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CPEA 28: Airborne Particulate Concentrations and Numbers in the United Kingdom (phase 2)

Annual Report - 2008

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Annual Report for 2008 on the UK Airborne Particulate Concentrations and Numbers Network

Executive Summary

This report was prepared by NPL as part of the UK Airborne Particulate Concentrations and Numbers contract (CPEA 28) let by the Department for the Environment, Food and Rural Affairs and the Devolved Administrations: the Scottish Executive; the Welsh Assembly Government; and the Department of the Environment in Northern Ireland. This is the Annual Summary Report for 2008 and contains:

- A summary of network operation and quality procedures
- A graphical presentation of all ratified network data from 2008
- Data capture per instrument per month
- Comparison of 2008 particle numbers and concentrations of sulphate, nitrate and carbon with levels in recent years.
- Update on relevant policy areas
- Update of the context of the project research and of equipment in the field

All equipment was audited during the annual audit round in December, and all instruments have been serviced and calibrated by the instrument manufacturer or Equipment Service Unit. Data capture was high, at a similar level to previous years, although some of the older instruments are starting to see a slight decline in reliability and, therefore, data capture.

In addition to the measurement programme, short-term research projects have been commissioned on specific topics related to the measurement programme. The measurements have been and are being used by the University of Birmingham to gain further understanding of particulate matter, its sources, composition and possible control options. King's College London is currently extending its volatile correction model and assessing methods to determine the oxidative potential of ambient samples. These research projects are reported through separate Topic Reports and are not discussed further here. A list of the completed Topic Reports is however given.

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1 Introduction

This report was prepared by NPL as part of the UK Airborne Particulate Concentrations and Numbers contract (CPEA 28) with the Department for the Environment, Food and Rural Affairs and the Devolved Administrations: the Scottish Executive; the Welsh Assembly Government; and the Department of the Environment in Northern Ireland.

This is the Annual Summary Report for the UK Airborne Particulate Concentrations and Numbers Network for 2008 and contains:

- Summary of network operation and quality procedures
- Data capture per instrument per month
- Graphical presentation of all validated and ratified network data from 2008
- Comparison of 2008 particle numbers and concentrations of sulphate, nitrate and carbon with levels in recent years
- Policy update on relevant areas
- Update of context of this project research and inventory of equipment in the field
- Network-related publications

In addition to the measurement programme, short-term research projects have been commissioned on specific topics. The measurements have been and are being used by the University of Birmingham to gain further understanding of particulate matter, its sources and possible control options. King's College London are currently extending its volatile correction model and assessing methods to determine the oxidative potential of ambient samples. These research projects are reported through separate Topic Reports and are not discussed further in this report. A list of the completed Topic Reports is however given.

2 Network Operation

2.1 Overview

The operation of the network in 2008 was structured in the same way as the previous year. King's College London (KCL) has continued in its role as the Central Management and Control Unit (CMCU). It has carried out activities including routine collection of data from sites, initial data validation and instrument fault finding, routine liaison with the Local Site Operators (LSO) and the Equipment Support Unit (ESU). The QA/QC activities were performed by NPL and included site audits, instrument calibrations, inter-laboratory performance schemes and data ratification.

In January 2009, NPL's contract with Defra to operate this network was extended by one year.

Network Structure

The current measurement programme is shown below:

Table 2-1: Network Structure

Site	Hourly $PM_{2.5}$ nitrate	Daily PM_{10} anions	Daily PM_{10} OC/EC	CPC	SMPS
Birmingham Centre (Urban centre)				x	
Harwell (Rural)	x	x	x	x	x
North Kensington (Urban background)	x	x	x	x	x
Marylebone Road (Roadside)	x	x	x	x	x

Windspeed and direction are reported for Harwell and Rochester.

2.3 Instrumentation

A list of network instruments can be found in Annex 1. A brief summary of the operation of each instrument is given here. More detailed descriptions of the theory of operation, calibration and the estimated uncertainty in the results are included in the NPL measurement uncertainty report [NPL, 2007a].

2.3.1 Particle Counting and Sizing Analysers

These instruments operate on the principle of passing the sample through clean air supersaturated with butanol, causing a butanol droplet to form around each particle so that they can be counted optically. In a CPC, total number concentrations of particles in the size range from ~7nm to several microns are determined in this way, either by individual number counting (at low concentrations) or using an optical integrating method (at high concentrations). In the case of an SMPS, the sample entering the CPC has passed through air ionised by a radioactive device (based on Krypton-85) that gives an electric charge to a known fraction of the particles, and then through a controlled electrical potential that separates the charged particles according to their electrical mobility.

2.3.2 Automated Nitrate Analyser ($PM_{2.5}$)

Ambient samples are pulled through a cyclone operated at 5.5 L/min to remove particles above 2.5 µm. Particles are collected by humidification and impaction, and assayed in place by flash heating and chemiluminescent analysis of the evolved nitrogen oxide vapors.

2.3.3 Inorganic Anions (Sulphate, Nitrate and Chloride) (PM_{10})

Daily measurements of the inorganic components of PM_{10} (sulphate, nitrate and chloride) were made using a Thermo Partisol 2025 sequential air sampler. Ultrapure quartz filters have been used to allow for the analysis of EC/OC and the inorganic components.

The partisol sampler provides uninterrupted sampling of ambient air and automatic exchange of filters for up to 16 days. The instrument used an airflow of 16.7 litres per minute through a PM_{10} inlet and the filter temperature was maintained to within ± 5 °C of ambient temperature. The exposed filters were stored in small polypropylene filter bags and kept in a cold room until analysis to prevent further loss of volatile components. Extracts from the filters were dissolved in an eluent of 3.5 mM sodium carbonate and 1 mM sodium hydrogen carbonate and analysed in the laboratory by ion chromatography, for sulphate, nitrate and chloride content. Ambient concentrations were derived from the mass measured on the filter and the airflow during the sampling period.

2.3.4 Elemental and Organic Carbon (PM_{10})

In the laboratory, a punch is taken from each filter and analysed for elemental and organic carbon in a procedure in which the measurand is method-defined. It involves heating the sample to remove the PM from the filter, conversion to methane, followed by detection by flame ionisation. In a helium atmosphere, the sample is gradually heated to 700°C to remove organic carbon on the filter. During this first phase there are usually some organic compounds that are pyrolitically converted to elemental carbon. Measuring the transmission of a laser beam through the filter continuously monitors this pyrolitic conversion and allows a correction to be made for it. Elemental carbon is detected in the same way after heating to 870°C in the presence of oxygen and helium.

3 Data Quality

A summary of the principal quality-assurance and quality-control procedures used during the measurement and ratification process is given below:

- Continued training of, and regular communication with, Local Site Operators (LSOs).
- The KCL Duty Officer is available to advise LSOs 365 days per year.
- Scheduled instrument services and calibrations are ongoing.
- An annual audit of all sites and instruments has been conducted by NPL.
- Calibration data produced at audit by the ESU, and regular calibrations carried out automatically or by the LSOs, are all used to produce an appropriate scaling factor to apply to the data.
- Routine maintenance is carried out on all instruments according to manufacturers' instructions.
- The Thermo 8400N nitrate analysers is calibrated with NO, which is certified at NPL and traceable to primary standards.
- The Equipment Support Unit (ESU) is contracted to respond to breakdowns within 48 hours.
- Data collection is automated by the MONNET system at KCL.
- Automatic and manual data validation is followed by rigorous ratification procedures.
- Research into particulate mass, chemical composition and speciation continues at NPL under the Department for Innovation, Universities and Skills' Chem-Bio Programme.

Data quality circle meetings are held at least annually to review the data. This may lead to tracking back through the measurements and analytical procedures to confirm the validity of specific measurements. Other measurements made in this monitoring programme and in other Defra monitoring programmes will also be used to check the validity of the measurements. For example, a high concentration of a PM component can be compared with available total PM mass measurements to check for consistency.

3.1 Scheduled Instrument Services and Calibrations

The automatic nitrate and the Partisols are serviced twice yearly by the ESU, Air Monitors. The service procedure includes replacing old or worn parts, calibration of the NOx analyser, temperature and flow calibrations, leak tests and pump refurbishment. The services completed during 2008 are indicated in Table 3-1:

Table 3-1: Equipment Services completed during 2008 for Partisol and Nitrate Analysers

Site	Instruments	Service 1	Service 2
Harwell	Partisol	30/08/08	18/11/08
	Nitrate	30/08/08	18/11/08
Marylebone Road	Partisol	31/01/08	24/10/08
	Nitrate	31/01/08	24/10/08
North Kensington	Partisol	03/06/08	----
	Nitrate	03/06/08	----

Since June 2005, CPCs have been serviced and calibrated annually, as recommended by the manufacturer (TSI Instruments) and detailed in Table 3-2. The instrument response is measured before and after the service to allow data to be corrected during ratification. Since January 2009, the CPCs have been serviced and calibrated by NPL. NPL received ISO 17025 accreditation for this calibration in 2008. For the CPC instrument at Marylebone Road site, only an 'as found' calibration service has been carried out.

Table 3-2: Annual CPC Service and Calibration Dates

Site	05/06 service	06/07 service	07/08 service	09 service
Birmingham	21/07/05	11/08/06	18/10/07	03/03/09
North Kensington	24/04/06	26/03/07	09/04/08	24/03/09
Marylebone Road	15/09/05	17/10/06	15/11/07	30/01/09(*)
Harwell	-	-	08/01/08	04/03/09

(*) Only 'as found' calibration

4 Network data

4.1 Instrument Performance And Concentration Data

The following sections discuss the different measurements made in the monitoring programme. The concentration data is also presented in a graphical format and unusual or interesting occurrences are noted and discussed. There is a monthly breakdown of data capture at each site along with reasons for data loss.

Full, ratified data from 2008 will be provided to Defra's Air Quality Information Archive and will be used to form the basis of future topic reports, produced in collaboration with the University of Birmingham.

4.2 Inorganic Anions

4.2.1 Partisol 2025 Measurements (PM_{10})

Daily measurements of particulate sulphate, nitrate and chloride in the PM_{10} fraction were made at 3 sites during 2008 (Harwell, North Kensington and Marylebone Road). The extracts from the filters exposed were analysed by ion chromatography at NPL. The filter extracts are analysed for sulphate, as required by Defra, and also for nitrate and chloride.

The measurements of particulate sulphate, chloride and nitrate concentrations made in 2008 are displayed in Figure 4-1 to Figure 4-4, respectively. Figure 4-4 also includes the automatic nitrate measurements for comparison (see Section 4.2.2).

There were high concentrations of chloride in February 2008, most notably at Marylebone Road site. All the UK experienced a high pollution event in February, which can be observed also in other measurements within Defra monitoring programmes.

Figure 4-5 shows a comparison of chloride concentrations in Marylebone Road with PM_{10} and $PM_{2.5}$ daily measurements.

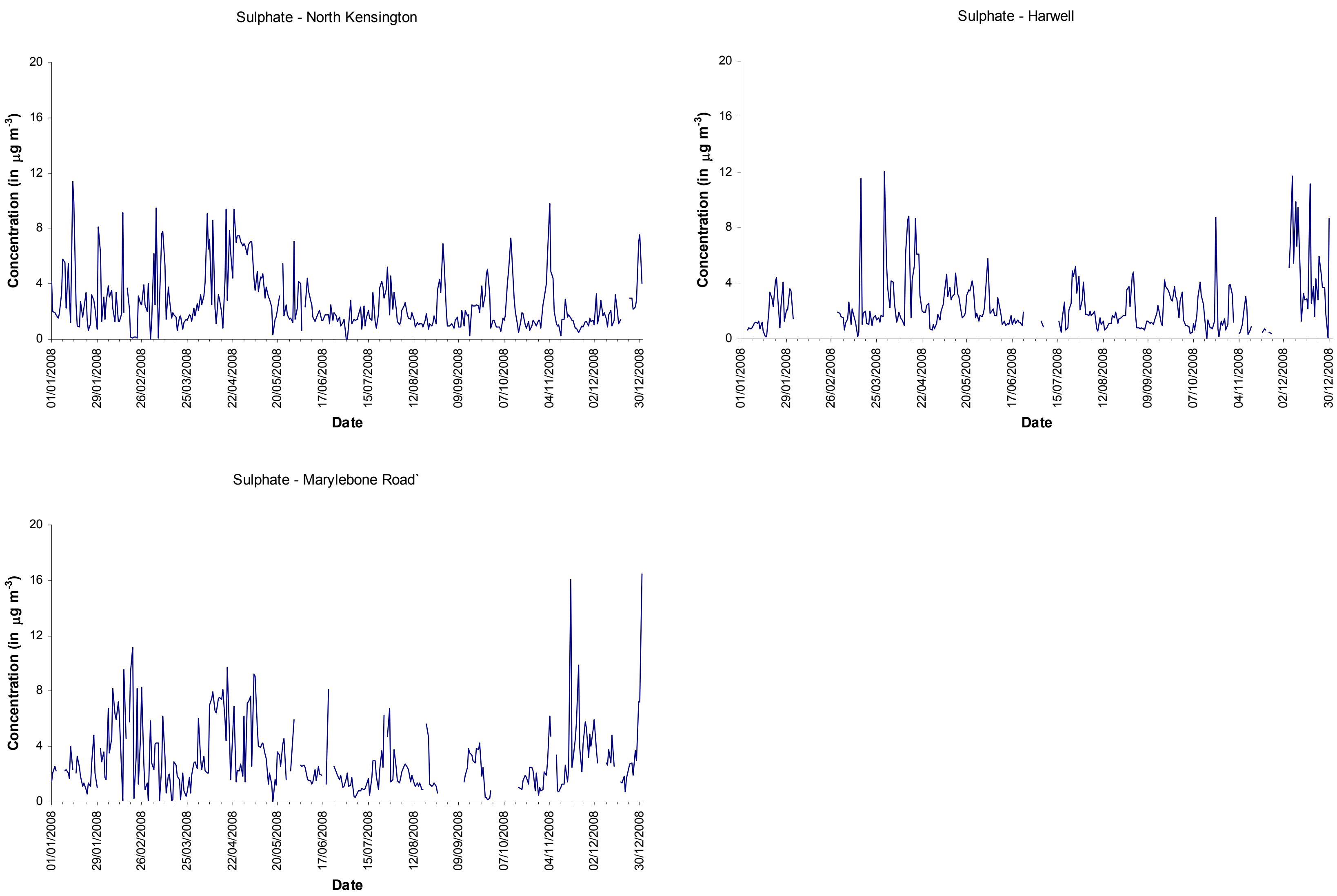


Figure 4-1: Partisol PM_{10} Sulphate Concentrations at Network Sites during 2008.

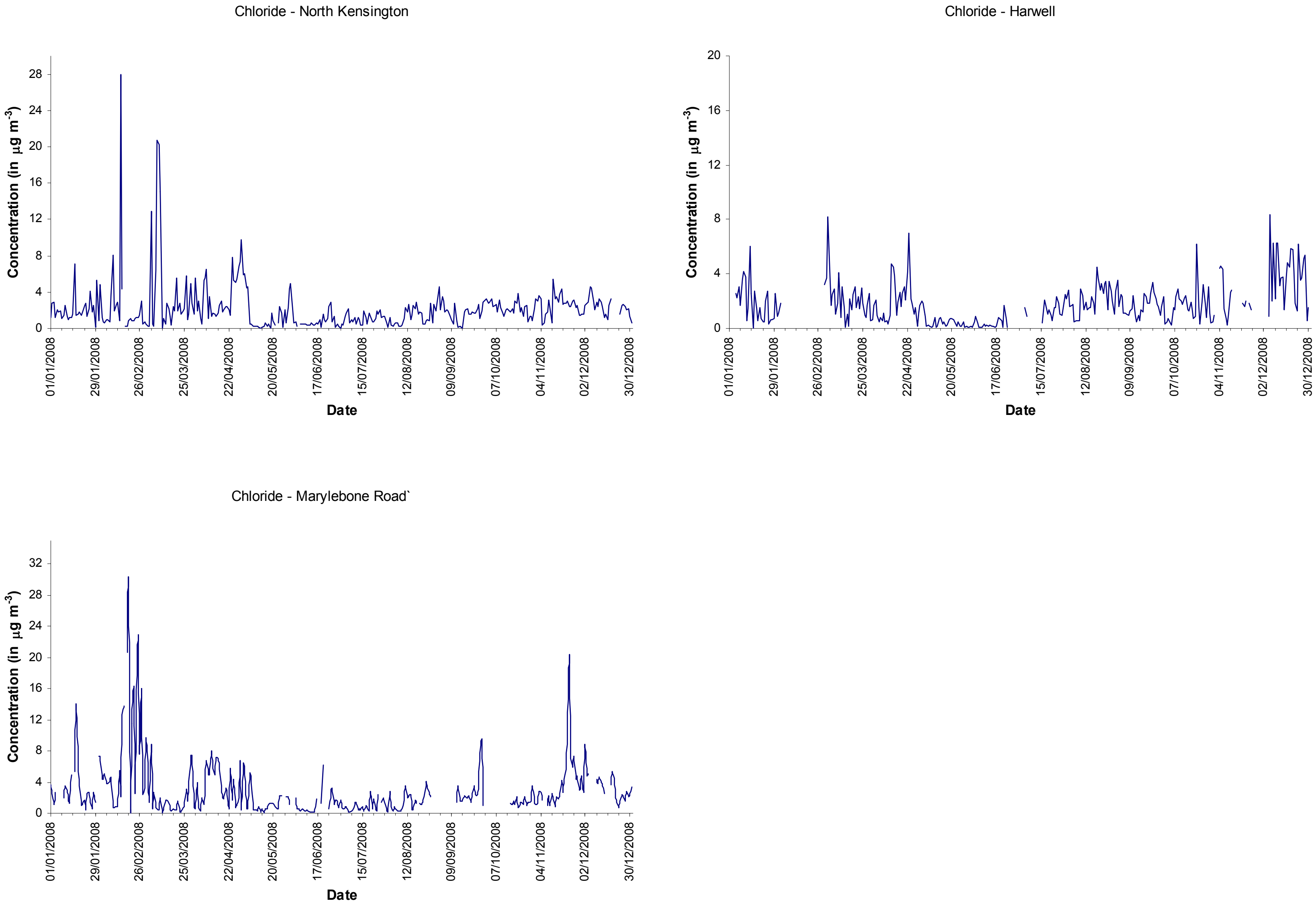


Figure 4-2: Partisol PM_{10}Chloride Concentrations at Network Sites during 2008.

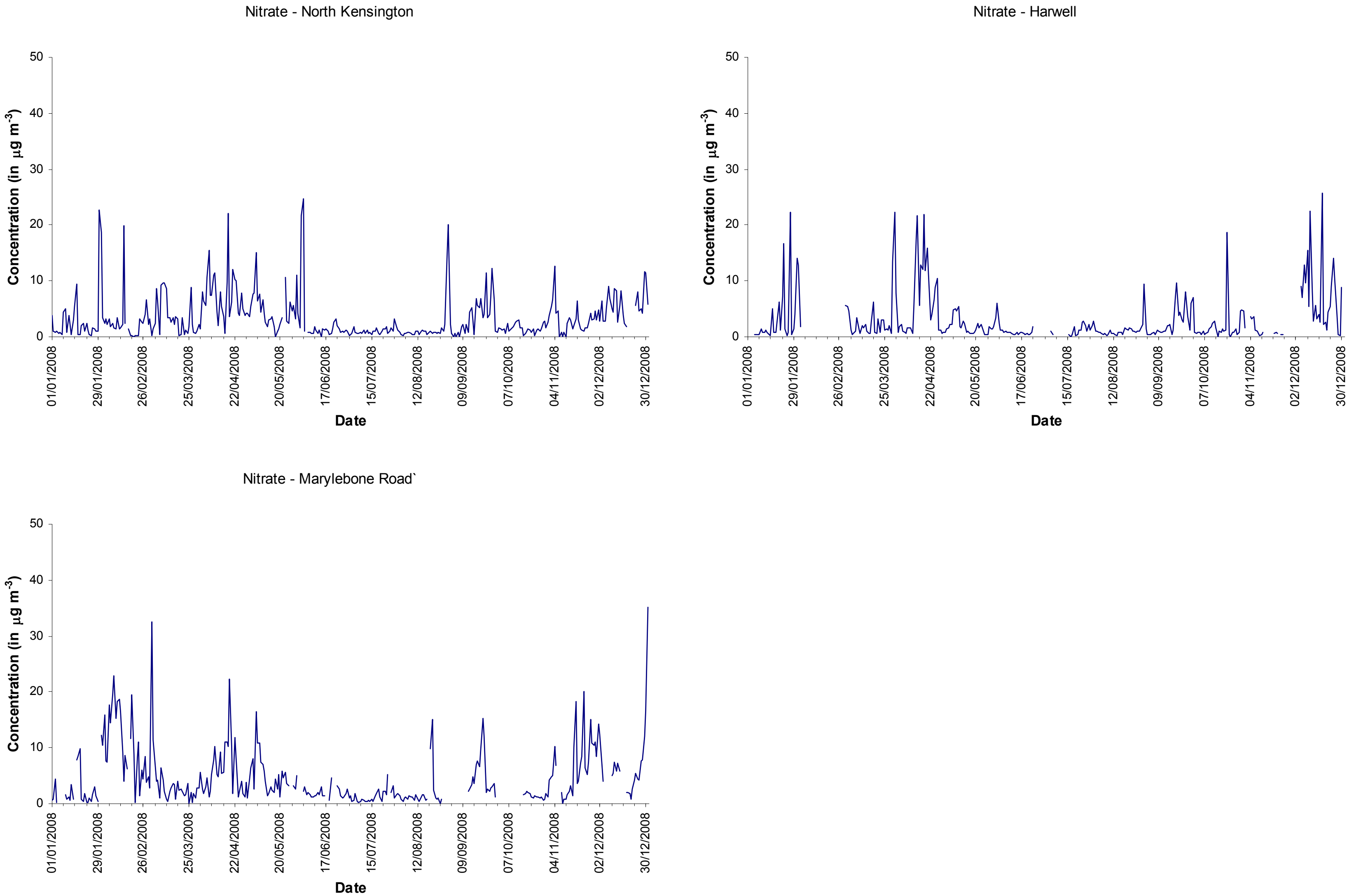


Figure 4-3: Partisol PM_{10} Nitrate Concentrations at Network Sites during 2008.

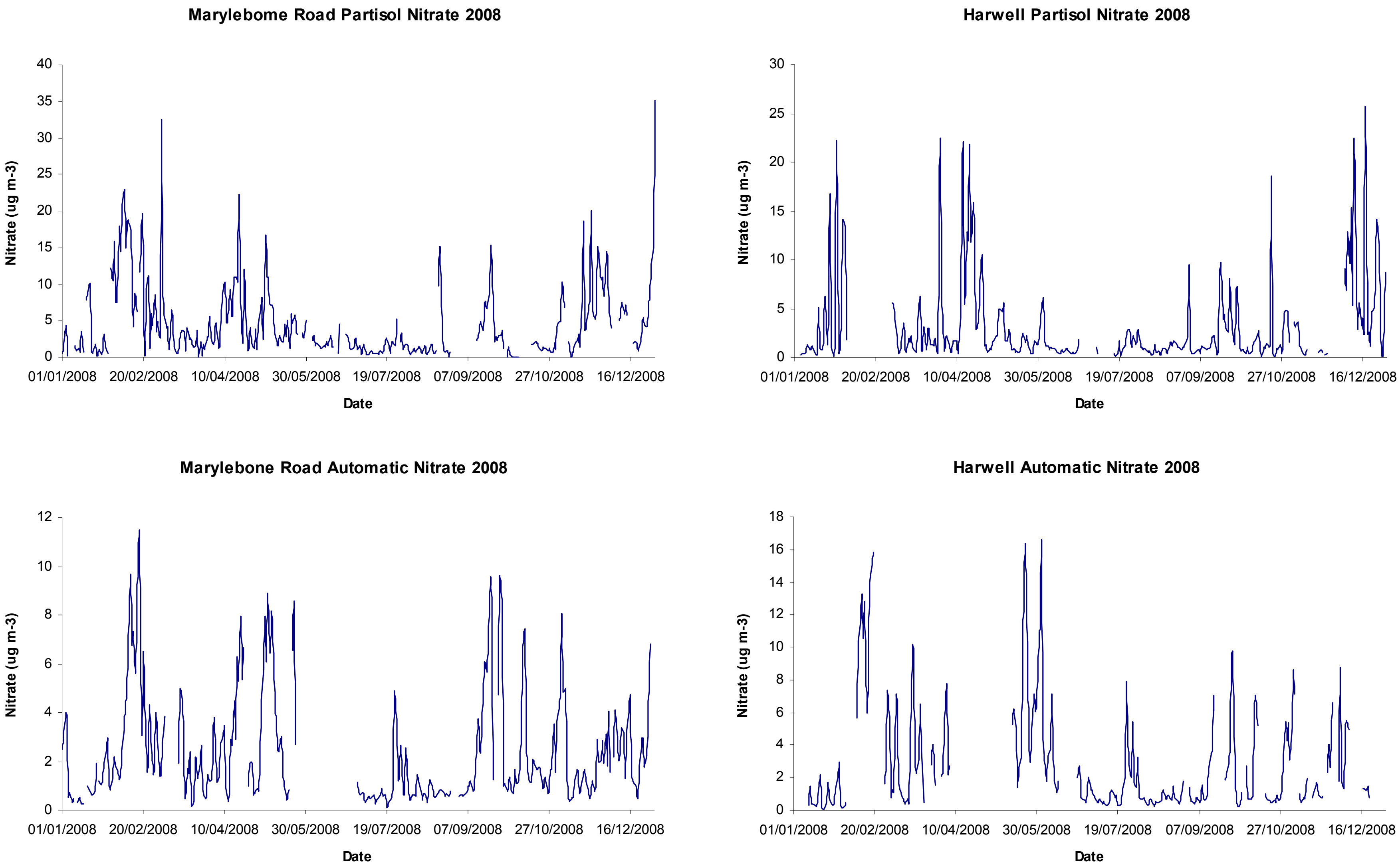


Figure 4-4: **Nitrate Concentrations at Network Sites during 2008. Partisol Measurements (PM_{10}) [Upper Panels] and Automatic Nitrate Analysers ($PM_{2.5}$)[Lower Panels]**

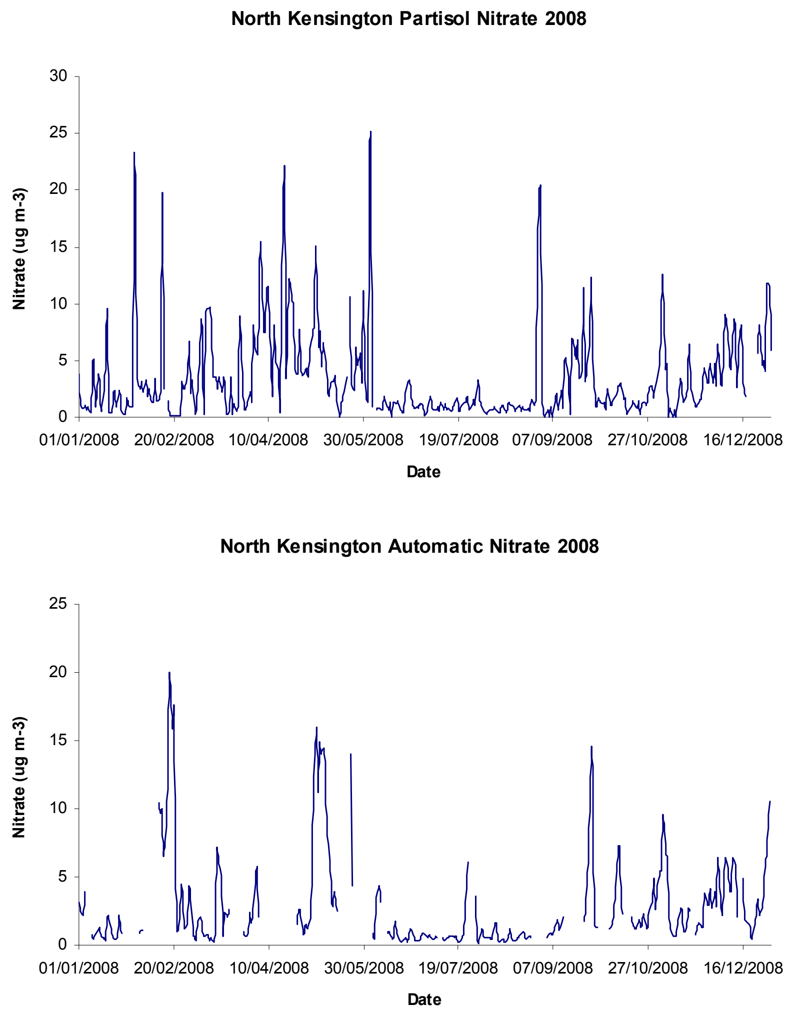


Figure 4-4: **Nitrate Concentrations at Network Sites during 2008. Partisol Measurements (PM_{10})[Upper Panels] and Automatic Nitrate Analysers ($PM_{2.5}$) [Lower Panels].(Continued)**

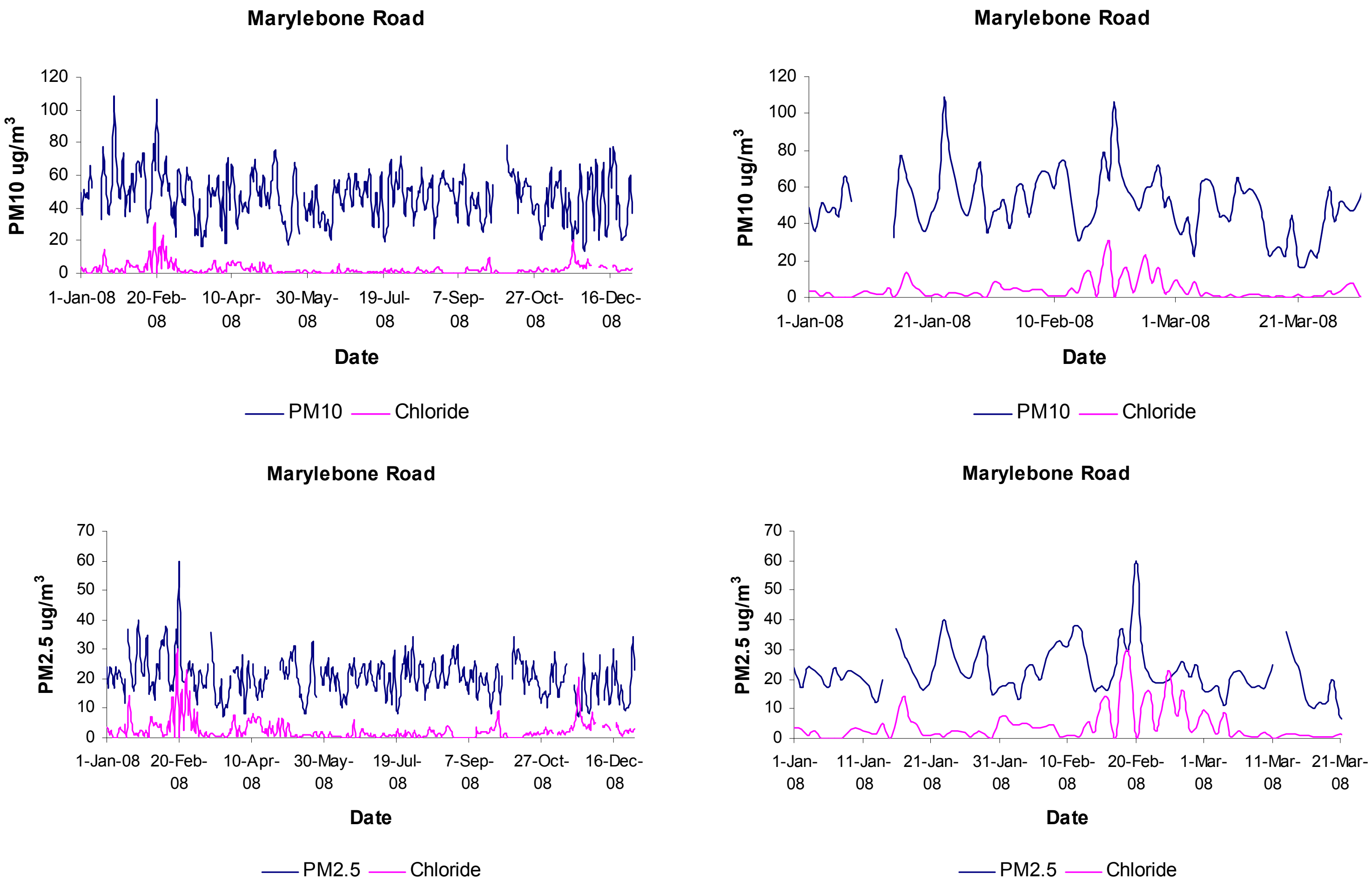


Figure 4-5: Time series of PM10, PM2.5 and Chloride Concentrations in Marylebone Road in 2008

Monthly data capture rates for the Partisol 2025 instruments during 2008 are given in Table 4-1.

Table 4-1: Monthly Data Capture for the Partisol 2025 Samplers during 2008

Site	Harwell	North Kensington	Marylebone Road
January	87%	100%	81%*
February	7%	97%	97%
March	100%	100%	100%
April	100%	100%	100%
May	100%	97%	90%
June	80%	97%*	77%
July	65%	100%	97%
August	100%*	100%	84%
September	100%	100%	60%
October	100%	100%	52%*
November	53%*	100%	93%
December	84%	84%	77%
Average	**81%**	**98%**	**84%**

Notes: '*' denotes the month in which the instrument service was performed.

The Equipment Support Unit carries out services and instrument calibrations twice a year. Up to one day has been allowed for each of these service visits and that is reflected in the data capture calculation.

4.2.2 Automatic Nitrate Analysers ($PM_{2.5}$)

The automatic daily measurements of particulate nitrate made in 2008 were displayed in the lower panels of Figure 4-4. Monthly data capture rates for the automatic nitrate instruments are presented in Table 4-2. The Equipment Support Unit carries out services and instrument calibrations twice a year.

Table 4-2: Monthly Data Capture for the Automatic Nitrate Instruments during 2008.

Site	Harwell	Marylebone Road	North Kensington
January	95%	89%*	59%
February	80%	90%	68%
March	78%	74%	75%
April	74%	89%	48%
May	79%	71%	67%
June	67%	2%	82%*
July	100%	98%	80%
August	76%*	86%	98%
September	54%	90%	59%
October	81%	97%*	74%
November	78%*	95%	70%
December	37%	93%	73%
Average	**75%**	**81%**	**71%**

Notes: '*' denotes the month in which the instrument service was performed.

4.2.3 Comparison of Automatic Nitrate ($PM_{2.5}$) and Partisol 2025 Nitrate (PM_{10})

Average daily concentrations of particulate nitrate have been derived from the hourly measurements made by the automatic analyser and these have been compared to the filter measurements of particulate nitrate.

Figure 4-6 presents scatter plots for each site. Only those days for which there are 20 or more hours of data have been included in the analysis.

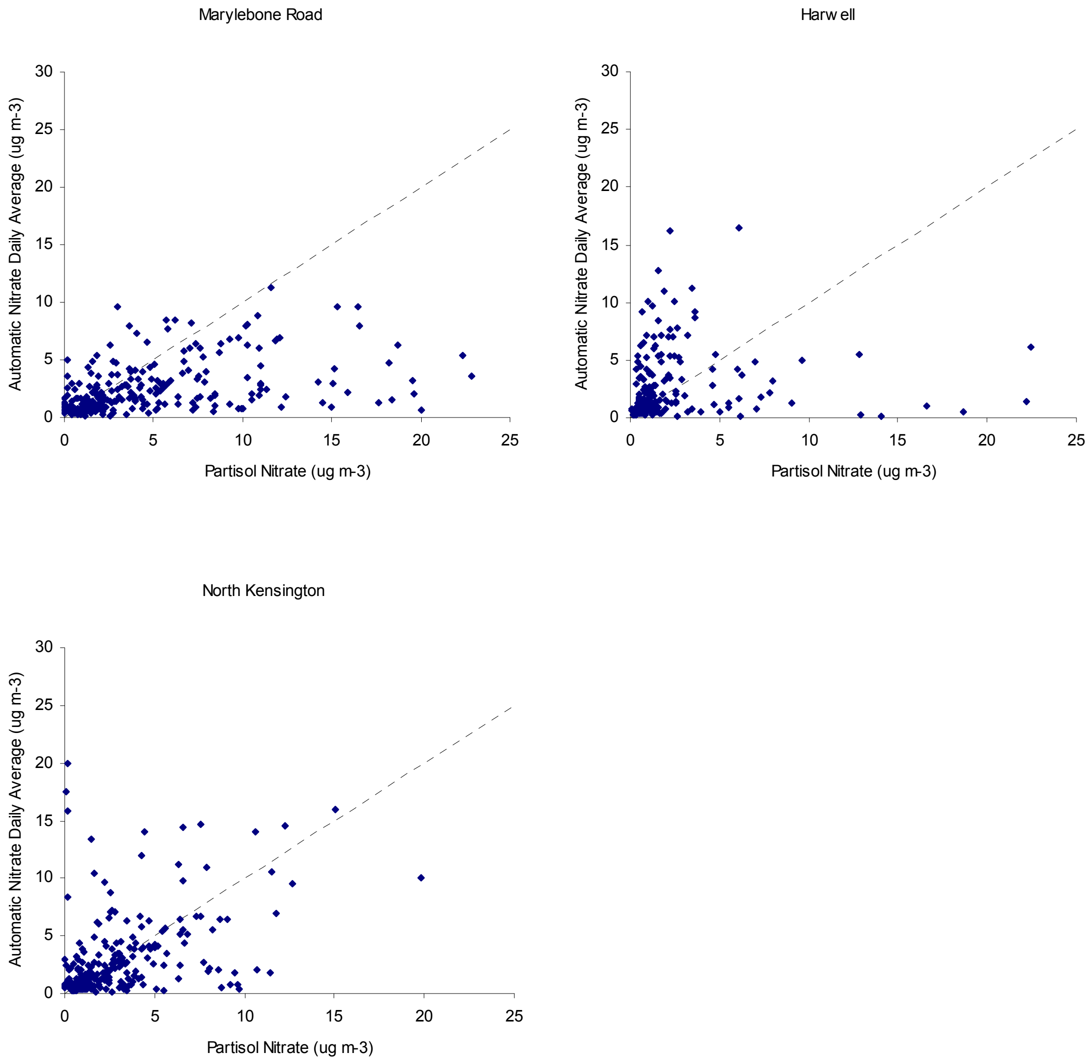


Figure 4-6: Scatter Plots of Nitrate Concentrations at the Network Sites during 2008.

Differences in the two measurement methods are expected to give rise to discrepancies in the results, and these are described in more detail in the NPL uncertainty report [NPL, 2007a]. As the measurements are from different PM size fractions (Partisol – PM_{10}, automatic nitrate – $PM_{2.5}$), a 1:1 correlation is not expected. Also, more sampling losses of volatile nitrate are expected from the daily Partisol method. The correlations at Marylebone Road and North Kensington are consistent with those found in previous years, while at Harwell the correlation close to unity found in 2007 was not found in 2008. The automatic nitrate concentrations gave considerably higher measurements in May and June 2008. The maximum temperature during those months was often over 20 °C and this could have led to a loss of nitrate from the filters.

4.3 Elemental and Organic Carbon

4.3.1 EC/OC Measurements (PM_{10})

The filter measurements of EC, OC and total carbon made in 2008 have been combined and are displayed in Figures 4-7and 4-8 for the 3 sites.

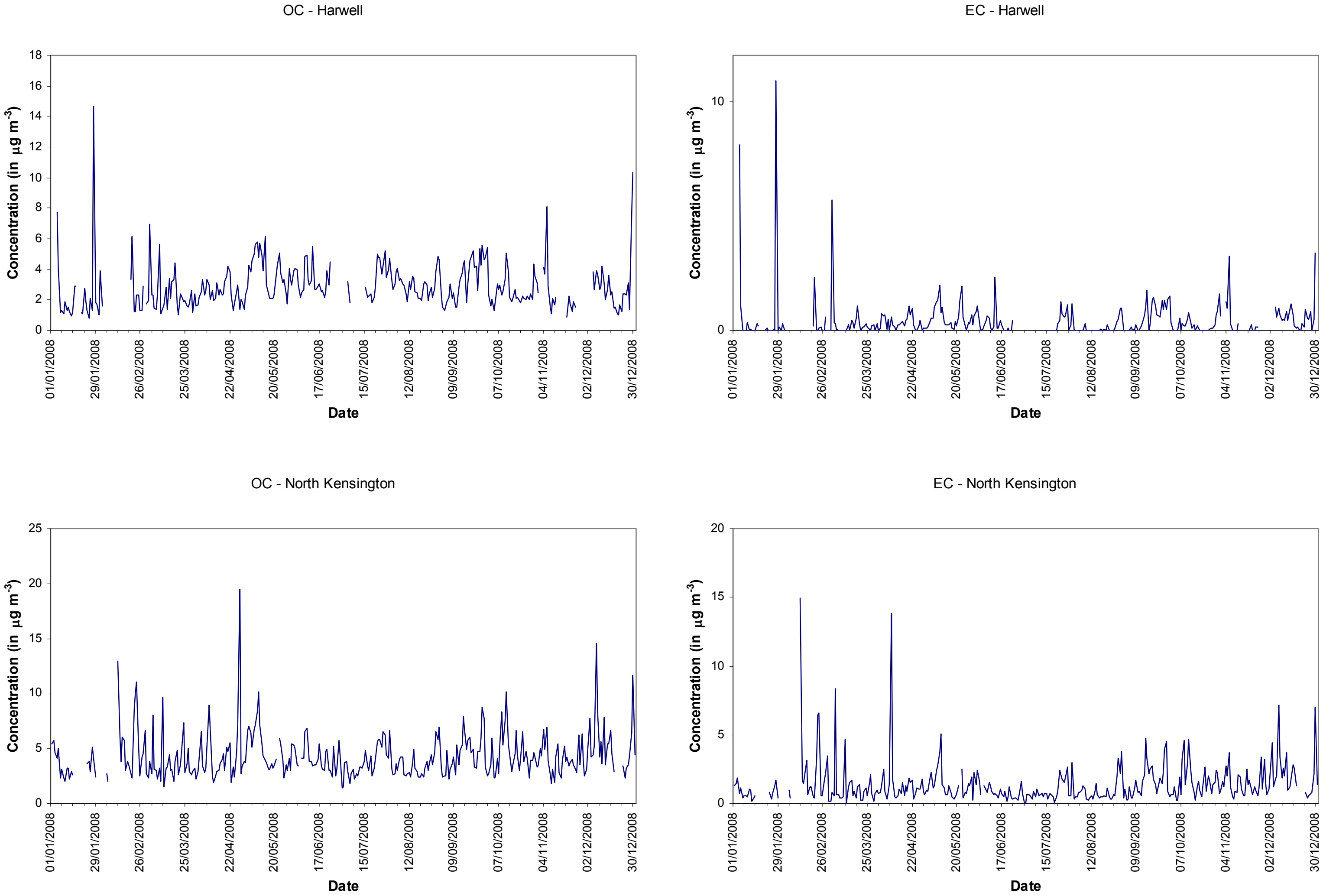


Figure 4-7: PM_{10} Organic and Elemental Carbon Concentrations in 2008 at Harwell and North Kensington

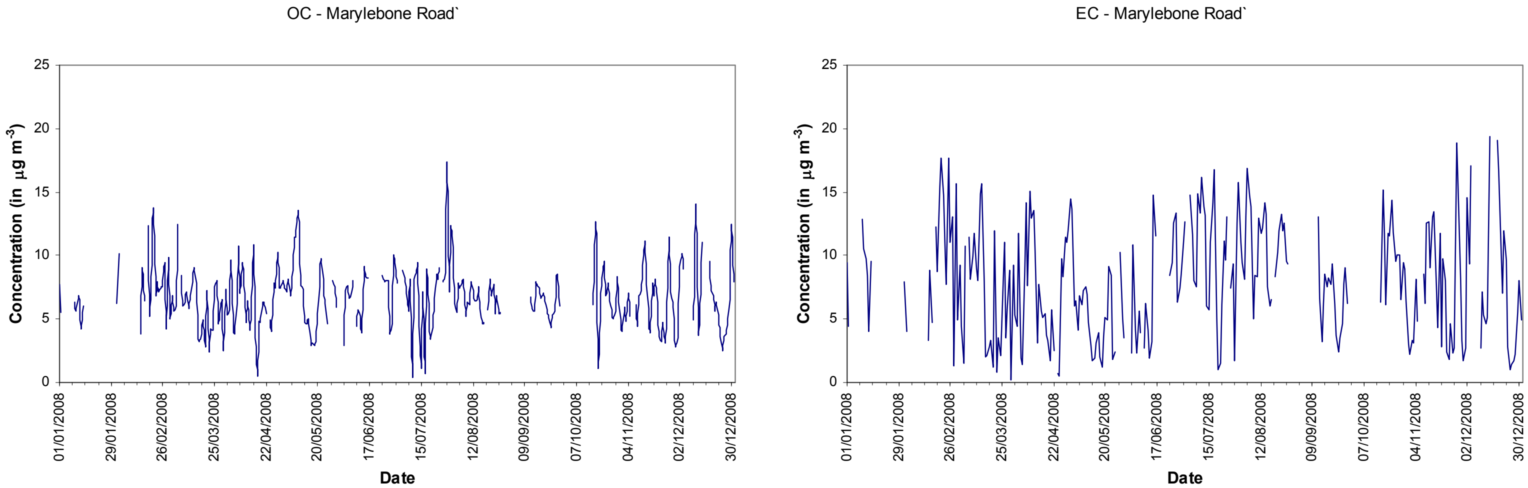
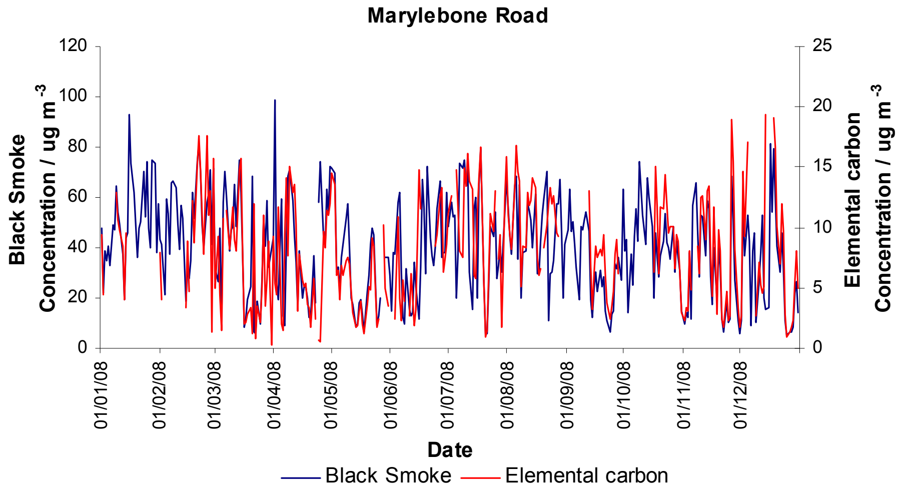


Figure 4-8: PM_{10} Organic and Elemental Carbon Concentrations at Marylebone Road

4.3.2 Comparison with Black Smoke

Co-located measurements of black smoke have been made at the North Kensington and Marylebone Road sites. The time series have been compared and are shown in Figure 4-9. Except few points, the correlation between the two measurements is good in both sites.



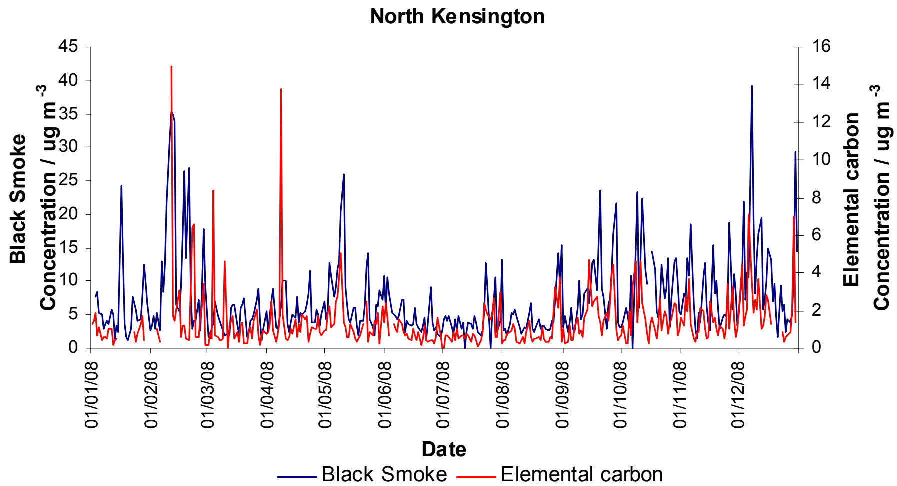


Figure 4-9: Time series of Black Smoke and Elemental Carbon Measurements at North Kensington and Marylebone.

4.4 Particle Number and Size Distributions

4.4.1 Particle Number Concentrations (CPC)

Time series of the particle number concentrations (between about 7nm and several microns in diameter) measured at network sites during 2008 are shown in Figure 4-10.
The following should be noted:

- **Harwell** – The instrument was removed in January for repair and a new phone line was installed on the 20th of February. A full calibration service was carried out in January.
- **Birmingham** – The instrument was removed from site and sent to TSI on the 19th of September for repair.
- **Marylebone Road** – The instrument was returned to TSI for unstable flow fault on the 21st of February and resumed normal operation on the 5th of March. It was again sent to TSI for stability flow problem on the 15th of May and reinstalled on the 28th of June. The instruments was removed from site for flow problems on the 29th of August and reinstalled on the 15th of October.
- **North Kensington** – The instrument was serviced and calibrated between March and April 2008.

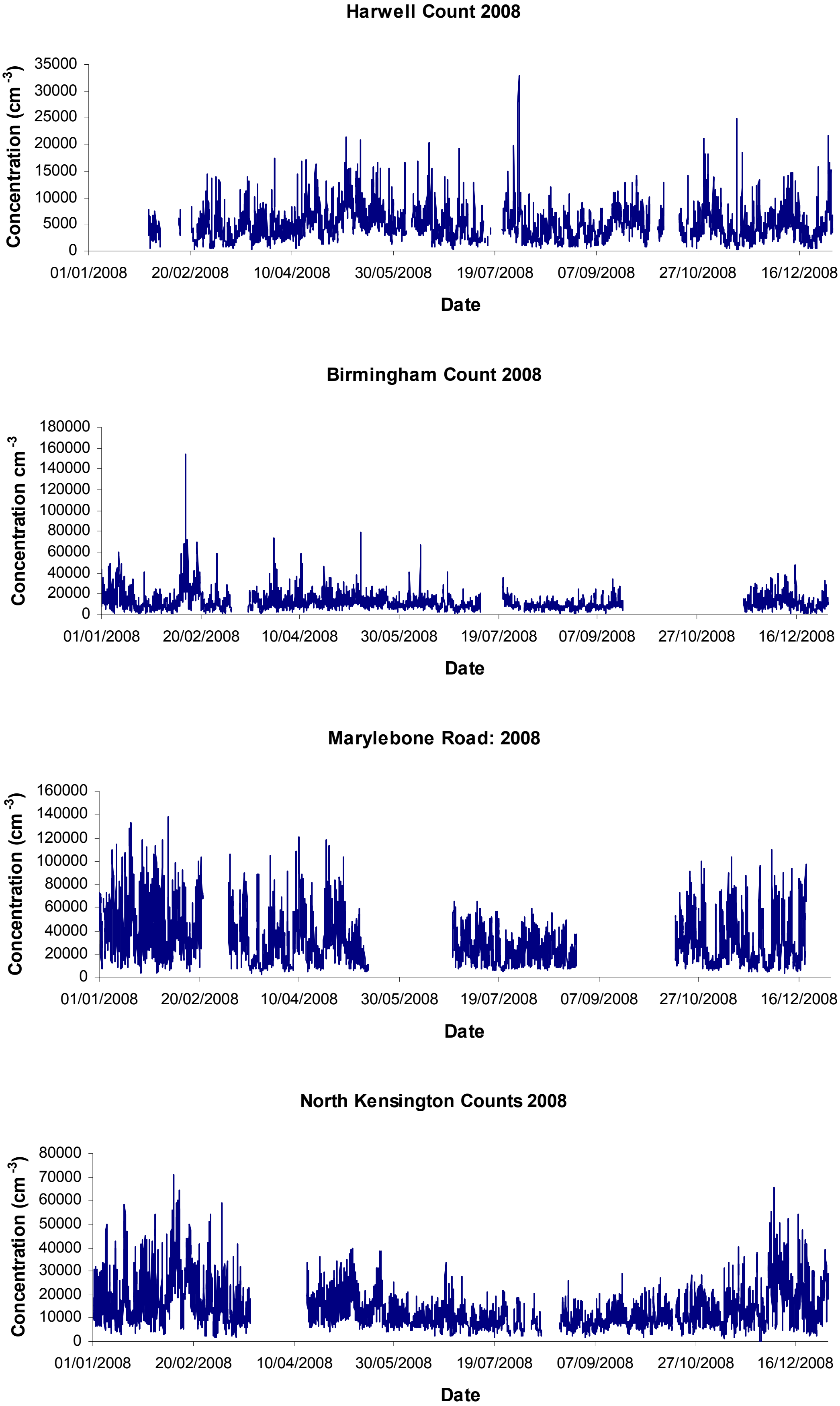


Figure 4-10: CPC Particle Count at the Network Sites during 2008.

There was a major peak in the number concentration of ambient particles at Harwell on the 30th of July. The measurements made during that period are shown in Figure 4-11 and are compared to the nitrogen oxides concentrations for the same period. A similar pattern is found although the major peak for the NO_x if found shifted of some hours. The same peak is present in the SPMS time trend (see Figure 4-13).

There was also a major peak in the number concentration of ambient particles at Birmingham on the 12th of February and this peak was mirrored in the NO_x concentration on the same day and same hour (see Figure 4-12).

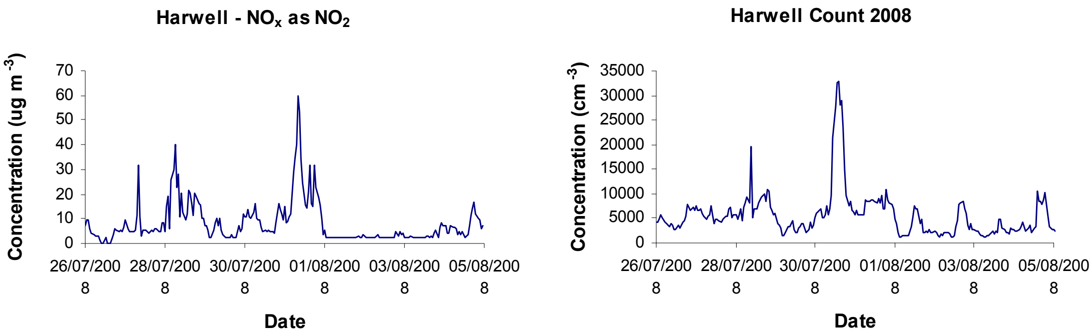


Figure 4-11: Correlation between the high concentrations of particles numbers and those of nitrogen oxides at Harwell in July 2008.

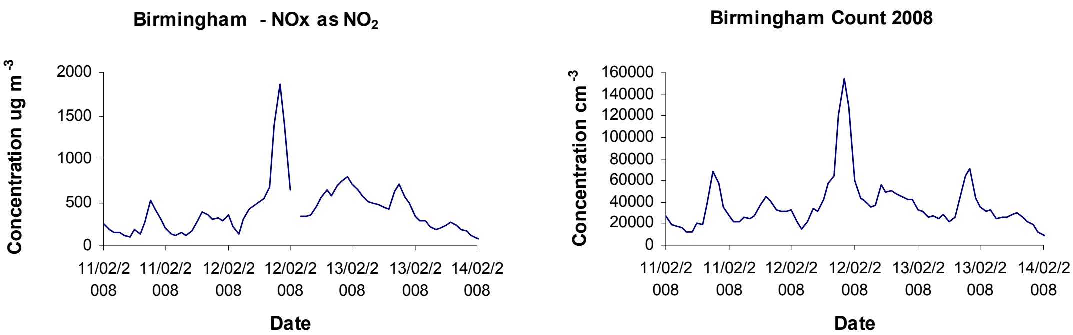


Figure 4-12: Correlation between the high concentrations of particles numbers and those of nitrogen oxides at Birmingham in February 2008.

Monthly data capture rates for the CPC instruments during 2008 are displayed in Table 4-3. Each instrument is removed from the site for a full service and calibration annually. This scheduled maintenance is expected to take three weeks, to include draining and drying, transit time, full service at TSI Instruments, and re-installation. In the month(s) where the CPC was serviced, the data capture quoted in the table takes into account the scheduled downtime, and is denoted with an asterisk.

Table 4-3: Monthly Data Capture for CPC Instruments during 2008

Site	North Kensington	Birmingham	Marylebone Road	Harwell
January	100%	100%	97%	72%*
February	94%	94%	66%	44%
March	100%*	72%	82%	100%
April	76%*	97%	97%	100%
May	100%	100%	44%	100%
June	97%	97%	16%	90%
July	95%	58%	100%	71%
August	60%	97%	84%	100%
September	97%	60%	0%	99%
October	94%	0%	53%	59%
November	97%	37%	97%	100%
December	100%	100%	60%	100%
Average	**92%**	**76%**	**66%**	**86%**

Notes: '*' denotes the month in which the instrument service was performed. '-' denotes that the site was not operational.

4.4.2 Particle Number and Size Distributions (SMPS)

Total particulate counts (between about 16 nm and 605 nm aerodynamic diameter) have been plotted in Figure 4-13. Full data sets, including size distributions, will be made available for public dissemination via the Defra Air Quality Information Archive (www.airquality.co.uk).

The following should be noticed:

- **North Kensington** – The instrument was removed from site in October and a full calibration serviced was carried out in December 2008.
- **Harwell** – The instrument was sent to TSI for repair twice in January and February and reinstalled on the 18th of March. It was removed from site on the 11th of December for calibration service.
- **Marylebone Road** - There are no measurements from the 26th of February and the 13th of June as the instrument was sent to TSI for repair. During this period the instrument was also serviced. Two faults occurred in July and August 2008. After the SMPS was sent to TSI for repair, the counts measurements for small particles appeared to be higher than usual.

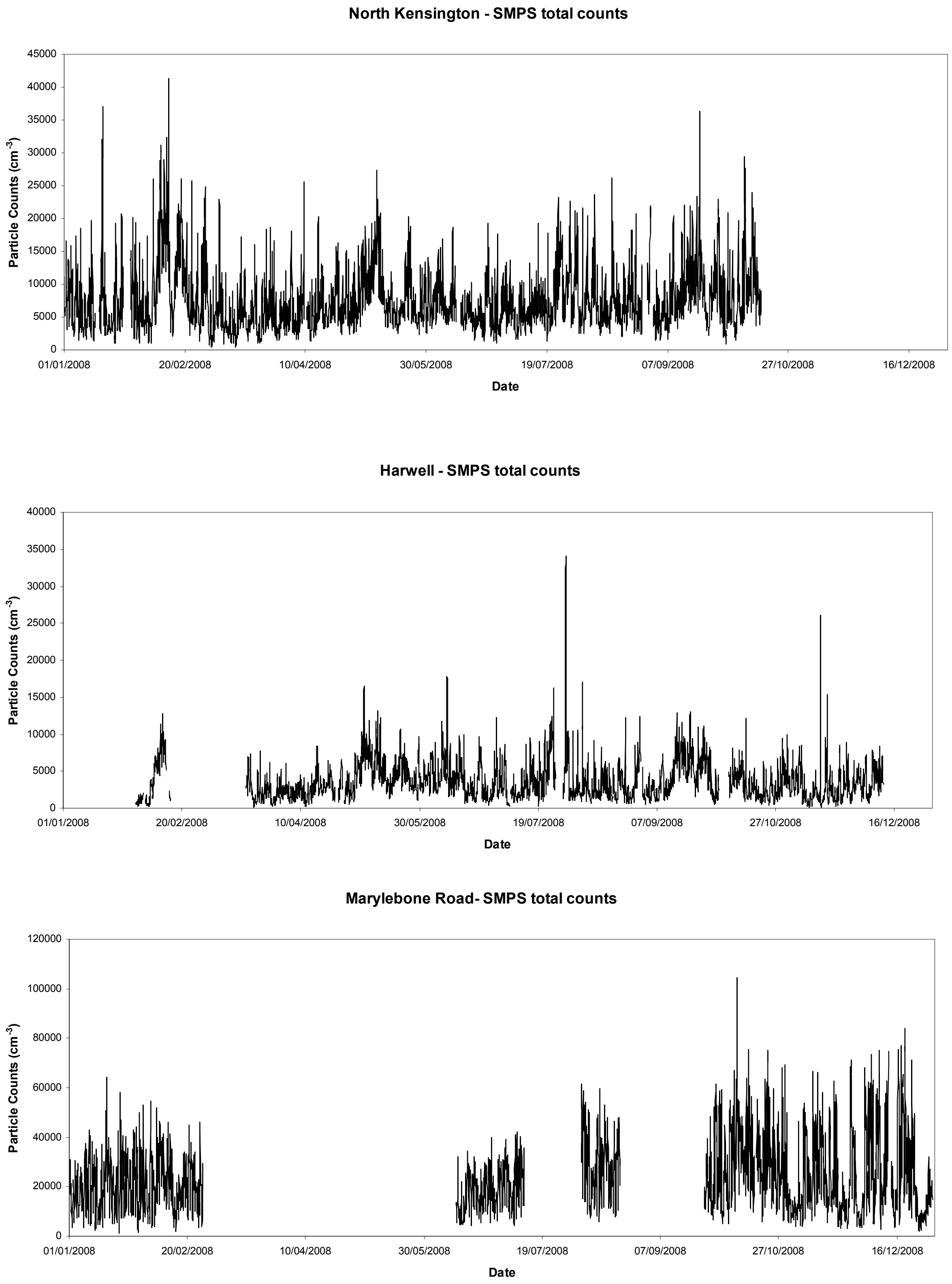


Figure 4-13: SMPS Total Particle Number Concentrations at the Network sites during 2008

The counts in each particle size bin measured during 2008 are presented as monthly averages in the left-hand panels of Figure 4-13 and as an annual average in the right-panel.

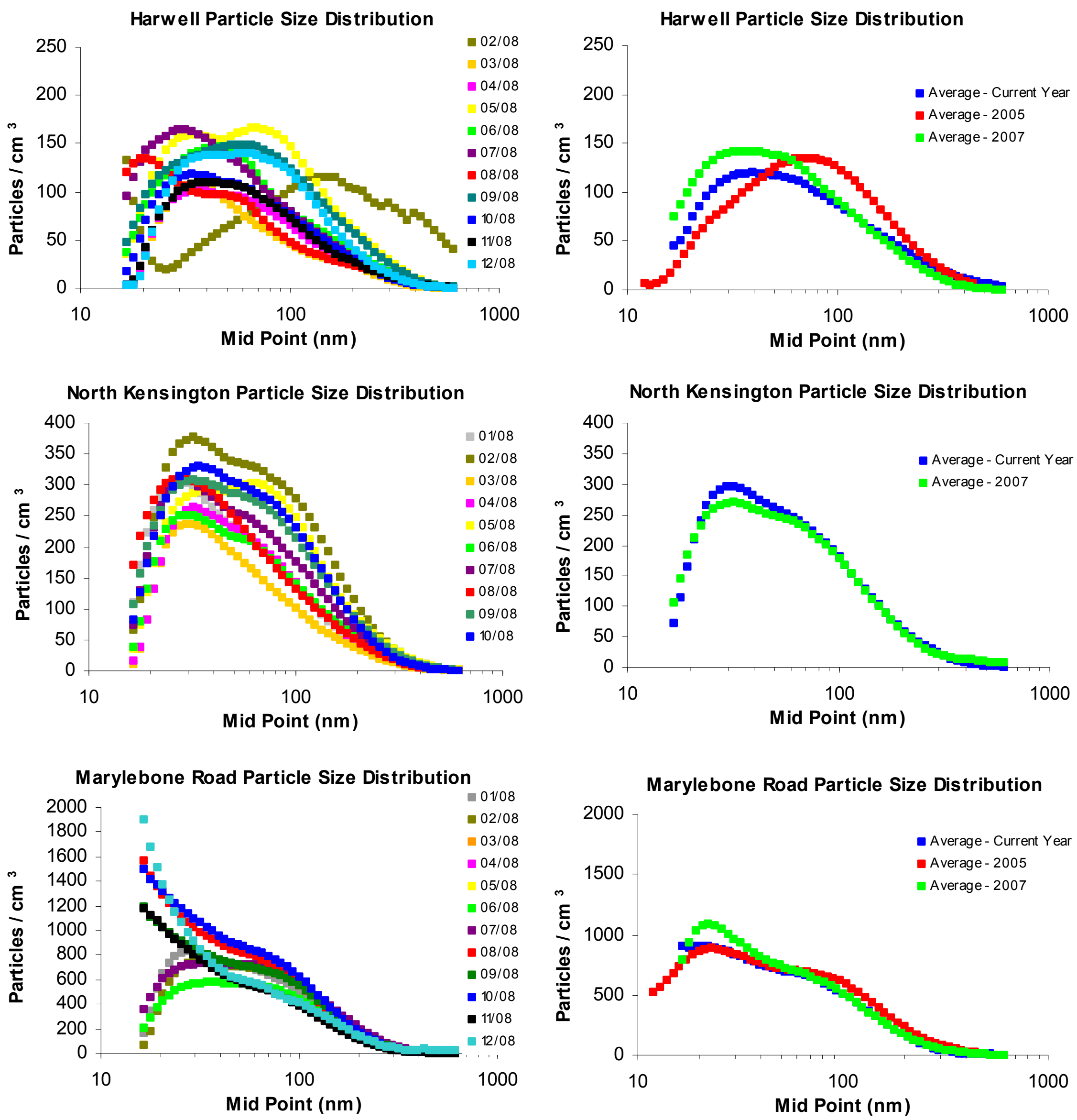


Figure 4-14: Monthly-averaged Particle Size Distributions at Network Sites during 2008 [Left-hand Panels] and Comparison of the 2005, 2007 and 2008 Annual-averged Size Distributions [Right-hand Panels].

The average size distributions for 2005, when a previous model of SMPS was in use, have also been included as a reference. There were insufficient measurements from 2006 to allow a valid comparison. There are some clear differences, which are due in part to the changes in instruments and the internal processing within the instruments. For example, the size of the maximum annual count at Harwell has shifted to smaller sizes, which is consistent with the changes expected from the corrections for multiple charge and diffusion loss, which were not applied to the 2005 measurements (see below). The average size distributions for all sites reproduced well the average size distributions obtained in 2007.

The counts at Marylebone Road show too high number concentrations for small particles from July 2008 onwards. Both the multiple charge and diffusion loss corrections were switched on during all the measurements and the high concentrations appeared after the instrument was sent to TSI in July 2008 following a butanol contamination.

Monthly data capture rates for the SMPS instruments during 2008 are displayed in Table 4-4.

Table 4-4: Monthly Data Capture for SMPS Instruments during 2008.

Site / Month	Harwell	North Kensington	Marylebone Road
January	1%	85%	100%
February	41%	100%	88%
March	45%	100%	0%
April	93%	96%	0%
May	100%	100%	68%*
June	100%	93%	61%
July	88%	100%	34%
August	97%	91%	53%
September	99%	100%	18%
October	86%	47%	97%
November	100%	0%	100%
December	100%*	68%*	96%
Average	**79%**	**82%**	**60%**

Notes: '*' denotes the month in which the instrument service was performed.

The production of data from SMPS instruments is a complicated process, summarised schematically in Figure 4-15. Many stages of data processing are carried out by proprietary manufacturer's software to convert the raw data (number count versus Differential Mobility Analyser voltage) into the final data (number concentration versus particle size). While the size axis can be reliably calibrated using certified spheres, the number concentration axis, and hence both the scale and shape of the size distribution, is much less amenable to direct evaluation.

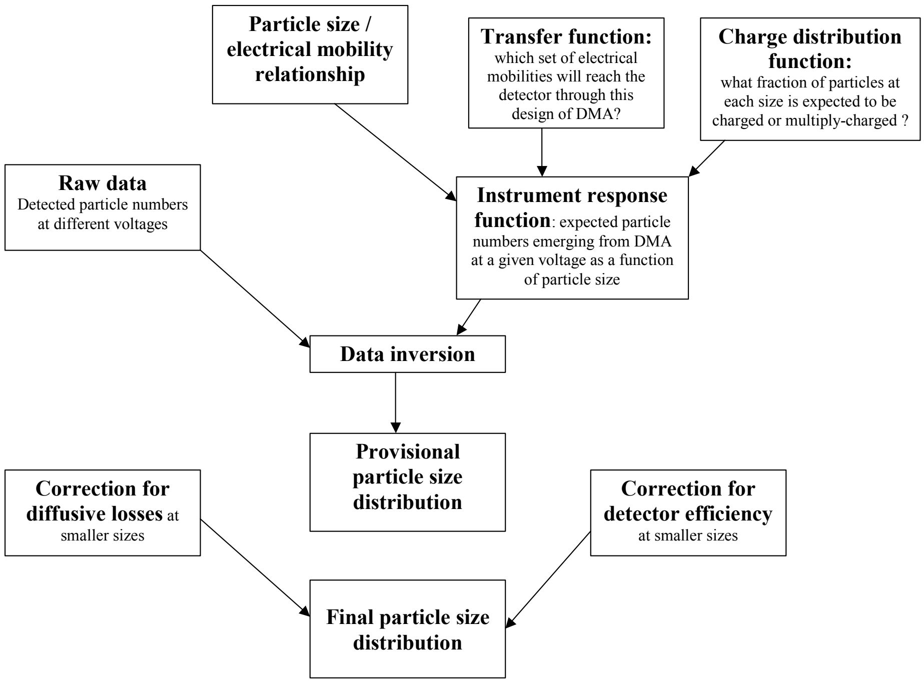


Figure 4-15: Schematic of the Internal Data Processing of the Current SMPS Instrument in the Network.

Some elements of the software in the current TSI instruments (Model 3936L75) are more transparent than for the previous TSI 3071 model used in the Network (in 2005). The multiple charge correction and diffusion loss correction software can be switched on and off by the user. Both of these corrections are used in the data reported here.

The effect of the diffusion loss and multiple charge corrections can be seen in Figure 4-16. The uncorrected spectrum is shown in black. The effects of the multiple charge correction and diffusion loss corrections are shown in green and red, respectively. The blue curve is the combined effect of the two corrections. The overall effect of the two corrections is to increase the particle number counts at smaller sizes and to increase the total particle count.

It is clear that great care needs to be applied when comparing SMPS data from similar instruments on different settings, and even more when comparing SMPS data from different instruments.

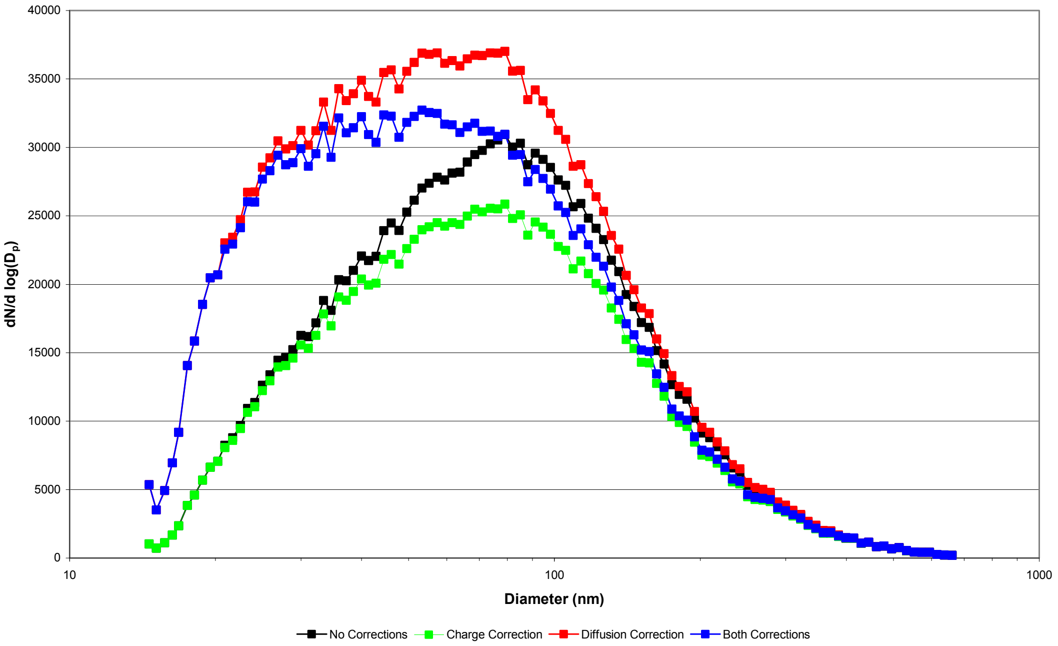


Figure 4-16: Effect of (i) the multiple charge, (ii) the diffusion loss and (iii) the combined correction on the SMPS size spectra.

4.4.3 SMPS versus CPC data

A scatter plot between the CPC particle counts and total SMPS particle counts (all size fractions) at all sites in 2008 is presented in Figure 4-17.

An example of the historical relationship of the ratios of the CPC to SMPS total counts is shown in **Table 4-5**.

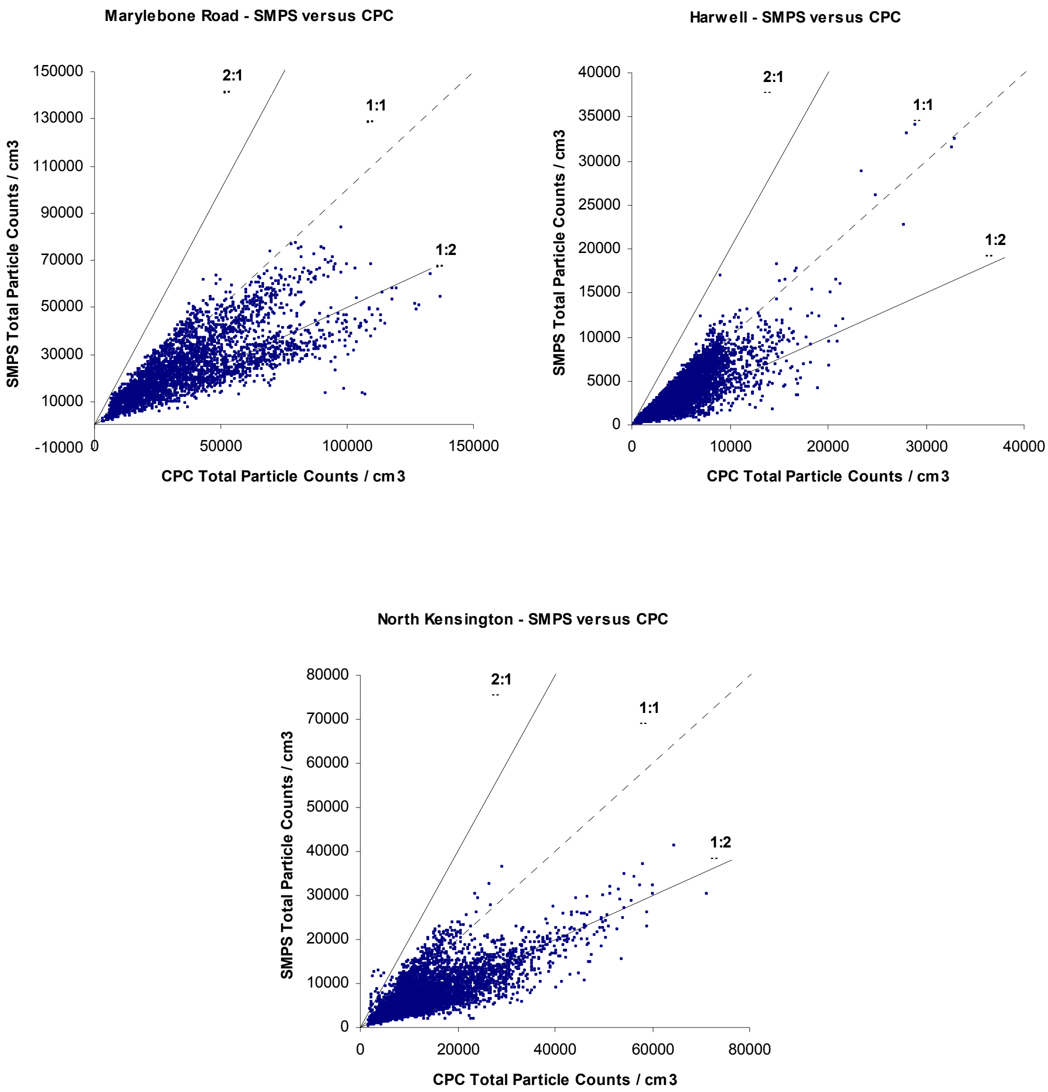


Figure 4-17: Scatter plot showing the relationship between CPC particle counts and total SMPS particle counts (all size fractions)

Table 4-5: Monthly Ratio of CPC to SMPS Particle Counts in 2005 and 2006 at Marylebone Road Site.

July 2005	2.7
August 2005	2.4
September 2005	2.3
October 2005	2.5
November 2005	2.6
December 2005	2.6
January 2006	3.0

CPC to SMPS particle count ratios for the three sites with co-located instruments in 2007 and 2008 are shown in Table 4-6 and Table 4-7 respectively.

Table 4-6: Monthly Ratio of CPC to SMPS Particle Counts in 2007.

Month	Marylebone Road	Harwell	North Kensington
January 2007			
February 2007			
March 2007	2.9		
April 2007			
May 2007	4.1		
June 2007	2.6		
July 2007	2.6		
August 2007	2.4		
September 2007	2.2		
October 2007	1.9	1.8	
November 2007	3.6		8.8
December 2007	3.4		3.5

Table 4-7: Monthly Ratio of CPC to SMPS Particle Counts in 2008

Month	Marylebone Road	Harwell	North Kensington
January 2008	2.4	5.1	2.6
February 2008	2.0	1.0	2.2
March 2008	-	1.8	2.6
April 2008	-	2.0	2.5
May 2008	-	1.4	1.9
June 2008	1.8	1.4	1.6
July 2008	1.1	1.3	1.1
August 2008	0.9	1.2	1.2
September 2008	-	1.1	1.1
October 2008	1.1	1.7	1.3
November 2008	1.3	1.6	-
December 2008	1.2	1.4	-

The complicated data processing within SMPS instruments, described in Section 4.4.2 above, means that the total particle number concentration obtained by integrating the SMPS size distribution is subject to much greater uncertainties than CPC instruments, which measure number concentrations much more directly. In addition, the results cannot be compared directly because the instruments measure particles over different size ranges – the SMPS covering approximately 16-600 nm aerodynamic diameter, and the CPC covering from around 7 nm to several microns. Clearly this means that the CPC should inherently record higher concentrations than the SMPS. However, the ratio from May 2008 appears to be smaller than in previous years at North Kensington and Marylebone Road sites.

4.5 Meteorological Data

Although not a formal part of this measurement programme, meteorological data have been collated from the measurements made at Harwell and Rochester in other Defra monitoring networks. Monthly data capture rates for the meteorological masts during 2008 are displayed in Table 4-8.

Table 4-8: Monthly Data Capture for Meteorological Instruments during 2008.

Site	Harwell	Rochester
January	99%	100%
February	97%	100%
March	100%	99%
April	100%	100%
May	99%	100%
June	100%	100%
July	100%	100%
August	100%	98%
September	100%	100%
October	97%	100%
November	100%	100%
December	100%	100%
Average	99%	100%

Wind roses have been derived for Harwell and Rochester for each month in 2008. These can be found in Annex 3.

4.6 Trends and Profiles

4.6.1 Annual Mean Concentrations

Annual mean concentrations have been derived for the inorganic components, as shown in Table 4-9. The table also includes the annual mean concentrations for the years 2003 to 2007 for comparison.

Table 4-9: Annual Mean Concentrations of Inorganic Anions, 2003–2008.

Component	2003 Mean	2004 Mean	2005 Mean	2006 Mean	2007 Mean	2008 Mean	Units
Harwell Nitrate ($PM_{2.5}$)	2.66	4.27	1.94	1.61	2.26	3.03	$\mu g.m^{-3}$
Marylebone Road Nitrate ($PM_{2.5}$)	-	-	3.33	3.18	3.25	2.33	$\mu g.m^{-3}$
North Kensington Nitrate ($PM_{2.5}$)	-	-	-	-	-	2.84	$\mu g.m^{-3}$
Harwell Daily Nitrate (PM_{10})	3.90	2.76	3.17	3.21	3.06	3.28	$\mu g.m^{-3}$
Marylebone Road Daily Nitrate	5.06	3.93	3.97	4.39	4.05	4.47	$\mu g.m^{-3}$
North Kensington Daily Nitrate	4.32	3.38	3.91	3.74	3.76	3.39	$\mu g.m^{-3}$
Harwell Daily Sulphate (PM_{10})	2.44	2.29	2.40	3.01	2.40	2.35	$\mu g\ m^{-3}$
Marylebone Road Daily Sulphate	3.18	3.16	3.21	4.00	3.15	2.89	$\mu g\ m^{-3}$
North Kensington Daily Sulphate	2.61	2.95	3.02	3.51	2.79	2.61	$\mu g\ m^{-3}$
Harwell Daily Chloride (PM_{10})	0.91	1.04	1.19	1.32	1.38	1.79	$\mu g\ m^{-3}$
Marylebone Road Daily Chloride	1.45	1.54	1.64	2.01	1.91	2.78	$\mu g\ m^{-3}$
North Kensington Daily Chloride	1.11	1.24	1.33	1.57	1.66	2.17	$\mu g\ m^{-3}$

4.6.2 Monthly Trends

Using data from this contract, and publicly available data from Defra's Air Quality Archive (www.airquality.co.uk), this section seeks to show the trends in the average monthly values for all species at all sites during the past several years (see Figure 4-18 to 4-23). All available data has been used, regardless of the data capture in any particular month.

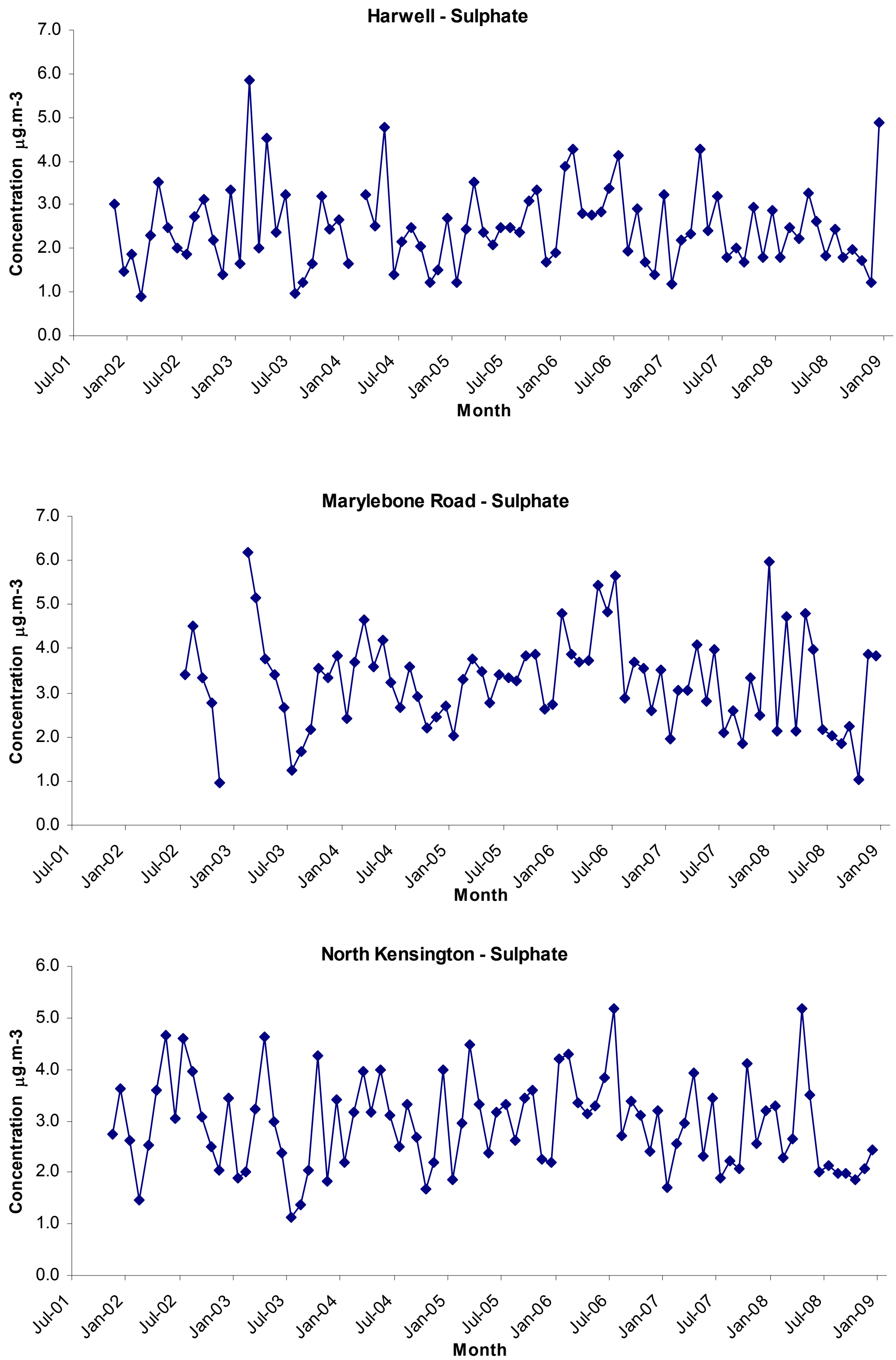
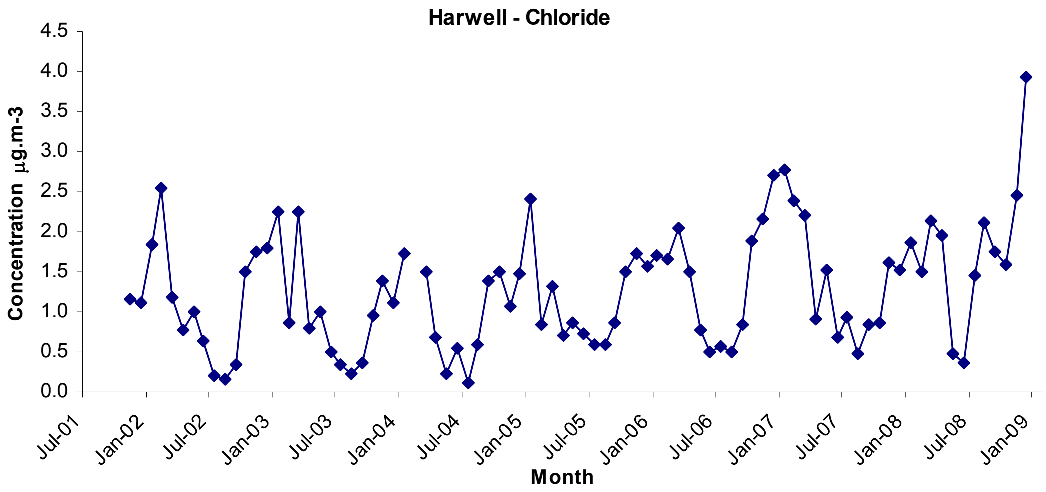
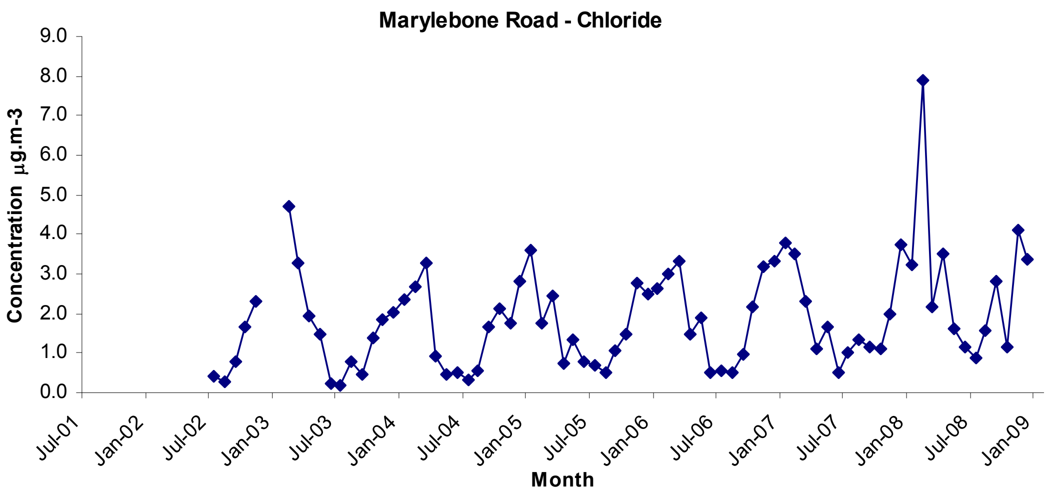


Figure 4-18: Monthly Averaged PM_{10} Sulphate Concentrations (Filter)





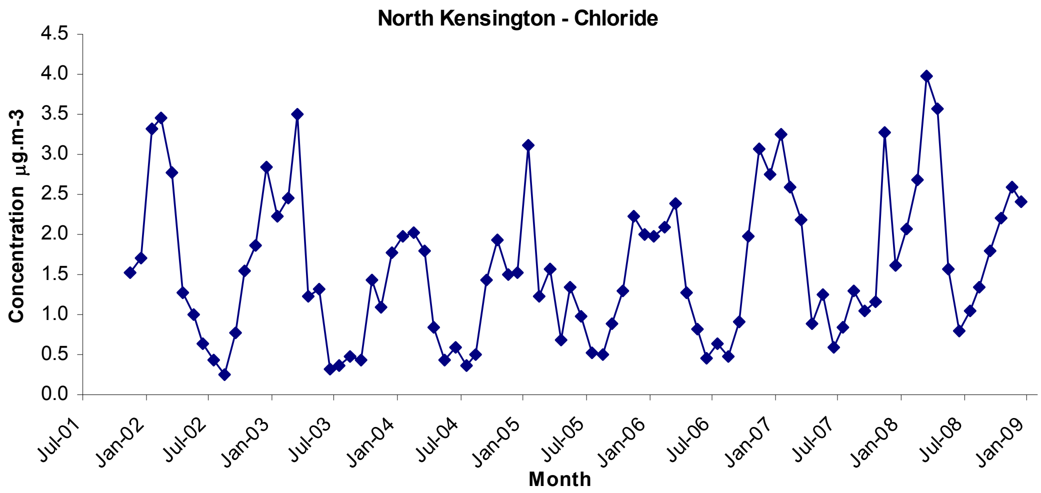
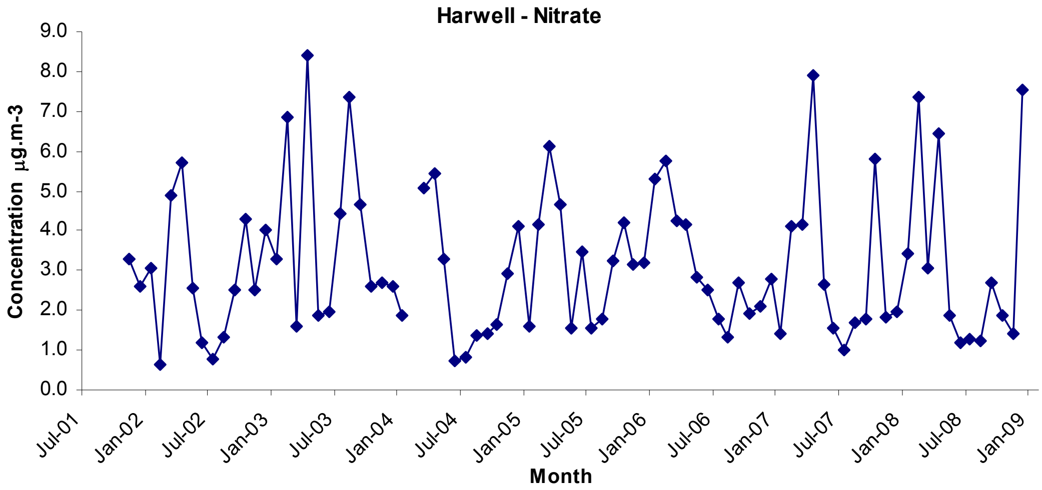
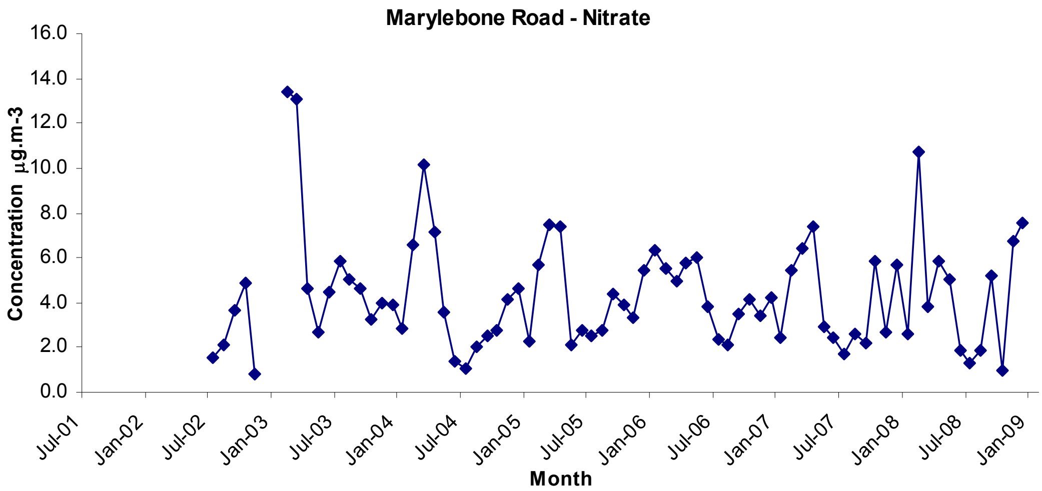


Figure 4-19: Monthly Averaged PM_{10} Chloride Concentrations (Filter).





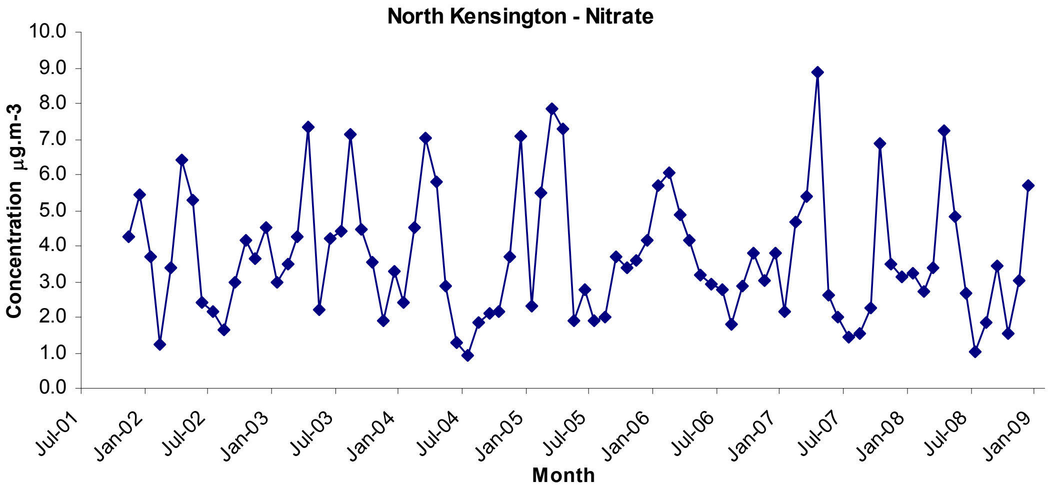


Figure 4-20: Monthly Averaged PM_{10} Nitrate Concentrations (Filter).

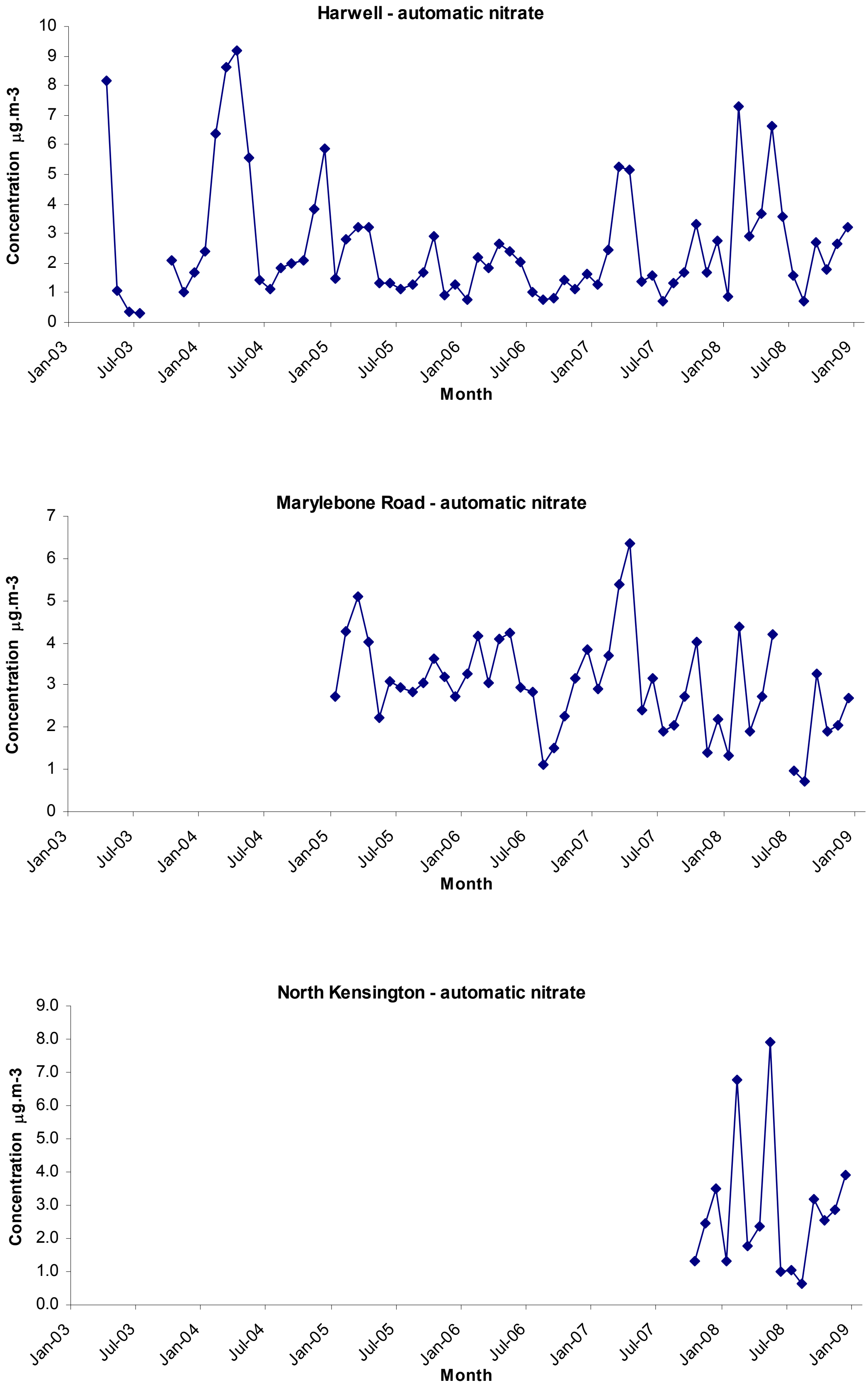


Figure 4-21: Monthly Averaged $PM_{2.5}$ Nitrate Concentrations (Automatic).

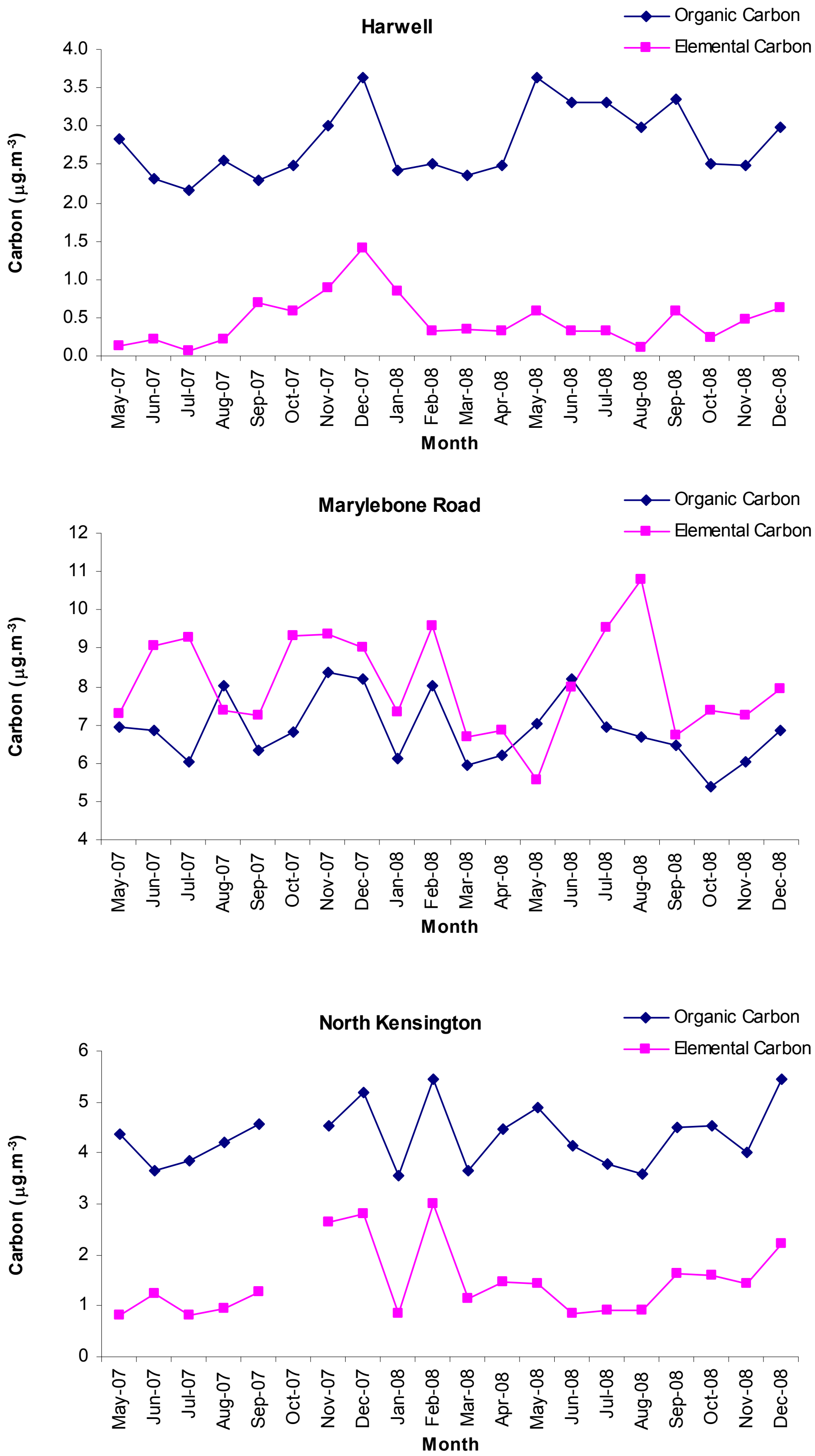


Figure 4-22: Monthly Averages – PM_{10} Daily Elemental and Organic Carbon

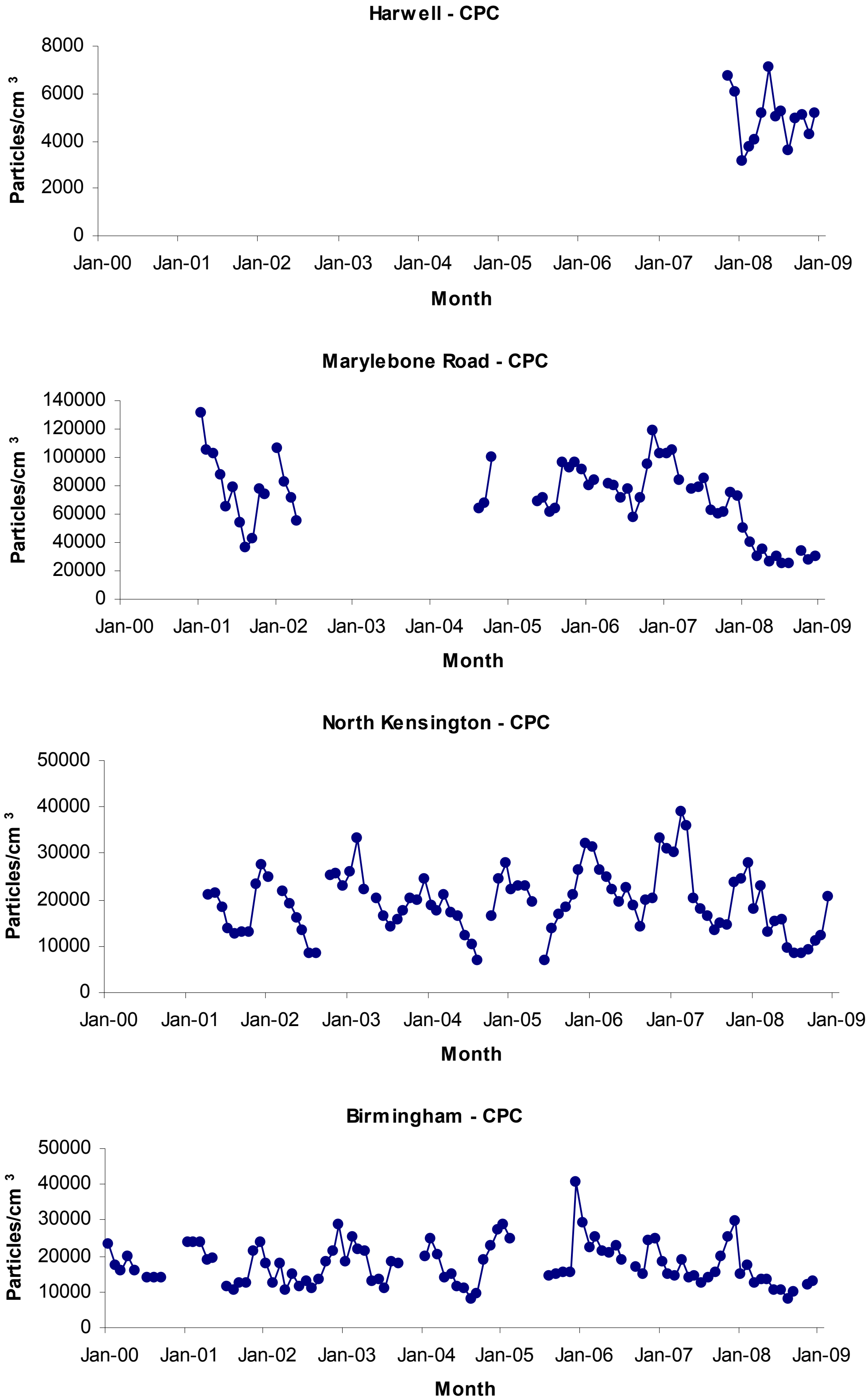


Figure 4-23: Monthly Averages –Particle Counts from CPC.

4.6.3 Diurnal Profiles

Diurnal profiles have been derived for the automatic 'continuous' instruments. The profiles by quarter (January-March, April-June, July-September and October-December) are shown in Figure 4-24 for the nitrate and in Figure 4-25 for the CPC measurements.

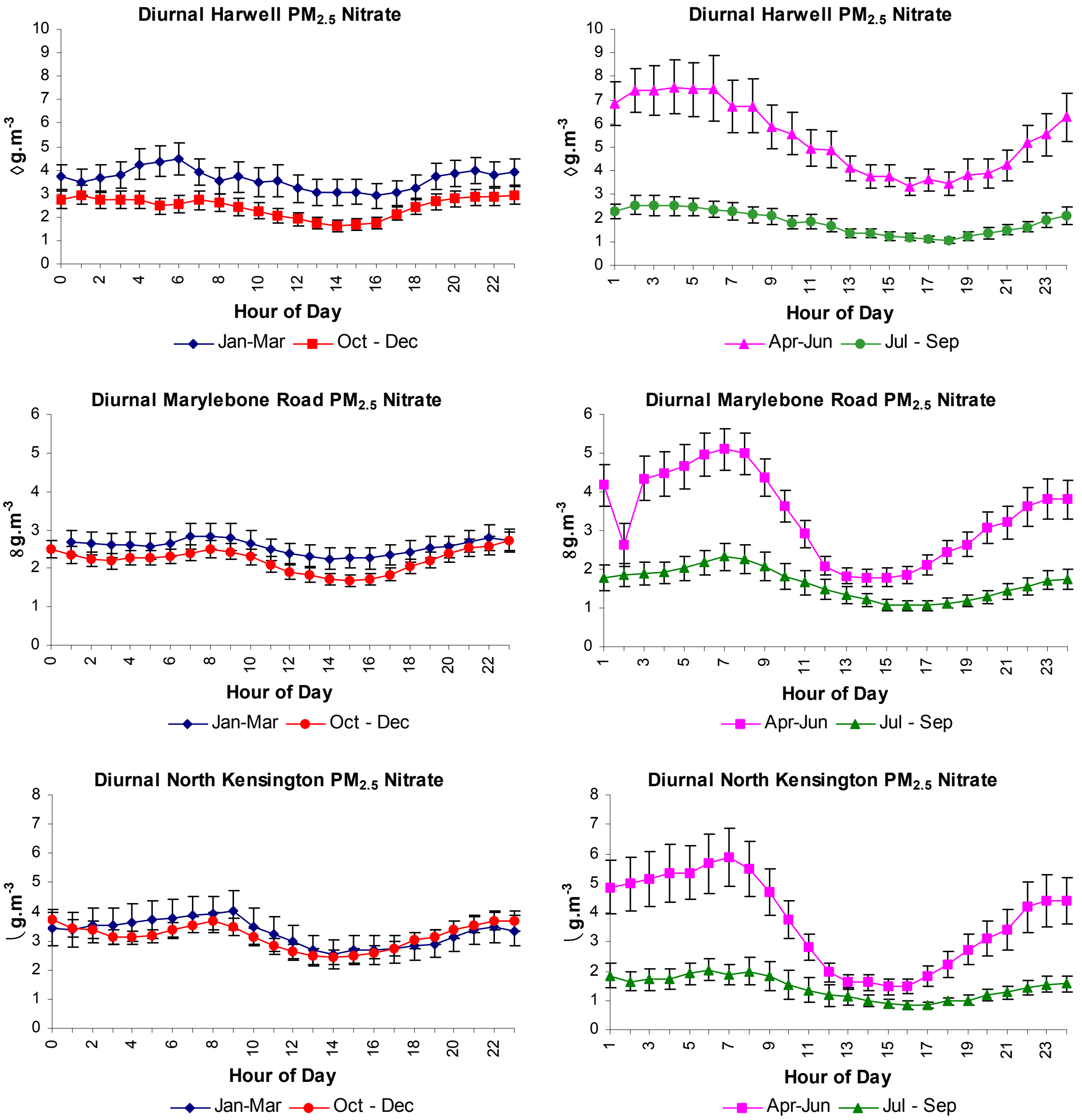


Figure 4-24: Diurnal Profiles of the Automatic Nitrate Concentrations at Network Sites during 2008 by Season.

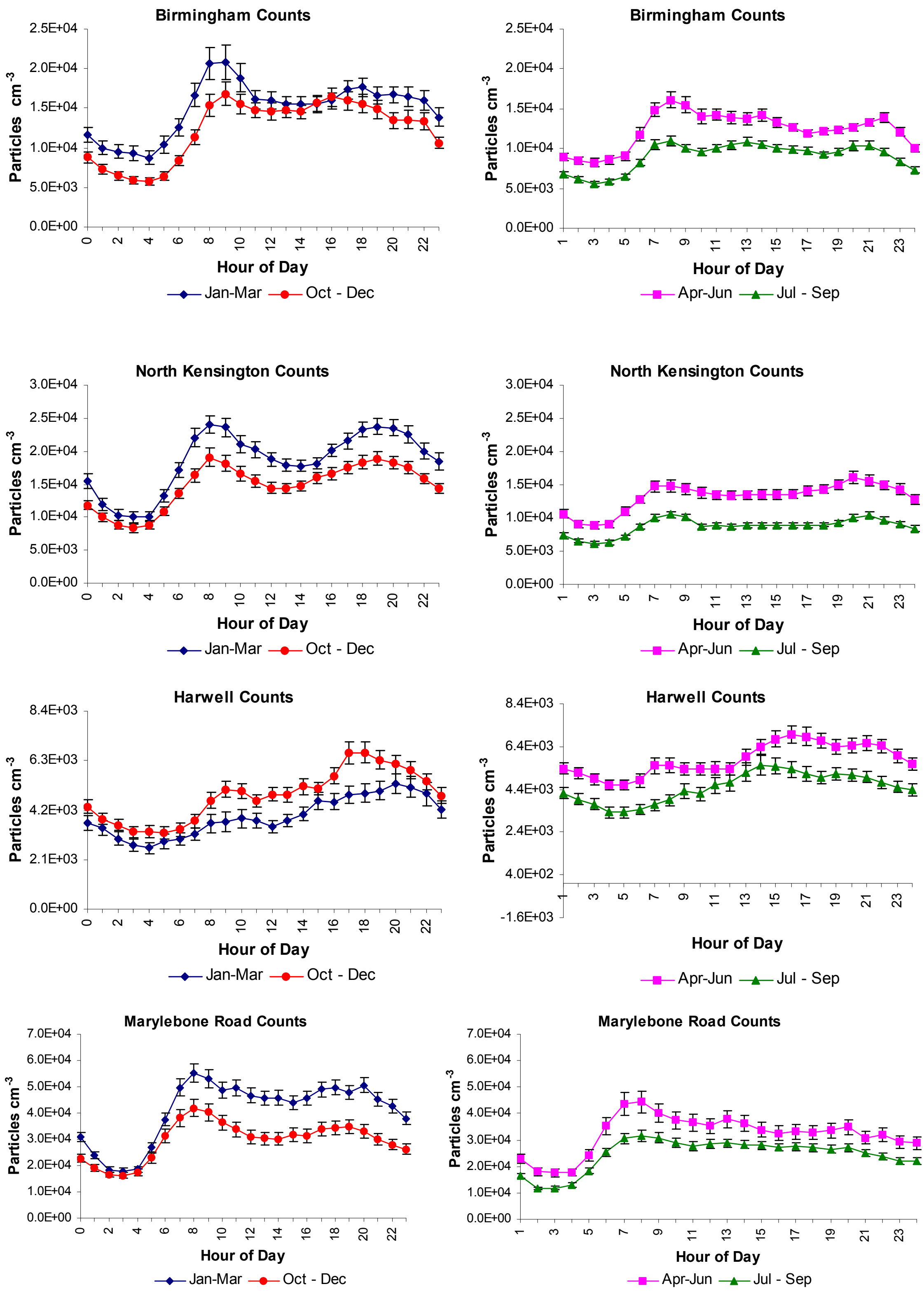


Figure 4-25: CPC Diurnal Profiles by Quarter in 2008

5 Update on the Wider Policy and Research Context

The measurements made within this Network are one research resource in the area of particulate matter. Other sources of data should be borne in mind. In this Section, we identify complementary measurement activities, which will provide additional data (a) to confirm the measurements made in this network or (b) to assist the interpretation of the measurements.

5.1 Update on Related UK Activities

5.1.1 Local Monitoring Activities

The London Air Quality Network (LAQN), operated by King's College London, has two sites, where particle number concentrations (using CPCs) and black carbon (using aethalometers) are determined in addition to PM_{10} and $PM_{2.5}$ mass measurements. These are the roadside sites at Blackwall Tunnel and the North Circular. These measurements are funded by Transport for London to investigate the impact of the London Low Emission Zone, the sites were chosen as they were predicted to see the largest changes in these particle metrics as a result of the LEZ abatement measures.

5.1.2 Defra and Other National Monitoring Activities

AURN measurements of PM_{10} and $PM_{2.5}$

Any investigation of PM must be linked to the officially reported PM_{10} and $PM_{2.5}$ measurements. The discrepancies between the reference gravimetric method and the standard TEOM instrument are well known, and it also become apparent during 2007 that the reference method needs to be very carefully implemented to produce reliable results. Results from this Particle Number and Composition Monitoring network are helping to resolve anomalies in historical gravimetric PM_{10} data, in part through a supplementary study looking at the effects of humidity on both filters and PM, to be reported in early 2009.

Black Smoke Measurements

There are currently 21 sites that make daily Black Smoke measurements using the reflectance of filter samples. Although the conventional Black Smoke index (given in units of $\mu g\ m^{-3}$) is quite different from a measure of elemental carbon, NPL has provided evidence that the black smoke index and the aethalometer measure of black carbon are closely related [Quincey, 2007]. In part because of this, the Black Smoke network instruments have been replaced with aethalometers during 2008, which will provide a much closer link with the elemental carbon data in this network. 3 of the instruments will be located at sites in this network (Harwell, North Kensington and Marylebone Road).

Rural Monitoring

Daily measurements of sulphate, and monthly measurements of nitrate, chloride and ammonium are made at a number of rural sites through the Ammonia and Acid Deposition Monitoring Networks.

As part of the UK implementation of the EMEP monitoring strategy, two sites, Auchencorth Moss and Harwell, have been established to monitor, *inter alia*, particulate matter. The measurements of relevance to this network are those of:

sulphate, nitrate, ammonium, sodium, potassium, calcium and magnesium ions in both the PM_{10} and $PM_{2.5}$ size fractions, on an hourly basis, using a steam-jet aerosol collector;

EC by aethalometry with supplementary analysis of filter samples for EC and OC.

As part of its monitoring activities, EMEP held an intensive monitoring campaign in September and October 2008. Data from Harwell from this Network for that period have been supplied to CEH Edinburgh to help interpret the data from the campaign.

5.2 Update on European Activities

5.2.1 New EU Air Quality Directive 2008/50/EC

The new Directive on Ambient air quality and cleaner air for Europe came into force in 2008. This directive revises and combines the Framework Directive 96/62/EC, the first three "Daughter" Directives, covering sulphur dioxide, NO_x, PM, lead, benzene, carbon dioxide and ozone, and the "Exchange of Information Decision".

Three aspects are relevant to this Network:

- the existing PM legislation is based on control of PM_{10}, while the new Directive places an emphasis on $PM_{2.5}$. Research-led measurements such as those on this Network should therefore make due emphasis on the $PM_{2.5}$ fraction.

- there is more explicit allowance for exceedences arising from "natural sources" to be excluded. Again, research-led measurements should make the determination of the "natural" fraction of PM a clear aim. Wind blown, long-range, transported mineral dust and sea salt are the most important natural sources, but there are many other sources with potentially significant effects that can be attributed to natural sources. The implications for Member States are still being discussed. The issues have been summarised in *Contribution of natural sources to air pollution levels in the EU – a technical basis for the development of guidance for the Member States*, Report EUR 22779 EN (2007).

- Annex IV includes the statement "Measurement of $PM_{2.5}$ must include at least the mass concentration and appropriate compounds to characterise its chemical composition. At least the list of chemical species below shall be included."

SO_4^{2-}	Na^+	NH_4^+	Ca^{2+}	Elemental carbon (EC)
NO_3^-	K^+	Cl^-	Mg^{2+}	Organic carbon (OC)

Many of these components are those currently measured by this Network. There is, however, an evident need to standardise these measurements for EU reporting purposes, which is being addressed as described in the next section.

5.2.2 CEN standards

2008 (and early 2009) has seen considerable CEN activity in the areas covered by this Network.

CEN TC 264 Working Group 15 is in the process of updating the gravimetric PM_{10} standard EN 12341:1998. One aim is to tighten the specifications for filter handling and transport in line with the EN 14907 standard for $PM_{2.5}$. The main outstanding issues are the specifications for "reference" filter material, and the humidity level during weighing. These issues have been the subject of experimental studies funded through JRC Ispra, that will be reported in June 2009.

The working group is also in the early stages of drafting a CEN standard for automatic PM_{10} measurement.

CEN TC 264 WG 32 is to cover particle number concentration and size distribution measurements (ie CPC and SMPS-type). It held its first meeting in January 2009. The main decision was to produce two separate Technical Specifications (as distinct from full Standards), covering:

1) A standard method for measuring "single parameter" particle number concentration, ie a "total" number concentration covering a broad size range, as typically covered by CPCs in ambient measurements. This will provide a "standard" low size cut-off, sampling, operating, QA/QC and calibration procedures, and be readily adoptable as a reference method.

2) Standard methods for measuring particle number concentration over more limited size ranges, as used to form size distributions, ie SMPSs, optical particle spectrometers, time-of-flight spectrometers, electrical low pressure impactors, etc, with appropriate sampling, operating, QA/QC and calibration procedures.

CEN TC 264 WG 34 will cover anion and cation analysis. CEN TC 264 WG 35 will cover Elemental Carbon and Organic Carbon. These two groups are due to hold their first meetings in May 2009. There was a preliminary workshop in February 2009 covering both topics.

5.2.3 EUSAAR

The EUSAAR project (European Super-sites for Atmospheric Aerosol Research) includes 20 sites across Europe including Harwell. Amongst other topics it makes recommendations for standardizing measurements with CPCs and SMPSs, and of EC/OC.

For example, it has recommended that SMPS instruments should standardise the aerosol size distribution by sampling under dry conditions (<40% RH). Changes to sampling systems in the UK Network to conform with this are currently being implemented. In early 2009 it has made wider-ranging proposals for CPC and SMPS measurements:

Sampling

Ambient sample to be "dry" (<40% RH); sample RH to be actively dried and the RH monitored.

Ambient sample flow rate to be monitored continuously, with corrective measures for deviations >5%.
Sheath air to be "dry" (<40% RH); sheath air RH to be actively dried and the RH monitored.
Sheath air flow rate to be monitored continuously, and actively controlled to +/- 2% (volumetric).
Temperature and pressure in the DMA to be monitored continuously.

Calibration and checks

Flow rates checked monthly with eg a bubble flow meter, and properly calibrated twice a year.
Humidity sensors calibrated initially and at least once a year.
The DMA voltage supply is calibrated "prior to deployment".
CPCs are calibrated at least once a year, including flow, "plateau" detection efficiency and efficiency curve at low size.
SMPS systems calibrated for size using 200 nm polystyrene latex spheres once a year.
SMPS systems to be compared with a "reference" system for a few days a year (on site or at a lab comparison)

Data storage and reporting

There is a formal hierarchy:

Level-0
Basic parameters of the system.
Storage of "raw" data - CPC concentration against nominal particle size (ie equivalent Stokes diameter for singly charged particles at the particular voltage).
Flagging system for missing data or problems.

Level-1
Processed data (corrections for multiple charge, CPC efficiency, diffusion losses within the SMPS, sampling losses, optional "system calibration" data) with the original time resolution of the instrument.
The corrections are to be described in a "Read-Me" file.

Level-2
Final size distributions with 1 hour time resolution, corrected to STP, with simple statistics (mean, median size, plus 15.87 and 84.13 percentiles).

NPL and KCL have commented on these proposals in the context of their effect in the UK Network.

EUSAAR’s ongoing development of recommendations for methods for EC/OC will be influential in CEN TC 264 WG 35 and in EMEP. It should be noted that their proposed methods (essentially revised temperature profiles for analysis using Sunset Labs-type instruments) have been optimized for rural PM samples, and may not be suitable for roadside samples.

5.3 ISO Standards

The most relevant standards being developed by ISO TC24 SC4 are:

ISO/DIS 15900, *Determination of Particle Size Distribution – Differential Electrical Mobility Analysis for Aerosol Particles* – i.e. measurements using SMPS. This is close to publication. This standard does not include requirements for calibrating the number concentration part of the measurement – i.e. CPCs.

ISO Preliminary Work Item 27891, *Aerosol particle number concentration – calibration of condensation particle counters* is at an early stage. It will be aimed at users (especially those with internal calibration programmes), instrument manufacturers who certify their equipment, and specialist calibration laboratories (including NMIs). Traceability is ultimately expected to be to the NMI structure.

Specifically the standard will cover calibration with an aerosol electrometer, and calibration with a "reference" ie certified CPC. There will be Informative Annexes on flow splitting, flow calibration, multiple charge issues, uncertainty due to size uncertainty, data recording, and effects of aerosol material and morphology.

The overlap in scope with CEN TC 264 WG32 has been noted. Paul Quincey (NPL) is a member of both committees.

5.4 Low Emission Zone

The characterization of the chemical composition of PM is of particular importance in London. Roadside locations in London were the only areas identified as likely to exceed the PM_{10} objective in the recent UK application to the European Commission for an extension to meet PM_{10} air quality limits. An understanding of the chemical composition is vital to understand the impact of local, regional, national and international emissions abatement.

London is also the subject of the largest Low Emission Zone in the UK, which began in February 2008 with emissions restrictions for heavy lorries. Further emissions restrictions for lighter lorries were bought in during July 2008; the emissions standards for both these vehicle classes will be further tightened in January 2012. The extension of the LEZ to large vans and minibuses, planned for 2010, is currently under review. These improved emissions standards will have the largest impact at traffic influenced locations in London, such as Marylebone Road. The detection of changes in PM concentrations and the change in chemical composition at these traffic influenced locations in London is therefore of particular interest. The chemical speciation of PM_{10} helps to source apportion the traffic related component of PM and detect changes in concentration due to emissions abatement.

6 Update on Instrumentation

6.1 Replacement Instruments

Hourly measurements of nitrate in the $PM_{2.5}$ size fraction are currently made using automatic analysers (Thermo/R&P 8400N), but the analyser is no longer made and supported by the manufacturer. Alternative instrumentations include the URG Ambient Ion Monitor (AIM), and the Applikon Particle Into Liquid Sampler (PILS). Both of these instruments consist of sample inlet and particle collection system followed by analysis by ion chromatography. Both are specifically designed for field operation and are similar in price. The AIM has been installed and assessed at NPL and it has been considered a good replacement for the current automatic nitrate analyser. A report will be written recommending the purchase.

6.2 EUSAAR Recommendations for SMPS measurements

The EUSAAR project (European Super-sites for Atmospheric Aerosol Research) includes 20 sites across Europe including Harwell. It has recommended that SMPS instruments should standardise the aerosol size distribution by measuring under dry conditions (<30% RH). The SMPS and CPC instruments at Harwell underwent an audit by the EUSAAR project team during November 2007. Several recommendations were made:

(1) Replace inherited copper pipe work and 'funnel' sampling inlet with a PM_1 sampling head and stainless steel tubing.

(2) Provide a calibrated flow meter (for example, a BIOS dry-cal meter or Gilian Gilibrator bubble meter) for the LSO to measure the flow rate of the CPC and SMPS fortnightly.

(3) Provide an ultrasonic bath for the cleaning of the SMPS impactor.

(4) Install humidity control and monitoring on the sample line, in the form of a drier and humidity sensor.

(5) Ensure that the Harwell site operator has access to documentation on instrument performance and measurement quality, either in written form at the site or as a detailed online log accessible form the site at any time.

Following from these recommendations, NPL has provided an ultrasonic bath at all SMPS sites and is in discussion with King's College on the provision of the Harwell instrument log to the site operator, either via e-mail or a web portal.

An upgrade of the SMPS instruments has been proposed and accepted by Defra to control humidity. As changes in humidity can affect the aerosol size distribution, the major change proposed to the sampling train is the introduction of driers to condition and regulate the humidity of the sample. This will greatly assist the analysis and interpretation of the SMPS measurements. It is expected that there will also be significant operational benefits. The lower water content of the samples will reduce contamination and the need to drain the CPC instruments, major reasons for instrument downtime. One system is being built and will be tested at NPL.

7 Topic Reports and Publications

Reports and papers produced or published since the start of the contract include:

7.1 Project and Topic Reports

May 2005-April 2006

CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2). State of Network Report, NPL Report DQL-AS 019, September 2005

CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2). Strategic Network Review, NPL Report DQL-AS 020, November 2005

CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2). Annual Report 2005, NPL Report DQL-AS 028, Revised July 2006

May 2006-April 2007

CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2). Annual Audit Report, NPL Report DQL-AS 031, July 2006

Comparison of Methods for Organic and Elemental Carbon PM_{10} Concentrations at Marylebone Road for the Period 07/09/06 to 31/12/06, NPL Report DQL-AS 035, February 2007

CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2). Estimation of Measurement Uncertainty in Network Data, NPL Report DQL-AS 037, March 2007

CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2). Annual Report 2006, NPL Report AS4, Revised April 2007.

May 2007-April 2008

Monitoring of Particulate Nitrate by Rupprecht & Patashnick 8400N Ambient Particulate Nitrate Monitors, A.M. Jones and R.M. Harrison, August 2007.

CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2). Annual Audit Report, NPL Report DQL-AS 016, October 2007.

Comparison of Cluster Analysis Techniques Applied to Rural UK Atmospheric Particle Size Data, D.C.S. Beddows and R.M. Harrison, Draft, December 2007.

Change in particle number concentration from 2000 to 2006 at four UK sites, A.M. Jones and R.M. Harrison, March 2008.

The weekday-weekend difference and the estimation of the non-vehicle contributions to the urban increment of airborne particulate matter, A.M. Jones, J.Yin and R.M. Harrison, *CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2). Annual Report 2007.*

7.2 Publications

Multisite Study of Particle Number Concentrations in Urban Air, R.M. Harrison and A.M. Jones, Environmental Science and Technology, **39**, 6063-6070 (2005).

The Use of Trajectory Cluster Analysis to Examine the Long-Range Transport of Secondary Inorganic Aerosol in the UK, S.S. Abdalmogith and R.M. Harrison, Atmospheric Environment, **39**, 6686-6695 (2005).

Interpretation of Particulate Elemental and Organic Carbon Concentrations at Rural, Urban and Kerbside Sites, A.M. Jones and R.M. Harrison, Atmospheric Environment, 39, 7114-7126 (2005).

Fine ($PM_{2.5}$) and Coarse ($PM_{2.5-10}$) Particulate Matter on a Heavily Trafficked London Highway: Sources and Processes, A. Charron and R.M. Harrison, Environmental Science and Technology, **39**, 7768-7776 (2005).

An Analysis of Spatial and Temporal Properties of Daily Sulphate, Nitrate and Chloride Concentrations at UK Urban and Rural Sites, S.S. Abdalmogith and R.M. Harrison, J. Environmental Monitoring, **8**, 691-699 (2006).

Particulate Sulphate and Nitrate in Southern England and Northern Ireland during 2002/3 and its Formation in a Photochemical Trajectory Model, S.S. Abdalmogith, R.M. Harrison and R.G. Derwent, Science of the Total Environment, **368**, 769-780 (2006).

Intercomparison of Secondary Inorganic Aerosol Concentrations in the UK with Predictions of the Unified Danish Eulerian Model, S.S. Abdalmogith, R.M. Harrison and Z. Zlatev, Journal of Atmospheric Chemistry, **54**, 43-66 (2006).

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9 Acknowledgements

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Annex 1. Network Instruments

Network Structure

Site	Hourly $PM_{2.5}$ nitrate	Daily PM_{10} (anions)	Daily PM_{10} (OC/EC)	CPC	SMPS
Birmingham Centre (Urban centre)				x	
Harwell (Rural)	x	x	x	x	x
North Kensington (Urban background)	x	x	x	x	x
Marylebone Road (Roadside)	x	x	x	x	x

Equipment models:

Hourly nitrate	Thermo 8400N
Daily PM_{10} filter	Thermo Partisol 2025
CPC	TSI model 3022A
SMPS	TSI model 3936

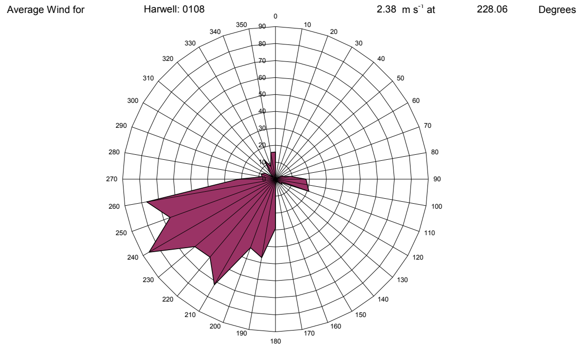
Annex 2. Automatic Nitrate Instrument Repairs

Site	Instrument	Date	Fault
Harwell	Nitrate	03/01/08	Analyser communication failure. CPU replaced.
		25/02/08	Temperature sensor replaced.
		14/05/08	Temperature sensor replaced.
		19/06/08	High and erratic flow.
		12/08/08	High and erratic flow.
		11/12/08	Strong smell of ozone. Charcoal bag to the exhaust replaced.
Marylebone Road	Nitrate	07/03/08	Ozone and sample flow warnings
		30/05/08	Analyser communication failure.
		06/12/07	NOx reaction cell changed.
North Kensington	Nitrate	28/03/08	Temperature and pressure sensors replaced.

Annex 3. Wind Roses at Harwell and Rochester

Wind Roses – Harwell, January-June 2008

January 2008



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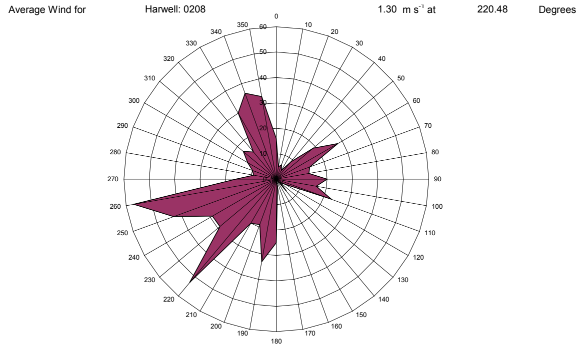

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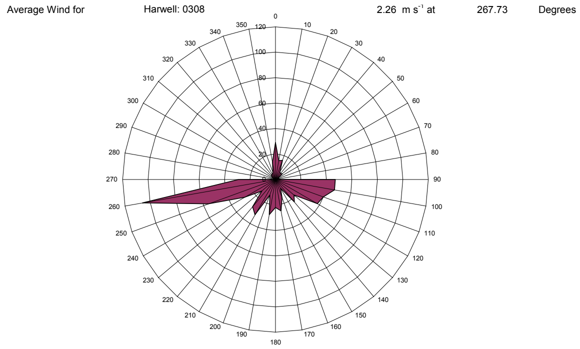

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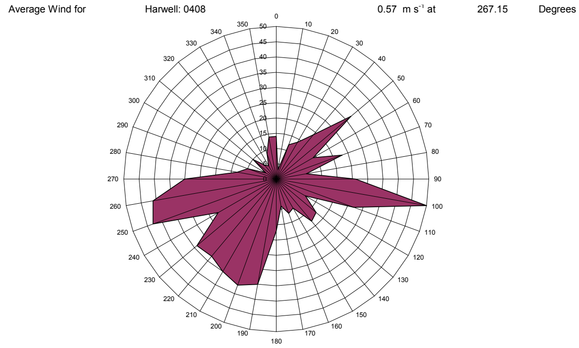

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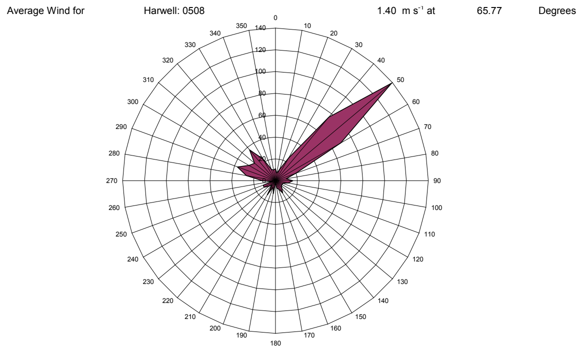
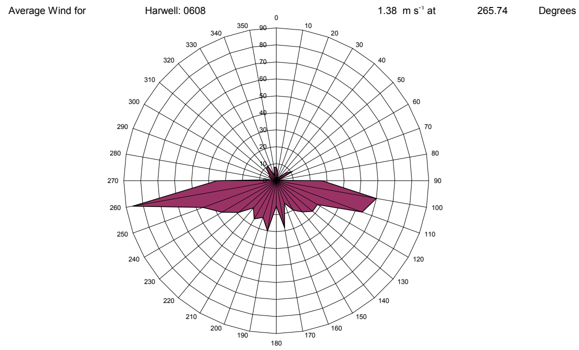
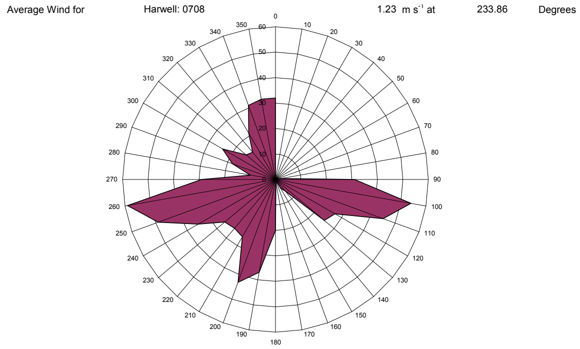


June 2008



Wind Roses – Harwell, July-December 2008

July 2008



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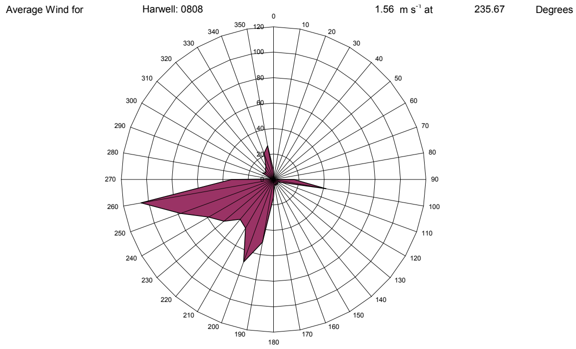

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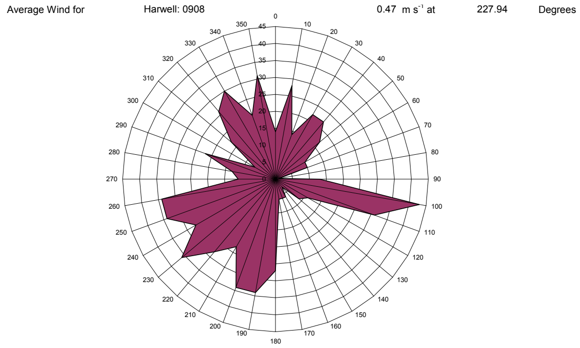

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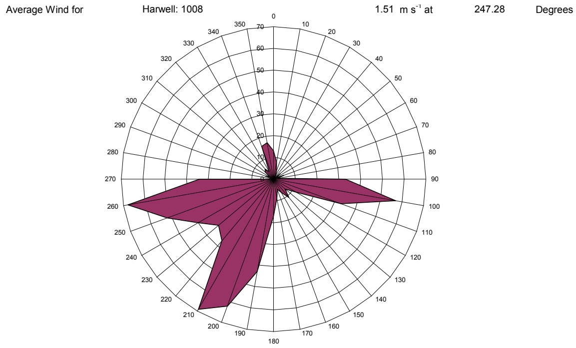

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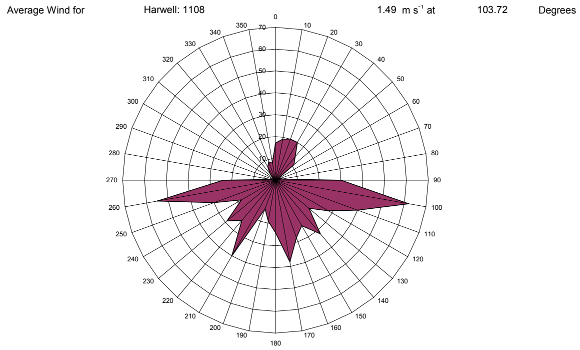

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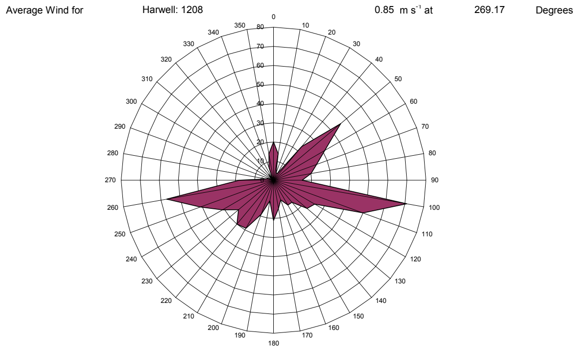
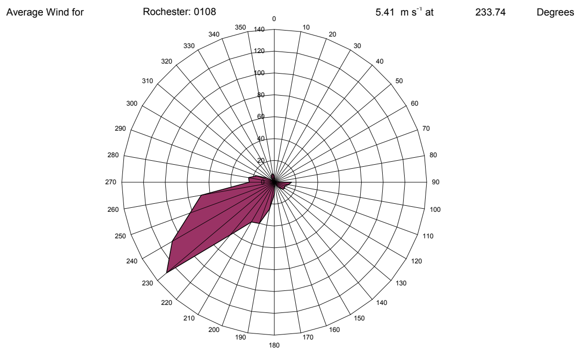


Wind Roses – Rochester, January-June 2008

January 2008



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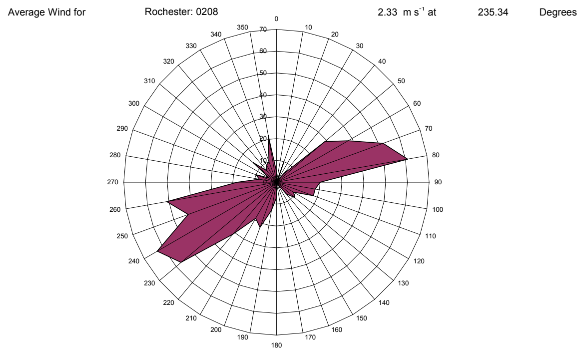

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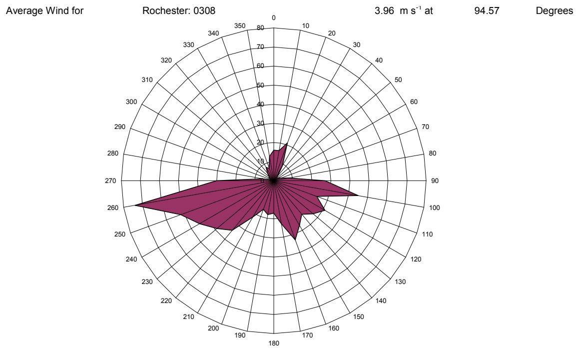

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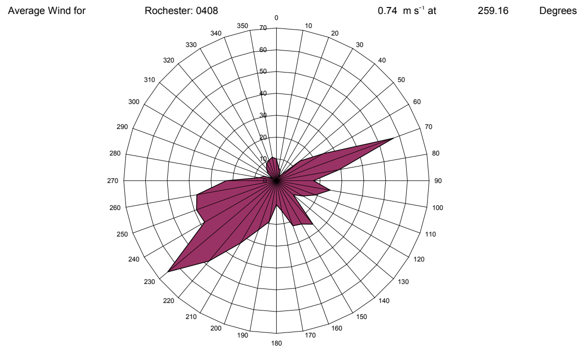

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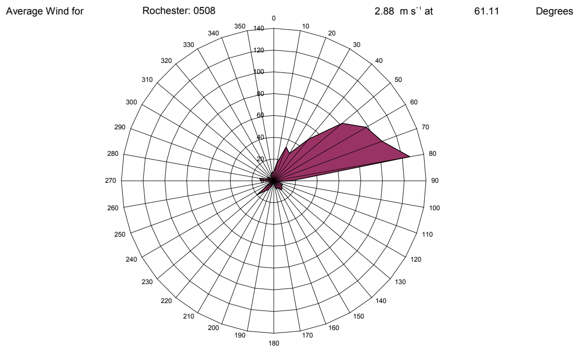

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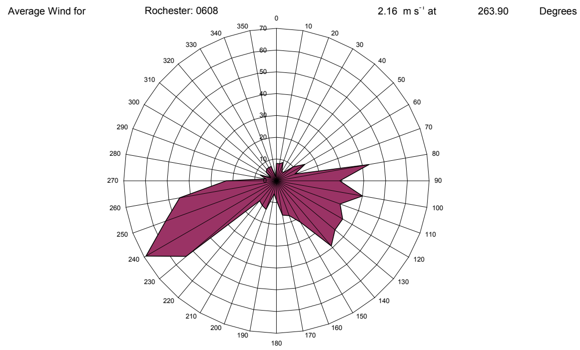
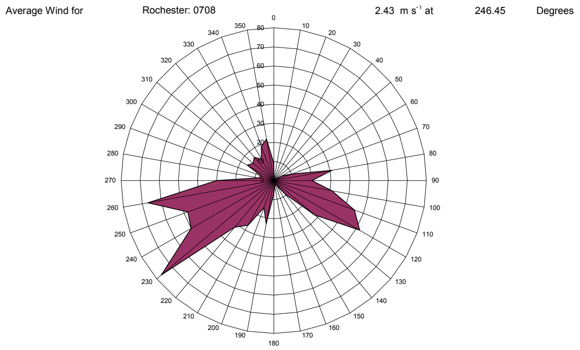


Wind Roses – Rochester, July-December 2008

July 2008



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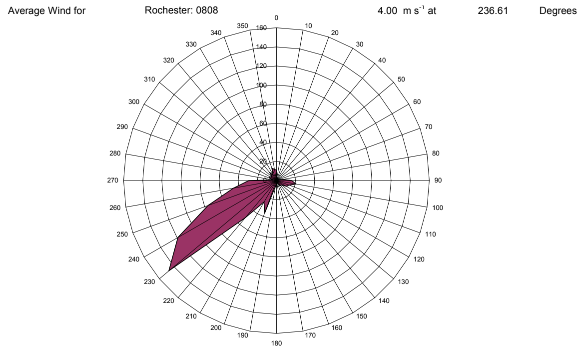

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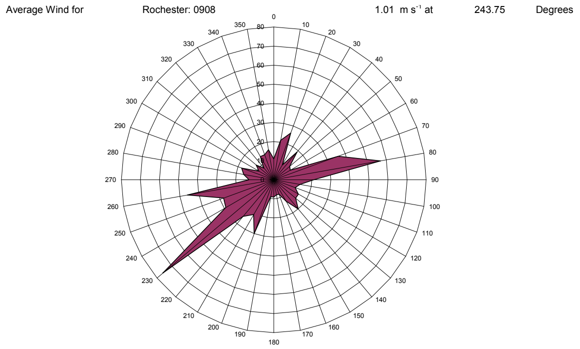

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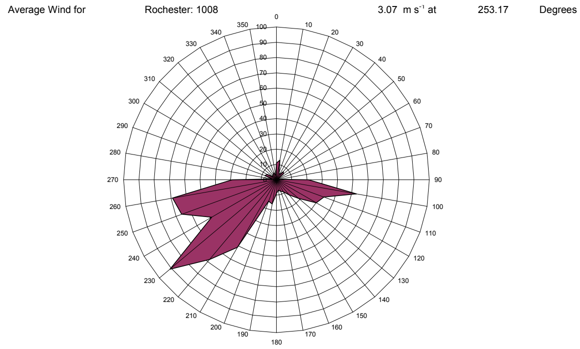

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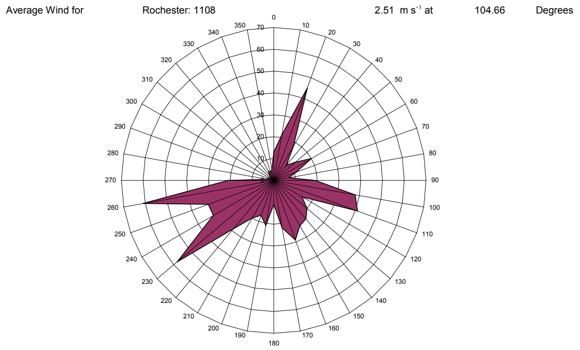

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