile material in the coarse fraction (PM₁₀-PM_{2.5}).

Undertaking the Limits of Agreement analysis, as described in section 2.5, quantified the comparability between the daily average concentrations of ammonium nitrate and the FDMS purge measurement (two standard deviations) as $\pm 1.3 \mu\text{gm}^{-3}$.

To investigate whether the agreement between the two metrics is as close as indicated by the correlation of daily means, the diurnal variation of the two measurements was calculated. Figure 14 shows the mean concentrations recorded during each hour of the day during 2004, only hours when measurements were available for both metrics were included in this analysis. This showed that, in general, the responses of the two instruments did not correlate on an hour-by-hour basis. This was supported by previous studies, which showed that the lag time between nitrate concentration measurement and vapourisation was between 40 minutes (at ambient temperatures of 14-15°C) and 100 minutes (at ambient temperatures of 22-23°C). This varied

depending on the main mechanism determining the vaporisation: either the difference in equilibrium vapour pressure or the difference in temperature. Unless the ambient temperature was within a degree or two of the filter temperature the difference in ambient temperature would be the driving force (Hering, S. *et al.*, 2004).

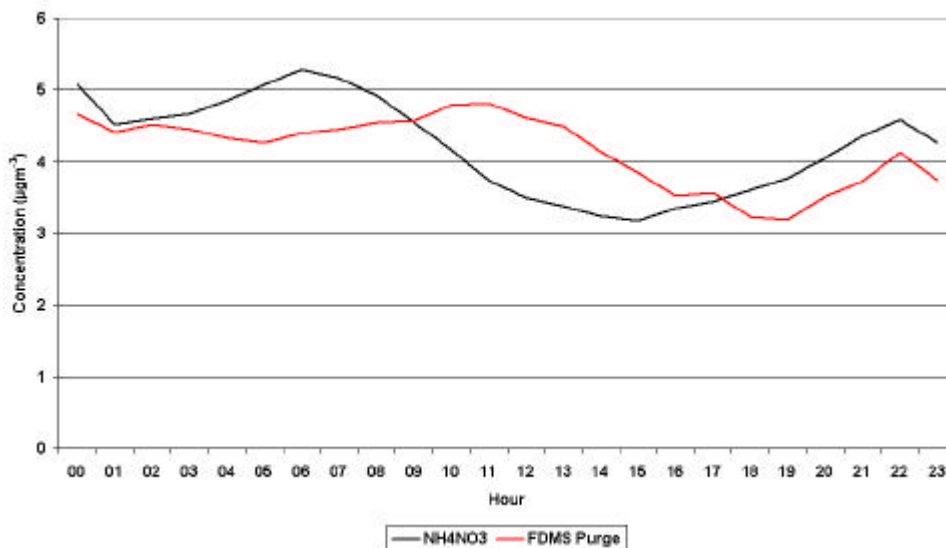


Figure 14: Diurnal variation of ammonium nitrate and the FDMS purge measurement from Marylebone Road during 2004

A lag in peak concentrations between the ammonium nitrate and the FDMS purge measurement of one to two hours could be identified from Figure 15, which shows the hourly concentrations of ammonium nitrate and the FDMS purge measurement during a period of elevated concentrations at Marylebone Road during August 2004.

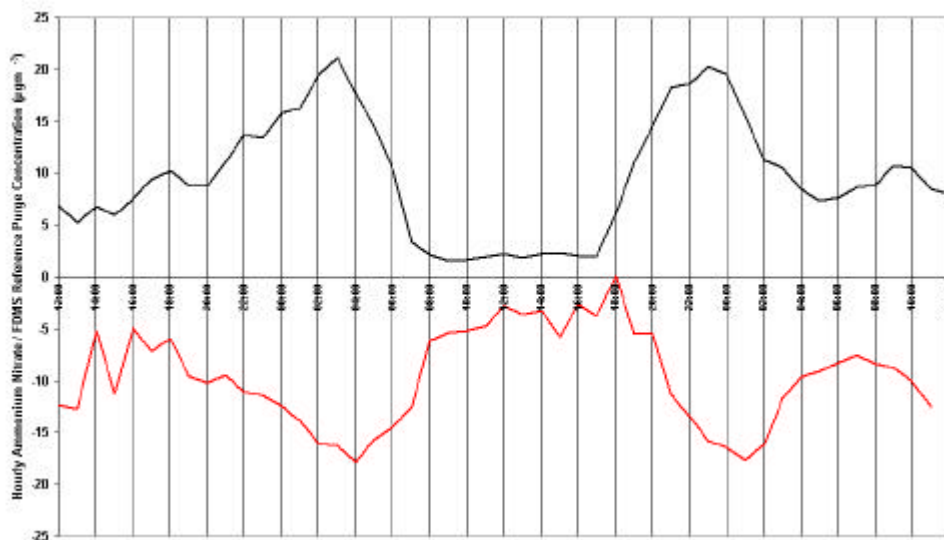


Figure 15: Hourly mean ammonium nitrate and FDMS purge measurement concentrations between 3^d and 5th August 2004 at Marylebone Road

To estimate the lag time between the deposition of the ammonium nitrate on the filter and its subsequent vaporisation for the whole of 2004, the hourly mean ammonium nitrate measurements were correlated against the FDMS purge measurements, time sifted by between 1 and 4 hours backwards. The result of the RMA regression analysis of this data is displayed in Table 3. This shows that the maximum correlation coefficient (R) of -0.82 was achieved with a time shift of two hours, comparable to the 40 – 100 minutes measured by Hering *et al* (2004).

This is obviously a mean value, the time taken for any deposited ammonium nitrate to vaporise from the FDMS filter would depend on the ambient temperature, relative humidity and the concentration of nitric acid in the atmosphere.

	Hourly time-shift of the FDMS purge measurement				
	0	-1	-2	-3	-4
Slope	-1.01	-1.01	-1.01	-1.01	-1.01
Intercept	0.08	0.07	0.07	0.07	0.06
R	-0.76	-0.81	-0.82	-0.81	-0.79

Table 3: RMA regression analysis of time-shifted hourly FDMS purge and ammonium nitrate measurements

3.3 Comparison Between PM₁₀ Measurements

Table 1 shows the PM measurement methods used in the LAQN at the selected sites. This range of instrumentation offered the opportunity to compare these different methodologies, to quantify differences between them and investigate whether the ammonium nitrate measurements could be used to approximate the difference between the TEOM and reference methods as described in previous studies (Allen, G. *et al.*, 1997; Charron, A. *et al.*, 2003). Additionally, having demonstrated that the relationship established between the nitrate measurements and the FDMS purge measurements made at Marylebone Road is linear, whether the FDMS purge measurement could be used to approximate the difference between the TEOM and reference method.

The demonstration of equivalence is not the aim of this study, this is currently being undertaken through a separate DEFRA research programme.

The measurements available to this study are shown in Table 1. The recent introduction of the FDMS instruments at many of the sites has resulted in low data capture for these instruments when examining the whole of 2004. Ideally, only days when data is available from all sites would be included in the analysis to avoid any bias caused by elevated or reduced concentrations measured at one site but not recorded at another. However, omitting data in this manner would result in a large drop in data capture for the more long-running sites. Therefore, to maximise both geographical and temporal coverage as well as data capture, all available measurements were analysed.

When comparing the relationships shown here, it is important to consider the data processing that has been undertaken on the TEOM data: the internal correction factor has been removed and the data has been reported to ambient temperature and pressure as described in section 2.4. The associations derived here should not be compared to previous studies (such as those used to estimate the '1.3 factor') where this pre-processing was not carried out.

3.3.1 Marylebone Road RMA Analysis

During 2004 there were four different instruments measuring PM₁₀ at Marylebone Road: TEOM, FDMS, Partisol and KFG. Due to the prevalence of the Partisol 2025 instruments at other sites within the LAQN, as well as the lower data capture for the KFG sampler (78% compared to 85%), the Partisol was chosen as the reference measurement for comparison purposes.

The results of the RMA regression analysis of the relationships between these instruments are shown in Table 4.

	TEOM PM ₁₀		FDMS PM ₁₀		FDMS Base PM ₁₀	
Partisol PM ₁₀	Slope	0.58	Slope	0.80	Slope	0.64
	Intercept	3.94	Intercept	0.45	Intercept	1.77
	Partisol Mean (µg m ⁻³)	41.41	Partisol Mean (µg m ⁻³)	41.41	Partisol Mean (µg m ⁻³)	41.41
	TEOM Mean (µg m ⁻³)	28.13	FDMS PM ₁₀ Mean (µg m ⁻³)	33.49	FDMS Base Mean (µg m ⁻³)	28.41
	R	0.75	R	0.92	R	0.90
TEOM PM ₁₀			Slope	1.34	Slope	1.08
			Intercept	-4.24	Intercept	-2.10
			TEOM Mean (µg m ⁻³)	28.14	TEOM Mean (µg m ⁻³)	28.14
			FDMS PM ₁₀ Mean (µg m ⁻³)	33.38	FDMS Base Mean (µg m ⁻³)	28.40
			R	0.85	R	0.92
FDMS PM ₁₀					Slope	0.81
					Intercept	1.34
					FDMS PM ₁₀ Mean (µg m ⁻³)	33.38
					FDMS Base Mean (µg m ⁻³)	28.40
					R	0.98

Table 4: Regression Analysis Results from Marylebone Road PM₁₀ Instruments during 2004

The general difference between the different measurement methodologies, which can be summarised as:

$$\text{TEOM} < \text{FDMS Base} < \text{FDMS} < \text{Partisol}$$

3.3.2 North Kensington RMA Analysis

During 2004 there were three different instruments measuring PM₁₀ at North Kensington: TEOM, FDMS and Partisol.

	TEOM PM ₁₀		FDMS PM ₁₀		FDMS Base PM ₁₀	
Partisol PM ₁₀	Slope	0.57	Slope	0.93	Slope	0.70
	Intercept	-0.08	Intercept	-2.09	Intercept	-0.76
	Partisol Mean (µgm ⁻³)	25.64	Partisol Mean (µgm ⁻³)	24.08	Partisol Mean (µgm ⁻³)	24.08
	TEOM Mean (µgm ⁻³)	14.62	FDMS PM ₁₀ Mean (µgm ⁻³)	20.21	FDMS Base Mean (µgm ⁻³)	16.19
	R	0.88	R	0.86	R	0.89
TEOM PM ₁₀			Slope	1.84	Slope	1.38
			Intercept	-5.99	Intercept	-3.43
			TEOM Mean (µgm ⁻³)	14.48	TEOM Mean (µgm ⁻³)	14.48
			FDMS PM ₁₀ Mean (µgm ⁻³)	20.66	FDMS Base Mean (µgm ⁻³)	16.59
			R	0.85	R	0.92
FDMS PM ₁₀					Slope	0.75
					Intercept	0.85
					FDMS PM ₁₀ Mean (µgm ⁻³)	20.57
					FDMS Base Mean (µgm ⁻³)	16.35
					R	0.97

Table 5: Regression Analysis Results from North Kensington PM₁₀ Instruments during 2004

The general difference between the different measurement methodologies, which can be summarised as:

$$\text{TEOM} < \text{FDMS Base} < \text{FDMS} < \text{Partisol}$$

3.3.3 Partisol and FDMS PM₁₀ Measurements

The PM₁₀ concentration that the FDMS reports is made up of the base concentration and the purge concentration, as described in section 2.2.1. The annual mean concentration at Marylebone Road was 33 $\mu\text{g m}^{-3}$, compared to the Partisol mean of 41 $\mu\text{g m}^{-3}$, a difference of 19%. The agreement between the methods was good: a small intercept (0.45 $\mu\text{g m}^{-3}$), a slope of 0.80 and a correlation coefficient of 0.92.

A limits of agreement analysis of the comparability between the Partisol and the FDMS at Marylebone Road is shown in Figure 16. This analysis indicated that the difference between the two instruments occurred throughout the concentration range. However, at higher concentrations the difference between the two instruments exceeded two standard deviations from the mean of the two instruments and reached concentrations as high as 50 $\mu\text{g m}^{-3}$. These large differences in the daily mean contribute to the 19% difference in the annual means measured at this site during 2004.

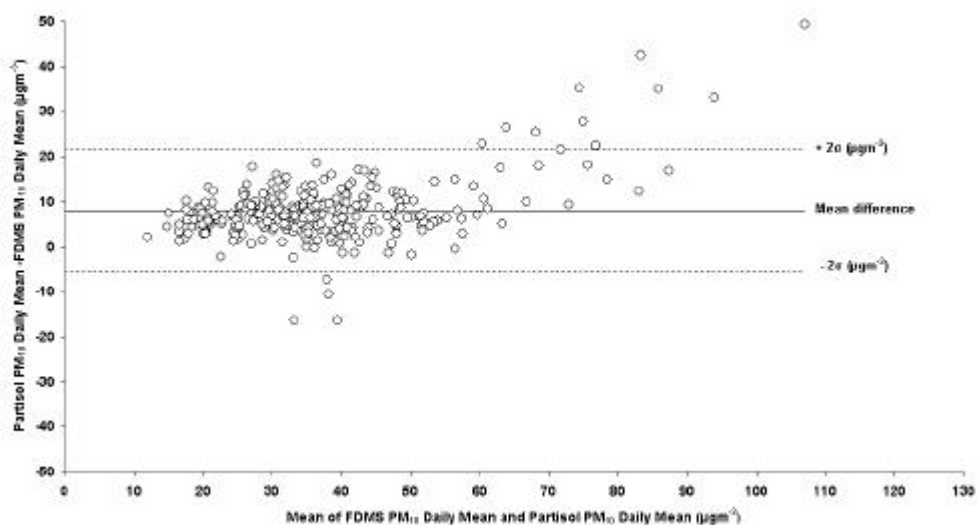


Figure 16: Limits of agreement analysis of daily mean Partisol and FDMS measurements at Marylebone Road

The FDMS PM₁₀ annual mean concentration at North Kensington was 20.2 $\mu\text{g m}^{-3}$, compared to the Partisol mean of 24 $\mu\text{g m}^{-3}$, a difference of 16%. This was close to the 19% difference found at Marylebone Road. The correlation coefficient between the methods as not as good as that produced at Marylebone Road, although the slope of 0.93 was closer to 1.

The differences between the FDMS and Partisol at North Kensington are shown in Figure 17. This demonstrated that there was a better agreement between the two instruments at North Kensington than at Marylebone Road. However, a closer examination of the measurements used in this analysis revealed that, due to instrument faults during the summer and a co-location exercise at Marylebone Road during December, the data capture at North Kensington was lower than at Marylebone Road. Specifically, the North Kensington FDMS was not monitoring during two periods of elevated ammonium nitrate concentrations.

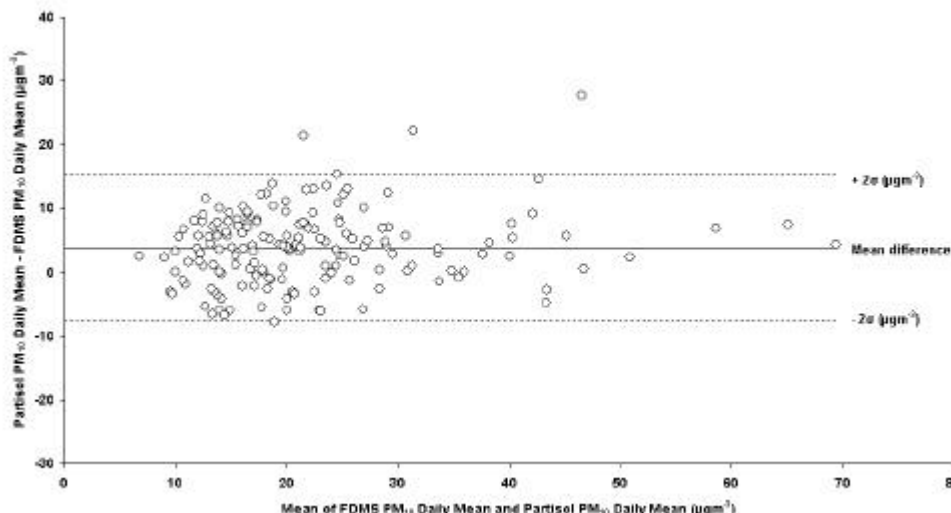


Figure 17: Limits of agreement analysis of daily mean Partisol and FDMS measurements at North Kensington

3.3.4 TEOM PM₁₀ and FDMS Base PM₁₀ Measurement

Four sites in the LAQN measured PM₁₀ using both the TEOM and the FDMS instruments. Two of these are roadside or kerbside sites (Marylebone Road and Westthorne Avenue) and two are background site (North Kensington and Belvedere).

The FDMS base measurement provided a similar annual mean concentration at Marylebone Road to the TEOM (both 28 µgm⁻³). The results of the RMA regression analysis (slope = 1.08, intercept = -2.1 µgm⁻³, R = 0.92) confirmed the strong agreement indicated by the annual mean. The difference between the FDMS base measurement and the TEOM measurement is simply their method of removing water from the sample stream. The TEOM heats the sample to 50°C, while the FDMS dehumidifies the sample using a dryer. It appears that the different drying methodology did not impact on the mass measurement of PM₁₀.

A further examination of the differences between these two measurements at Marylebone Road is shown in Figure 18. This analysis indicated that the difference between the two instruments occurred throughout the concentration range, the instruments could be expected to agree within ±8 µgm⁻³ (2s).

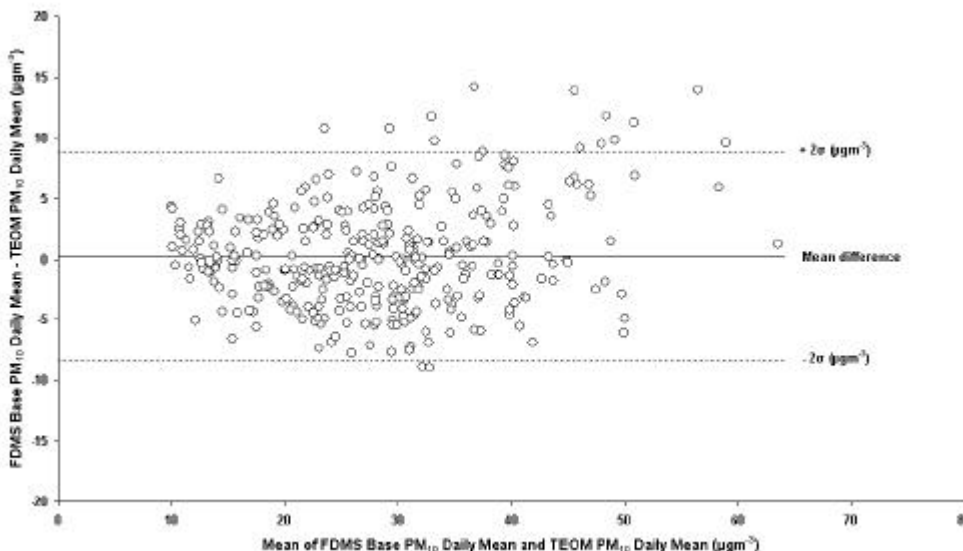


Figure 18: Limits of agreement analysis of daily mean TEOM and FDMS base measurements at Marylebone Road

The annual mean concentrations measured at North Kensington for the TEOM and FDMS base measurement were $14.5 \mu\text{g m}^{-3}$ and $16.6 \mu\text{g m}^{-3}$ respectively. The results of the RMA regression analysis (slope = 1.38, intercept = $-3.43 \mu\text{g m}^{-3}$, $R = 0.92$) indicated that there is a greater difference between the two methods at this site than at Marylebone Road; this is supported by the limits of agreement analysis shown in Figure 19. There is a clear concentration dependence demonstrated, the FDMS base measurement records a higher PM_{10} mass than the TEOM at elevated concentrations. The mean difference and the limits of agreement are skewed leading to a bias of $3.6 \mu\text{g m}^{-3}$, however, the instrument can be expected to agree $\pm 9 \mu\text{g m}^{-3}$ (2s).

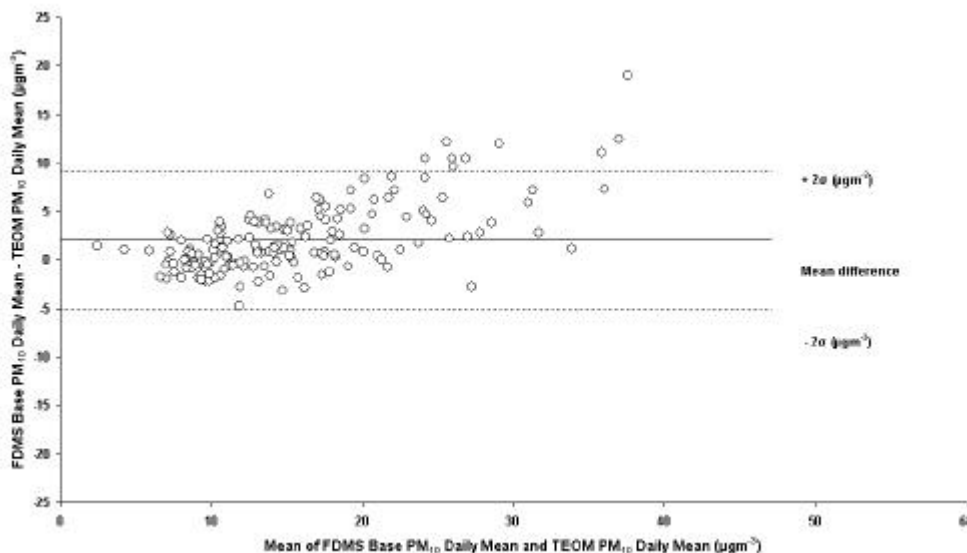


Figure 19: Limits of agreement analysis of daily mean TEOM and FDMS base measurements at North Kensington

Repeating this analysis for the TEOM and FDMS base PM_{10} measurements at the Belvedere monitoring site revealed a similar pattern to that demonstrated at North Kensington, this is shown in Figure 20. The annual mean concentrations measured at Belvedere for the TEOM and FDMS base measurement were $14 \mu\text{g m}^{-3}$ and $18.3 \mu\text{g m}^{-3}$ respectively. The results of the RMA regression analysis were also similar to those found at North Kensington (slope = 1.30, intercept = $0.06 \mu\text{g m}^{-3}$, $R = 0.95$); this is supported by the limits of agreement analysis shown in Figure 19. There is a clear concentration dependence demonstrated, the FDMS base measurement

records a higher PM₁₀ mass than the TEOM at elevated concentrations. The mean difference and the limits of agreement are skewed a bias of 4.2 µg m⁻³, however, the instruments can be expected to agree ±10 µg m⁻³ (2s).

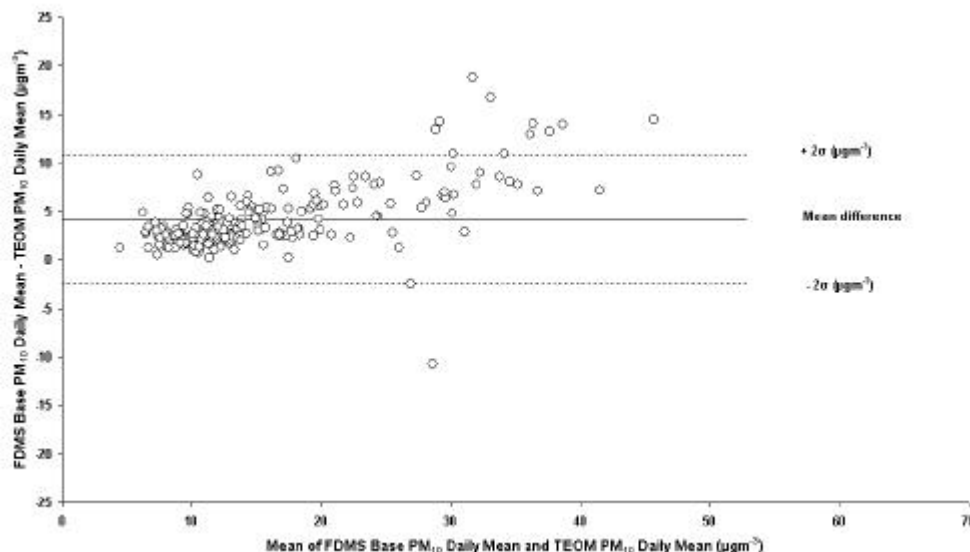


Figure 20: Limits of agreement analysis of daily mean TEOM and FDMS base measurements at Belvedere

The Thames Road North monitoring site is positioned 22 metres from a major road. The annual mean concentrations measured at Thames Road North for the TEOM and FDMS base measurement were both 21.8 µg m⁻³. The results of the RMA regression analysis were slope =0.94, intercept = 1.38 µg m⁻³ and R = 0.93. The limits of agreement analysis shown in Figure 21 demonstrate that there is little bias between the instruments; the instruments can be expected to agree ±9 µg m⁻³ (2s).

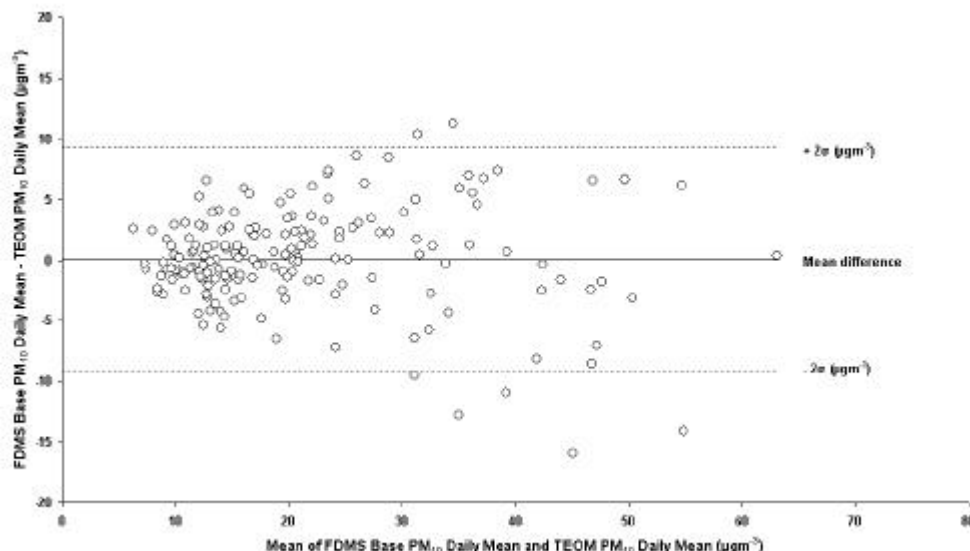


Figure 21: Limits of agreement analysis of daily mean TEOM and FDMS base measurements at Thames Road North

3.3.5 TEOM and Partisol PM₁₀ Measurements

TEOM and Partisol measurements have been compared many times in the UK (Salter, L F. *et al.*, 1999; Green, D. *et al.*, 2001; Charron, A. *et al.*, 2003). Nevertheless, as this study seeks to infer the difference between the TEOM and Partisol using alternative methods, such as the

FDMS purge measurement, an examination of the differences and any influencing factors is necessary.

The annual mean PM₁₀ concentrations measured by the Partisol and the TEOM at Marylebone Road were 41.1 µgm⁻³ and 28.1 µgm⁻³ respectively, a difference of 32%. A previous study, using data that had not been processed as described above found differences in the annual mean of 13% and 18% in 1998 and 1999 respectively (Green, D. *et al.*, 2001). The RMA regression analysis results are the weakest correlation between any of the methods (slope = 0.58, intercept = 3.94 µgm⁻³, R = 0.75). The limits of agreement between the Partisol and the TEOM at Marylebone Road are shown in Figure 22. This analysis indicates that the difference between the two instruments occurs throughout the concentration range. There is a bias of 13 µgm⁻³ between the two instruments, however, at concentrations above approximately 50 µgm⁻³ the difference between the two instruments exceeds two standard deviations and reaches daily mean concentrations as high as 82 µgm⁻³.

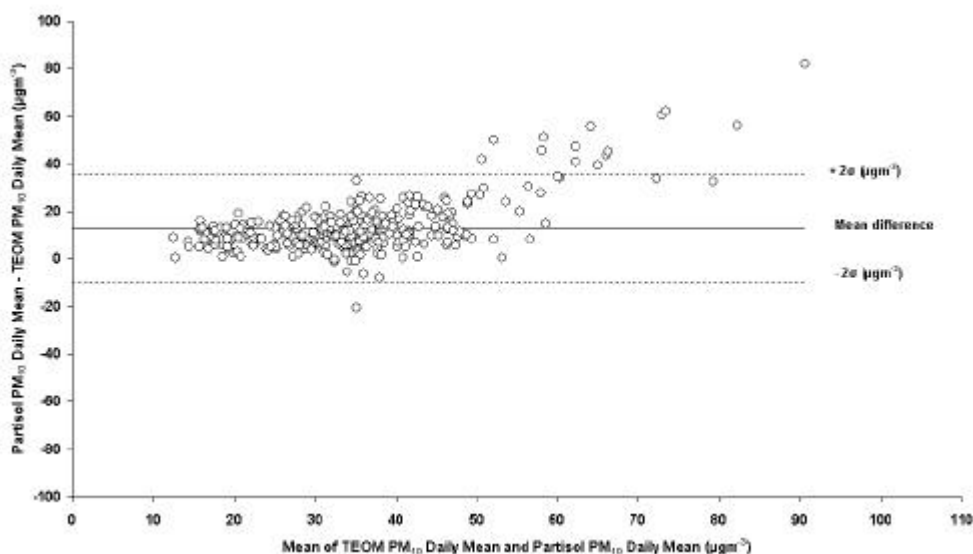


Figure 22: Limits of agreement analysis of daily mean Partisol and TEOM measurements at Marylebone Road

The annual mean PM₁₀ concentration measured by the Partisol and the TEOM at North Kensington were 25.6 µgm⁻³ and 14.6 µgm⁻³ respectively, a difference of 42%. The results of the RMA regression analysis (slope = 0.57, intercept = -0.08, R = 0.88) indicate a better agreement between the two instruments when compared to Marylebone Road. The differences between the Partisol and the TEOM at North Kensington are shown in Figure 23. The bias between the two instruments is 11 µgm⁻³. Maximum daily mean concentration differences reached 43 µgm⁻³.

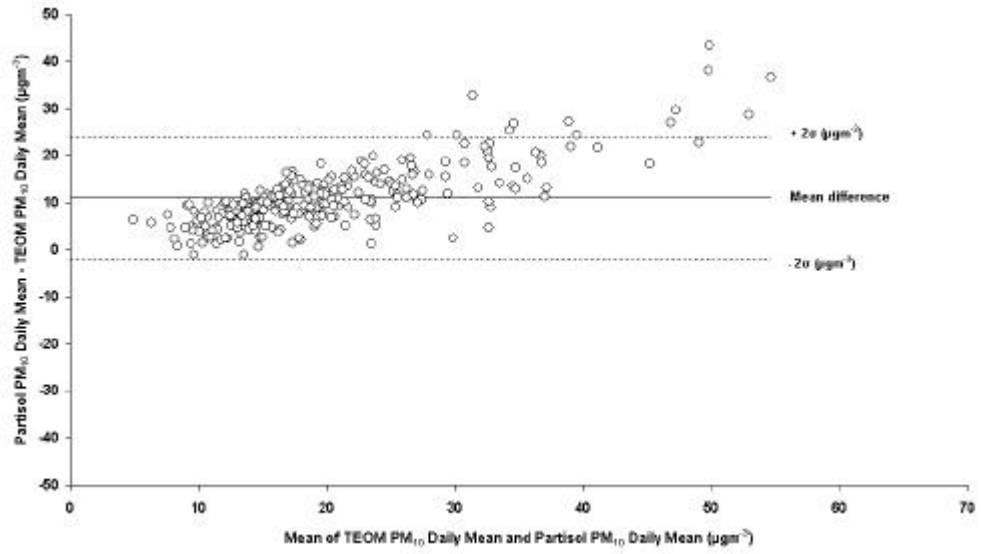


Figure 23: Limits of agreement analysis of daily mean Partisol and TEOM measurements at North Kensington

3.3.6 The relationship between the FDMS Purge Measurements and the difference between the measurements of PM₁₀ made by the Partisol and the TEOM

As discussed, ammonium nitrate was used to account for the differences between the TEOM and the reference method in the US (Allen, G. *et al.*, 1997). When this approach was applied to correct both PM₁₀ and PM_{2.5} measurement by Charron *et al* (2003) in the UK. A similar approach was attempted here, however, the FDMS purge measurement is used as a substitute for the ammonium nitrate measurement made at Marylebone Road. This has been carried out to investigate the potential for the FDMS instruments to be used to correct the more widely used TEOMs for the loss of volatile material.

The difference between the TEOM and Partisol (*i.e.* Partisol Daily Mean PM₁₀ – TEOM Daily Mean PM₁₀) was compared directly to the daily mean FDMS purge concentration at Marylebone Road in Figure 24. Although the relationship was linear, with a correlation coefficient of –0.71, the slope of –0.23 shows that the FDMS purge measurement did not fully account for the difference between the TEOM and the Partisol. Additionally, there are several periods, especially during the summer, where the TEOM measured a higher PM₁₀ concentration than the Partisol. The loss of ammonium nitrate from the TEOM filter, as approximated by the FDMS purge measurement will clearly not account for this.

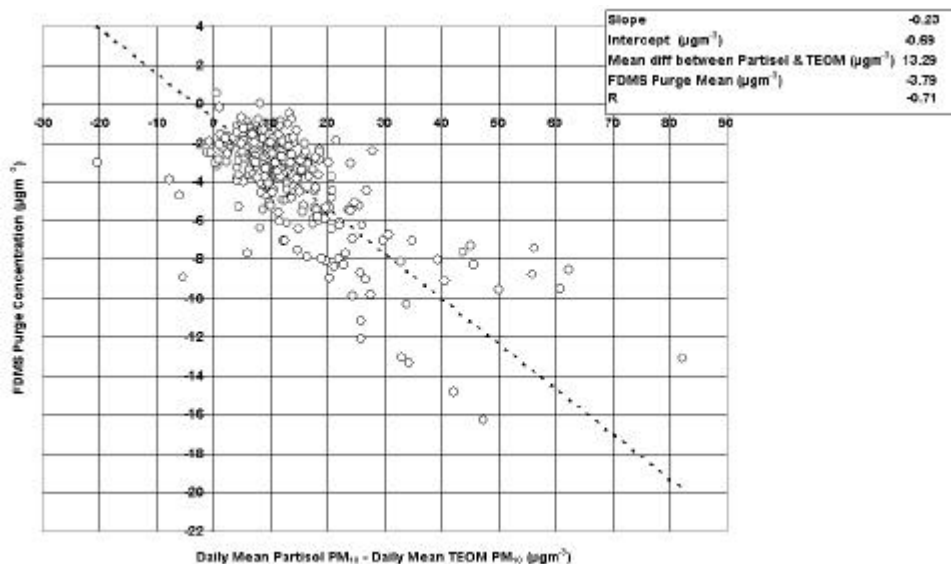


Figure 24: Correlation between Partisol Daily Mean minus TEOM Daily mean and FDMS purge concentration measurements made at Marylebone Road during 2004

The same analysis was undertaken for the instruments at North Kensington. The difference between the TEOM and Partisol (*i.e.* Partisol Daily Mean PM₁₀ – TEOM Daily Mean PM₁₀) was compared directly to the daily mean FDMS purge concentration at North Kensington in Figure 25. Again a linear relationship was clear, especially at the higher concentrations, although the agreement between the two instruments was not as strong as that between the same instruments at Marylebone Road.

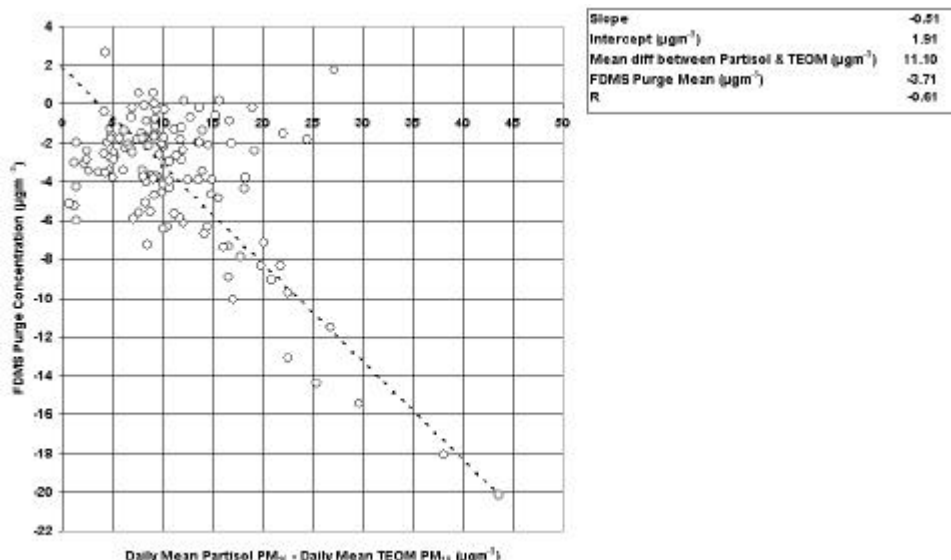


Figure 25: Correlation between Partisol Daily Mean minus TEOM Daily mean and FDMS purge concentration measurements made at North Kensington during 2004

Due to instrument faults during the summer, and a co-location exercise at Marylebone Road during December, the data capture at North Kensington was lower than at Marylebone Road. Specifically, the North Kensington FDMS was not monitoring during two of the periods identified as causing the greatest differences between the measurement methods:

- The elevated ammonium nitrate concentrations, associated with high ambient temperatures that led to the TEOM measuring higher PM_{10} concentrations than the Partisol.
- The elevated ammonium nitrate concentrations measured during a two week period in December.

To investigate the impact of these missing measurements the correlations shown in Figure 24 and Figure 25 were repeated only with data present at both sites, this is shown in Figure 26. After the exclusion of this data, the relationships between the Partisol minus TEOM and the FDMS purge measurement from each site were closer to each other. However, the lack of agreement at lower concentration differences is still present. The slopes of the lines of best fit indicate that the FDMS purge measurement can account for 50% of the difference between the instruments at North Kensington, while only 30% can be accounted for in this way at Marylebone Road. The FDMS purge measurement alone is therefore not an adequate measurement to account for the difference between these instruments. The cause of the difference between the two instruments is evidently more complex.

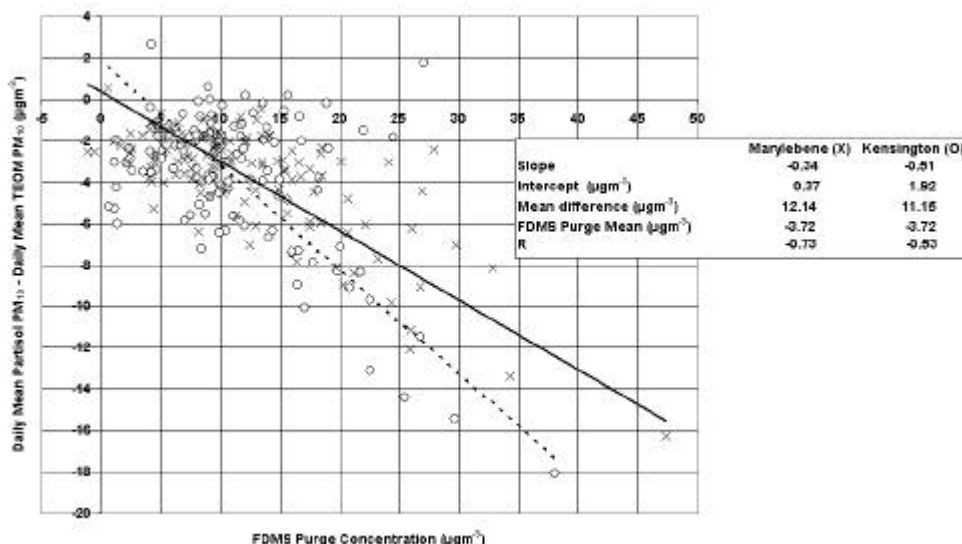


Figure 26: Correlation between Partisol Daily Mean minus TEOM Daily mean and FDMS Purge concentration measurements made on common days at Marylebone Road and North Kensington during 2004

Many factors, including filter media, sampling and weighing conditions, are known to induce measurement artefacts when using gravimetric methods (such as the Partisol) to measure PM_{10} . In particular, environmental conditions (including temperature and relative humidity) have been shown to affect the measurements made using this method (Charron, A. *et al.*, 2003). Figure 27 shows a time series of difference between the TEOM and Partisol at Marylebone Road during 2004 alongside the FDMS purge measurement. For most of the year the difference between the two instruments remains within two standard deviations of the mean difference. However, between 1st and 15th December the Partisol can be seen to record daily mean concentrations far in excess of the TEOM instrument, these are the high concentration differences identified in Figure 22.

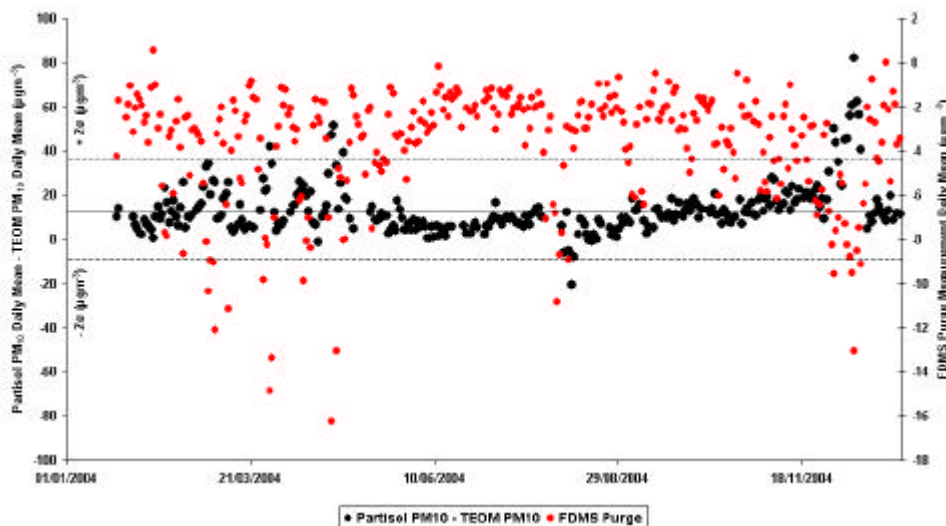


Figure 27: Difference between the Partisol and TEOM measurements as a time series alongside the FDMS purge measurements at Marylebone Road during 2004

Comparing the differences between the instruments to the FDMS purge measurement as shown in Figure 27 allows the identification of three periods during the year when the differences are greatest:

- During February, March and April secondary PM₁₀ is frequently transported from continental Europe on light easterly winds. This leads to elevated PM₁₀ concentrations, most notably during 1996 and 2003. The pattern is repeated here, to a lesser extent, and leads to high FDMS purge measurements.
- Between the 6th and 10th August 2004, the TEOM instrument recorded PM₁₀ concentrations higher than those measured by the Partisol. Figure 27 shows that this period was also characterised by elevated FDMS purge measurements and, as demonstrated in section 3.2, elevated ammonium nitrate concentrations.
- The high concentration differences during December coincided with a period of elevated FDMS purge concentrations. The FDMS purge concentrations measured during this period were amongst the highest recorded, however, similar measurements during February, March and April did not lead to the large differences between the instruments experienced during December.

The pattern of collection and subsequent evaporation of volatile material from the Partisol filter compared to the TEOM will be a function of the varying ambient concentration of PM as well as gaseous components and the temperature and relative humidity that this deposit experienced during and after collection. This relationship will be complex, requiring a more detailed modelling approach, similar to that undertaken by Hering *et al* (2004).

It should be noted that there are likely to be other influences on the mass measured by the Partisol. The effect of water retained due to the hysteresis effect of some particles has been demonstrated in the UK (Price, M. *et al.*, 2003). The adsorption of organic compounds onto quartz fibres has also been shown to affect mass estimates of PM₁₀ (Kirchstetter, T. W. *et al.*, 2001).

3.4 Assessing of the differences in volatile PM concentration in London using measurements from the six FDMS instruments.

FDMS instruments are currently monitoring at six locations in London, these are shown in Figure 1 and described fully in section 2.1. As described in section 3.2, the FDMS purge measurement has a strong relationship to the ammonium nitrate concentration in PM_{2.5} measured at Marylebone Road. The analysis undertaken in section 3.3 showed that the FDMS purge measurement could partly, but not entirely, account for the differences between the measurements of PM₁₀ made by the TEOM and the Partisol at either Marylebone Road or North Kensington due to volatile organic compounds, particle bound water or ambient temperature effects on the instrumentation. Nevertheless, information regarding the variability of the FDMS purge measurement on a regional scale may be informative should a correction factor based on the FDMS purge measurement (or ammonium nitrate measurements) be desired.

Table 6 shows the mean concentrations for all the FDMS sites in the LAQN. With the exception of Westthorne Avenue, which had a start date of 20th December 2004, the mean concentrations do not vary by more than 0.6 µgm⁻³ from the network mean (excluding Westthorne Avenue). The FDMS purge measurement can therefore be considered uniform over the London area for long term averages.

Site	Mean Concentration ($\mu\text{g m}^{-3}$)
Marylebone Road	-3.7
North Kensington	-4.2
Millennium Village	-3.3
Westthorne Avenue	-1.5
Belvedere	-3.1
Thames Road North	-3.6
Network Mean (ex Westthorne Avenue)	-3.6

Table 6: Mean concentrations of the FDMS purge measurements during 2004

Figure 28 shows the time series of FDMS purge measurements made in the LAQN during 2004, it is clear that the measurements did not vary substantially between sites.

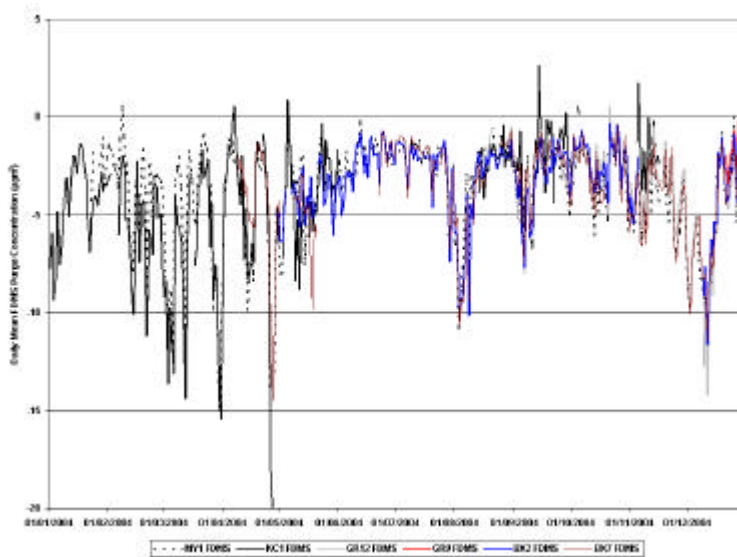


Figure 28: Time series plot of FDMS purge measurements made in the LAQN during 2004

To quantify the variation between individual sites, the daily mean FDMS purge measurement from each was compared to an independent network mean, calculated from all sites except the site being analysed. The results of this analysis are shown in Figure 29 alongside the number of sites in the network. This illustrates that an individual site could vary from the network mean by as much as $6 \mu\text{g m}^{-3}$ on an individual day. However, it is clear that the agreement between any one site and the annual mean of the other sites was much better than this. The standard deviations of the measurements from the network mean can be examined to quantify this day-to-day variability. These standard deviations are shown in Table 7, these range from $0.6 \mu\text{g m}^{-3}$ to $1.7 \mu\text{g m}^{-3}$ with a network average of $0.9 \mu\text{g m}^{-3}$. Assuming a normal distribution, two standard deviations would represent a 95% confidence interval. Therefore, any daily mean FDMS purge measurement could be expected to agree with another instrument $\pm 1.8 \mu\text{g m}^{-3}$.

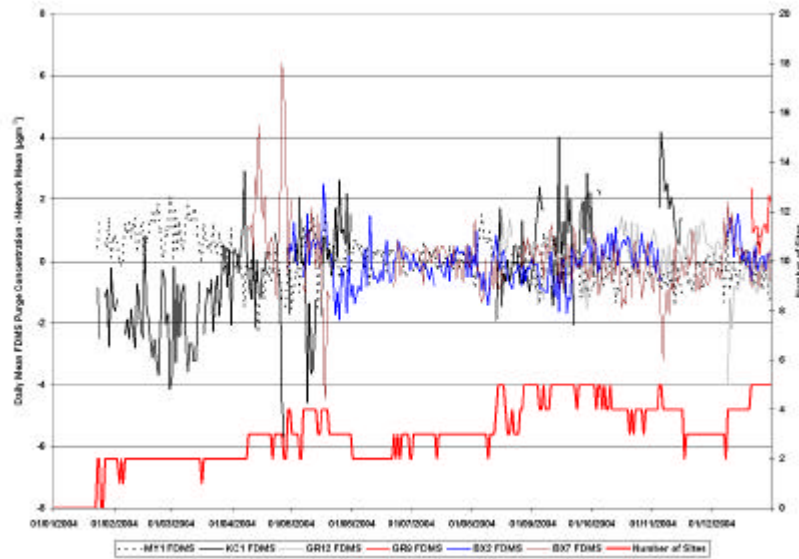


Figure 29: Time series plot of FDMS purge measurement variation from a network mean during 2004

Site	Standard Deviation (μgm^{-3})
Marylebone Road	0.7
North Kensington	1.7
Millennium Village	0.8
Westthorne Avenue	0.6
Belvedere	0.7
Thames Road North	1.1
Network Average	0.9

Table 7: Standard deviations of the difference between FDMS purge measurement and a network mean

4 CONCLUSIONS

The wide range of PM monitoring equipment at Marylebone Road and North Kensington (as well as sites in Bexley) allowed comparisons to be made between the measurements methods. At all these sites, the PM₁₀ mass measurements made using the different instruments followed the mass hierarchy below:

$$\text{TEOM PM} < \text{FDMS Base} < \text{FDMS} < \text{Partisol}$$

Comparisons between individual instruments showed that the FDMS does not measure PM₁₀ concentrations equivalent to the Partisol. However, whether these differences are due to measurement artefacts in the reference method (Partisol) or in the FDMS is unclear.

The FDMS base measurement (a component measurement of the FDMS) showed an inconsistent agreement with the standard TEOM mass measurements. The FDMS base measurement is made on a dehumidified sample at 30°C compared to the 50°C of the standard TEOM and is therefore seen as analogous. The 2004 annual mean concentrations for both instruments were identical at Marylebone Road and Thames Road North. However, the annual mean FDMS base concentrations at North Kensington and Belvedere are higher than the TEOM, by 3.6 µg m⁻³ and 4.2 µg m⁻³ respectively. The relationship between these two measurements requires further investigation.

Comparing the measurements made by the R&P 8400N, expressed as ammonium nitrate, with the FDMS PM₁₀ purge measurement produced a slope of -1.01, a negligible intercept and a correlation coefficient of -0.89. This showed that the FDMS purge measurement is a good surrogate for the concentration of ammonium nitrate in PM_{2.5}.

It was hypothesised that the FDMS purge measurements, as a surrogate for ammonium nitrate concentration could be utilised to correct for the difference between the TEOM and the Partisol measurements. In previous studies the measured ammonium nitrate concentration was added back to the TEOM mass concentration, providing a better estimate of the PM mass as measured by the reference method. This approach was modified in this study to use the FDMS purge measurement as a surrogate for ammonium nitrate concentration. The FDMS purge measurement was subtracted from the TEOM PM₁₀ mass measurement (the FDMS purge measurement is generally a negative number). The linear relationship shown by the correlation between the two metrics (TEOM - FDMS purge) vs Partisol was encouraging, nevertheless, the FDMS purge measurement, and by implication the ammonium nitrate concentration in PM_{2.5}, did not account for the difference between these instruments alone. This is consistent with previous studies in the UK.

A further investigation of why the FDMS purge measurement does not account for more of the mass measured by the Partisol showed that the greatest differences between the Partisol and TEOM were associated with high FDMS purge measurement concentrations, as indicated by the linear correlation. These differences were clustered during three periods:

- During spring, the Partisol measured PM₁₀ concentrations above those of the TEOM, these periods were characterised by high ammonium nitrate concentrations and light easterly winds.
- During a few days in August the TEOM measured PM₁₀ concentrations above those of the Partisol. These days were typified by high ammonium nitrate concentrations and high ambient temperatures. It is likely that the ammonium nitrate and other volatile components deposited on the Partisol were subsequently evaporated by the high ambient temperatures, whereas, temperatures on the TEOM filter were not high enough to evaporate the volatile material to the same degree before the measurement was made.
- The Partisol measured PM₁₀ concentrations substantially above those of the TEOM during a two week period in December. This period was characterised by high ammonium nitrate concentrations and low ambient temperatures. The

differences between the two instruments during this period were greater than those experienced during spring, despite lower ammonium nitrate concentrations. The cause of these differences are:

- The inability of the TEOM to sample ammonium nitrate efficiency due to the 50°C sample temperature. The difference between the TEOM and the Partisol sampling temperatures was greater during the winter period, therefore, the proportion of ammonium nitrate lost will be greater.
- The limitations of the equilibration conditions of the Partisol filters when overcoming the effects of hysteresis, which would lead to water remaining bound to the PM.
- The adsorption of organic gases onto the Partisol filters.

In summary, the FDMS improves our understanding of PM and its components. Specifically, the FDMS PM₁₀ purge measurement was found to agree very well with measurements of ammonium nitrate mass in PM_{2.5}. The comparisons between the measurements provided by the FDMS and other instruments have highlighted the difficulty in measuring PM and its volatile components. Nevertheless, the FDMS did not measure mass concentrations equivalent those reported by the Partisol. However, further work is needed to improve the reference method to eliminate the effects of particle bound water, the adsorption of organic gases and the volatilisation of ammonium nitrate and other semi-volatile components, during and after collection.

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London Borough of Bexley

London Borough of Greenwich

Royal Borough of Kensington and Chelsea

Westminster City Council

6 SITE LOCATIONS

Details of all the sites used in this study are shown in the following sections.

6.1.1 Marylebone Road

Marylebone Road is a kerbside monitoring site in central London shown in Figure 30, grid reference 528120 182000, and is affiliated to the AURN. Marylebone Road is a major route in and out of Central London, running north-east to south-west and carries approximately 90,000 vehicles per day. The tall buildings on either side form a broad street canyon and 40m across. The monitoring cabin is located 1m from the kerb on the southern side of the road.



Figure 30: Marylebone Road site picture and location

6.1.2 North Kensington

North Kensington is an urban background monitoring site to the north and west of central London shown in Figure 31, grid reference 524040 181740, and is affiliated to the AURN.

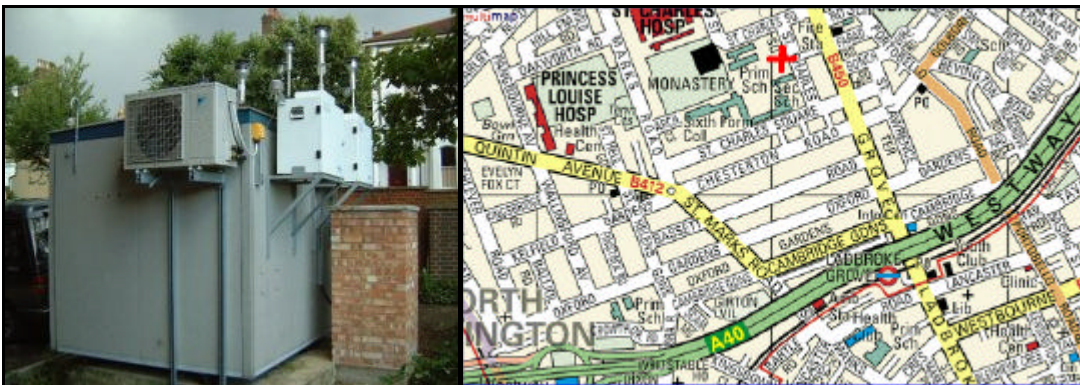


Figure 31: North Kensington site picture and location

6.1.3 Millennium Village

Millennium Village is an urban background monitoring site to the south east of London shown in Figure 32, grid reference 540175 179000.

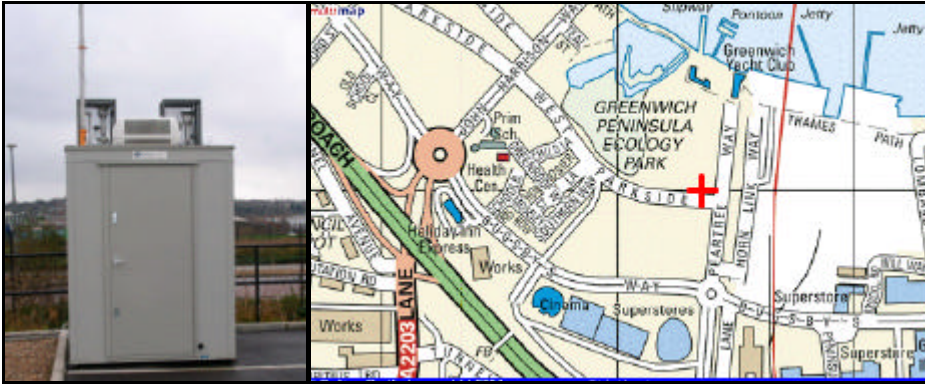


Figure 32: Millennium Village site picture and location

6.1.4 Westthorne Avenue

Westthorne Avenue is a roadside monitoring site to the south east of London shown in Figure 33, grid reference 541883 175016.



Figure 33: Westthorne Avenue site picture and location

6.1.5 Belvedere

Belvedere is a suburban monitoring site to the south east of London shown in Figure 34, grid reference 550000 179070.

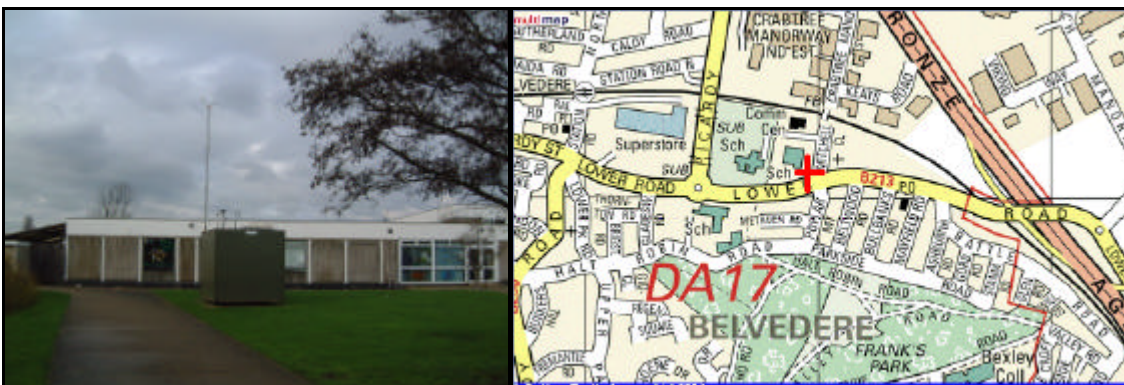


Figure 34: Belvedere site picture and location

6.1.6 Thames Road North

Thames Road North is a roadside monitoring site to the south east of London shown in Figure 35, grid reference 551862 176380. This site has been installed to monitor the changing pollution

concentrations that result from the forthcoming conversion of the close by road to a dual carriageway.



Figure 35: Thames Road North site picture and location

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