NPL
National Physical Laboratory

Report

NPL REPORT AS 25

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

Annual Report - 2007

Garry Hayman
Rachel Yardley
Paul Quincey
David Butterfield
David Green
Jon Alexander
Paul Johnson
Anja Tremper

NOT RESTRICTED

June 2008

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

Annual Report - 2007

National Physical Laboratory:
Garry Hayman
Rachel Yardley
Paul Quincey
David Butterfield

King's College London:
David Green
Jon Alexander
Paul Johnson
Anja Tremper

ISSN 1754-2928

National Physical Laboratory
Queens Road, Teddington, Middlesex, TW11 0LW

Approved on behalf of Managing Director, NPL
By Martyn Sené, Division Director, Division of Quality of Life

Annual Report for 2007 on the UK Airborne Particulate Concentrations and Numbers Network

Version History

Version	Version Number	Date Available
Initial Draft For internal review	Particles Network Annual Report 2007 v2_08Apr.doc	11th April 2008
Draft to Defra Submitted for external review by Defra and Devolved Administrations	NPL REPORT AS 25 Particles Network Annual Report 2007 Draft_08Apr.doc	30th April 2008
Issue 1 Incorporating comments from Defra and the Devolved Administrations	Particles Network Annual Report 2007 Final_08Jun.doc	19th June 2008

Annual Report for 2007 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 2007 and contains:

- A summary of network operation and quality procedures
- A graphical presentation of all validated and ratified network data from 2007
- Data capture per instrument per month
- Comparison of 2007 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

There has been a major restructuring of the network during 2007. This has involved removing instruments from some sites, in a bid to focus attention on a few key sites where the resulting data will be most useful to policy-makers and researchers. Particle–sizing equipment was introduced at three key sites, Marylebone Road, North Kensington and Harwell, in March 2007, and the manual analysis of daily concentrations of elemental and organic carbon began in May 2007.

All equipment was audited during the annual audit round in July, 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.

In conclusion, the network has operated smoothly during 2007 despite the several changes made to the network to improve operation and data quality. This report outlines plans for future improvements to the network.

Table of Contents

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 2007 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 2007
- Comparison of 2007 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 2007 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 May 2007, NPL's contract with Defra to operate this network was extended by two years. The contract extension included restructuring the network and details of this are given in the sections below.

2.2 Improvements to Network Operation

2.2.1 Computer Installations

Following several laptop failures resulting in loss of data in 2006, new computers were purchased in 2007 to replace the old and unreliable hardware. Three rugged laptops were purchased for the data handling of CPCs and SMPSs at sites where space was limited. The remaining CPCs and SMPSs were issued with a small-form 'shoebox' computer. Since the installation of this new hardware there has been no data lost through computer failure.

2.2.2 North Kensington Site

Space restrictions at North Kensington prompted NPL to make some modifications to the site hut prior to the installation of an SMPS and automatic nitrate analyser. The North Kensington monitoring station is situated in the grounds of Sion-Manning RC Girls' School. Approval was sought from the school governors and the Royal Borough of Kensington and Chelsea Council to build an external cylinder cage and to install a radioactive source (Kr-85 neutraliser in the SMPS). These modifications were carried out during August 2007.

2.2.3 Anion and Carbon Analysis

Analysis of the daily Partisol filters for nitrate, sulphate and chloride is carried out by ion chromatography. Between January and April 2007 these analyses were performed by King's College London. From May to December 2007 the work was done by NPL. In order to allow the analysis of organic and elemental carbon from the same filter, the filter type was switched from Emfab (PTFE-coated glass fibre) to ultrapure quartz fibre in October 2007. There has been no step-change in the results.

2.2.4 Nitrate Analysers

Previous audit reports have highlighted potential problems with the converter efficiency of the molybdenum converters in the automatic nitrate instruments. The converters were changed, tested and recalibrated by Air Monitors during routine service visits in 2007.

Local site operators have reported difficulties carrying out the manual aqueous calibrations. Until December 2007 one standard nitrate solution was supplied, and LSOs were required to apply different volumes of the standard to the analyser flash strip to generate a calibration curve. However, the calibrations were sometimes unreliable due to problems caused by small droplets refusing to leave the syringe, and large volumes overflowing the flash strip. In December 2007 NPL issued an updated procedure and four nitrate solutions of varying concentrations. Now the spiking volume is always constant and the repeatability is much improved.

2.2.5 SMPS Analysers

Following an NPL intercomparison of two commercially available SMPS analysers in 2006, the TSI analyser (model 3936L75) was judged to be most suitable for the network. Three new systems were installed at Bloomsbury, Harwell and Marylebone Road in March 2007. NPL have registered the three Kr-85 sources with the Environment Agency, in accordance with the 1993 Radioactive Substances Act.

Shortly after the installations, the three SMPS units started to suffer from blocked orifices and restricted flows. This was traced back to a problem during the instrument manufacture. None of the new CPCs in the SMPS systems were fitted with make-up air filters and the orifice pressure limits were set up incorrectly during installation. The affected instruments were each returned to TSI for corrective action. The instruments are now operating correctly.

In November 2007, the SMPS and CPC at Harwell underwent an audit by the European Supersites for Atmospheric Aerosol Research (EUSAAR) project team. This is discussed further in Section 6.3. Following from these recommendations, NPL has provided an ultrasonic bath at all SMPS sites. The other proposals are being investigated and costed for Defra's consideration in the future.

2.3 New Network Structure

There has been a major restructuring of the network during 2007. This has involved (a) closure of some sites (and subsequent removal of the instruments), in a bid to focus attention on a few key sites where the resulting data will be most useful to policy-makers and researchers; and (b) change in instrumentation to address performance issues, for example, with the automatic EC/OC measurements. Particle–sizing equipment was introduced at the three key sites, Marylebone Road, North Kensington and Harwell, in March 2007, and the manual analysis of daily concentrations of elemental and organic carbon began in May 2007.

By June 2007, the following instrumentation had been removed from sites as part of the network restructuring:

Belfast:	Carbon, Nitrate, CPC and Partisol
Bloomsbury:	SMPS
Manchester:	CPC
Port Talbot:	CPC
Glasgow:	CPC (no longer operated under the contract CPEA 28, but the instrument remains at the site for operation by Strathclyde University).

Additional equipment has been installed at Harwell (CPC) and North Kensington (SMPS and Nitrate). The new network structure is detailed in Table 2-1.

Table 2-1: New Network Structure

Site	Hourly $PM_{2.5}$ nitrate	Daily PM_{10} filter (anions)	Daily EC/OC	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 (Kerbside)	x	x	x	x	x

Safety assessments have been reviewed and Portable Appliance Testing carried out at the retained sites.

During 2008, aethalometers are to be installed at Marylebone Road, North Kensington and Harwell, to provide hourly concentrations of black carbon (related to elemental carbon) at these sites. These installations are scheduled to take place between May 2008 and October 2008.

2.4 Instrumentation

A list of network instruments can be found in Annex 1. Annex 2 contains a map showing the locations of the deployed instruments. 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].

2.4.1 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 ~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.

2.4.2 Automated Nitrate and Carbon Analysers

Both systems operate on broadly similar principles. For the nitrate analyser the particulate content of the air is sampled onto a flash strip via an internal cyclone inlet. For the carbon analyser the particulate content of the air is sampled through a size selective inlet and then collected by an impactor. In the case of the nitrate analysers, the system flash heats the particulate matter and the quantity of NO_x produced is analysed, and in the case of the carbon analysers, CO_2 is produced. In the latter case the combustion is initially performed at a temperature of 320°C to 370°C to determine the organic carbon content and subsequently at a temperature of 650°C to 700°C to determine the elemental or 'soot' carbon content.

2.4.3 Inorganic Anions (Sulphate, Nitrate and Chloride)

Daily measurements of the inorganic components of PM_{10} (sulphate, nitrate and chloride) were made using a Thermo Partisol 2025 sequential air sampler. Until October 2007, the PM_{10} samples were collected on glass fibre filters (Emfab, PTFE-bound glass fibre). From October 2007, ultrapure quartz filters have been used to allow for the analysis of EC/OC in addition to 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.

2.4.4 Elemental and Organic Carbon

From May 2007, elemental and organic carbon (EC/OC) concentrations in ambient air have been determined from filters. Between May 2007 and October 2007, the determination has been made from quartz fibre filters provided by Bureau Veritas. As indicated above, NPL switched the filter type in the ‘anion’ Partisol samplers from Emfab (PTFE-coated glass fibre) to ultrapure quartz to allow for the analysis of EC/OC.

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 carbon 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 all 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, and the results were published in October 2007
- 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 5400 carbon and 8400N nitrate analysers are calibrated with CO_2 and NO, which are certified at NPL and are 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 (see Section 6.3).

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 carbon analysers, and the Partisols are serviced twice yearly by the ESU, Air Monitors. The service procedure includes replacing old or worn parts, calibration of NOx analyser and CO_2 sensor, temperature and flow calibrations, leak tests and pump refurbishment. The services completed during 2007 are indicated in Table 3-1:

Table 3-1: Equipment Services completed during 2007 for Partisol, Carbon and Nitrate Analysers

Site	Instruments	Service 1	Service 2
Belfast	Partisol	14/03/07	Shut down
	Carbon	14/03/07	Shut down
	Nitrate	14/03/07	Shut down
Harwell	Partisol	27/03/07	27/09/07
	Carbon	27/03/07	Shut down
	Nitrate	27/03/07	27/09/07
Marylebone Road	Partisol	29/05/07	23/10/07
	Carbon	09/05/07	Shut down
	Nitrate	09/05/07	23/10/07
North Kensington	Partisol	06/04/07	09/10/07
	Carbon	06/04/07	Shut down
	Nitrate	Not installed	24/09/07

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.

Table 3-2: Annual CPC Service and Calibration Dates

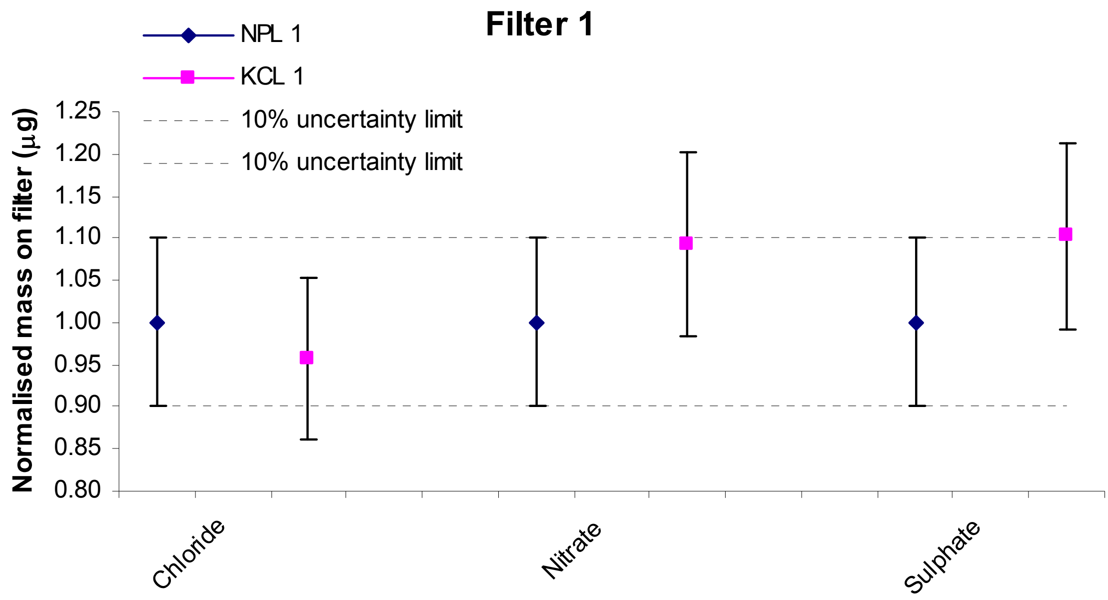
Site	05/06 service	06/07 service	07/08 service
Belfast	16/02/06	24/02/07	Shut down
Birmingham	21/07/05	11/08/06	18/10/07
Glasgow	17/11/05	24/11/06	Shut down
North Kensington	24/04/06	26/03/07	09/04/08
Marylebone Road	15/09/05	17/10/06	15/11/07
Manchester	10/10/05	03/11/06	Relocated
Port Talbot	10/08/05	20/09/06	Shut down
Harwell	-	-	08/01/08

3.2 Intercomparisons of Anions on Filters

The daily Partisol filters are analysed for nitrate, sulphate and chloride using ion chromatography. Between January and April 2007, these analyses were performed by King's College London. From May to December 2007, the work was done by NPL. To ensure the continuity of the data produced, an intercomparison between the two laboratories was carried out during the handover period.

In July 2007, NPL gravimetrically prepared two standard solutions, each containing a different concentration of each anion (in the range expected from the network). An aliquot of each solution was analysed by KCL using its standard operating procedure and each result was found to agree with the gravimetric value within the uncertainty of the measurement at the 95% level of confidence.

Additionally, NPL accurately bisected two sampled filters and both laboratories analysed one half of each filter to compare the extraction efficiency of the laboratories. The results from this intercomparison are shown in Figure 3-1, and demonstrate agreement within an acceptable uncertainty.



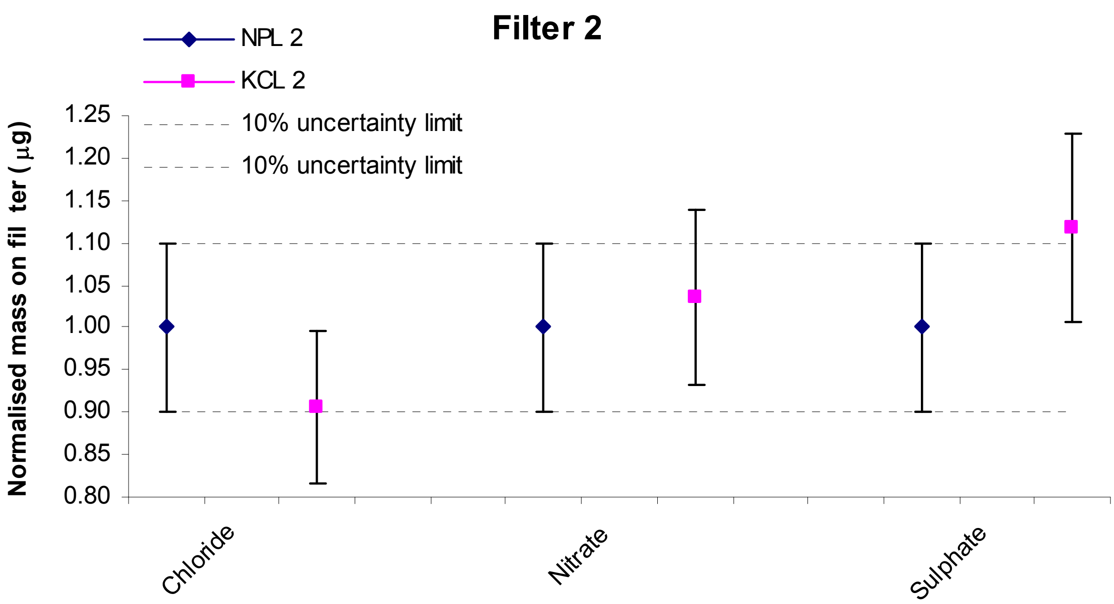


Figure 3-1: Results of the Ion Chromatography Intercomparison between NPL and King's College London – Filter 1 [Upper Panel] and Filter 2 [Lower Panel].

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 2007 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

Daily measurements of particulate sulphate, nitrate and chloride in the PM_{10} fraction were made at 4 sites during 2007 (Belfast, Harwell, North Kensington and Marylebone Road). The extracts from the filters exposed between January to May (inclusive) were analysed by ion chromatography at King's College London. The extract from the filters exposed from June to December were analysed at NPL by a similar method. 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 2007 are displayed in Figure 4-2 to Figure 4-4, respectively. Figure 4-4 also includes the automatic nitrate measurements for comparison (see Section 4.2.2).

There were a number of periods of elevated sulphate and nitrate concentrations, most notably in March and April 2007. The nitrate episode at the end of March is seen at a number of sites and is also seen in the automatic nitrate measurements (see lower panels of Figure 4-4). As an example, the FLEXTRA trajectory arriving at Harwell at midday on 28th March 2007 (see Figure 4-1) is typical of airflows from the east associated with elevated concentrations over the UK.

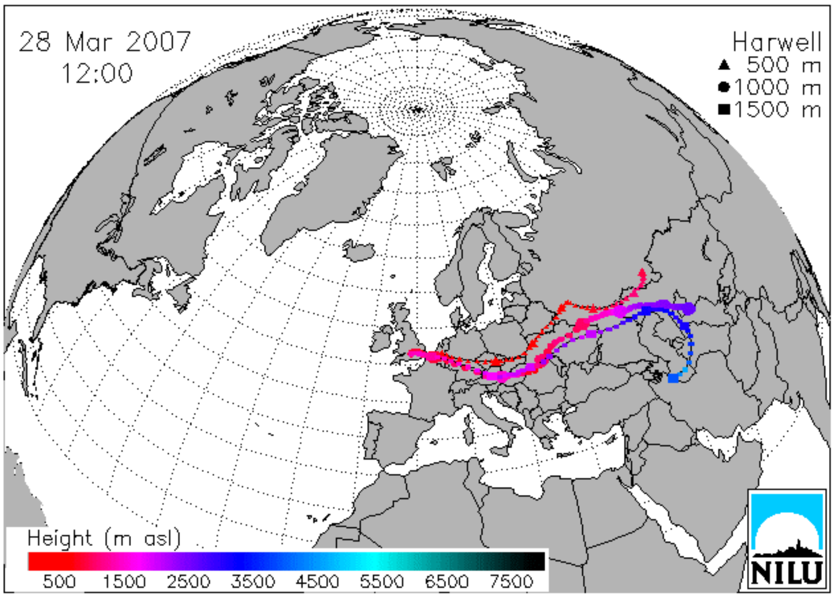


Figure 4-1: FLEXTRA Airmass Trajectories arriving at Harwell at Midday on 28th March 2007.

The elevated sulphate concentrations at Marylebone Road around mid-December 2007 were seen in a number of other PM measurements at this site and also North Kensington (see Figure 4-13 later).

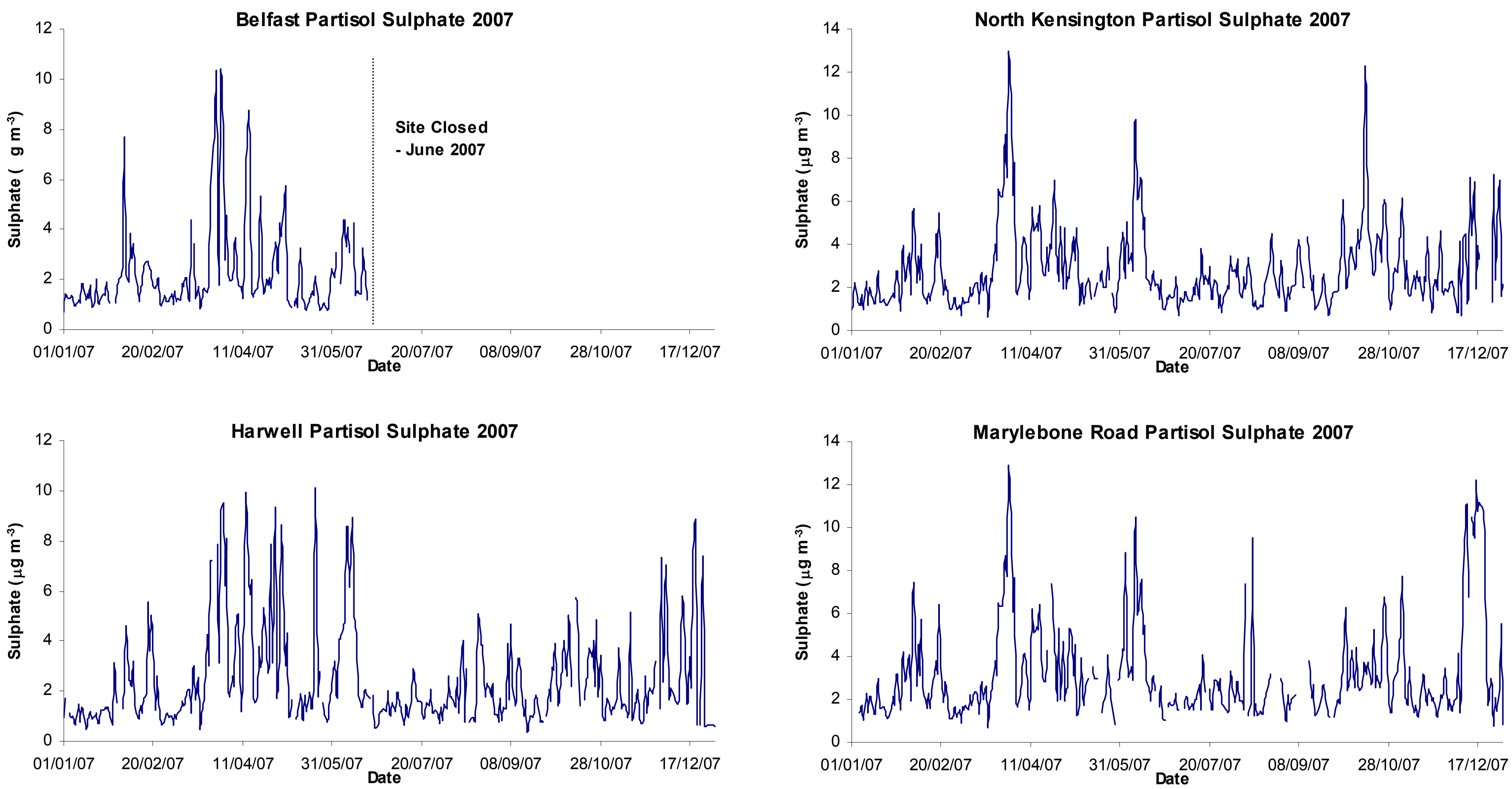


Figure 4-2: Partisol Sulphate Concentrations at Network Sites during 2007.

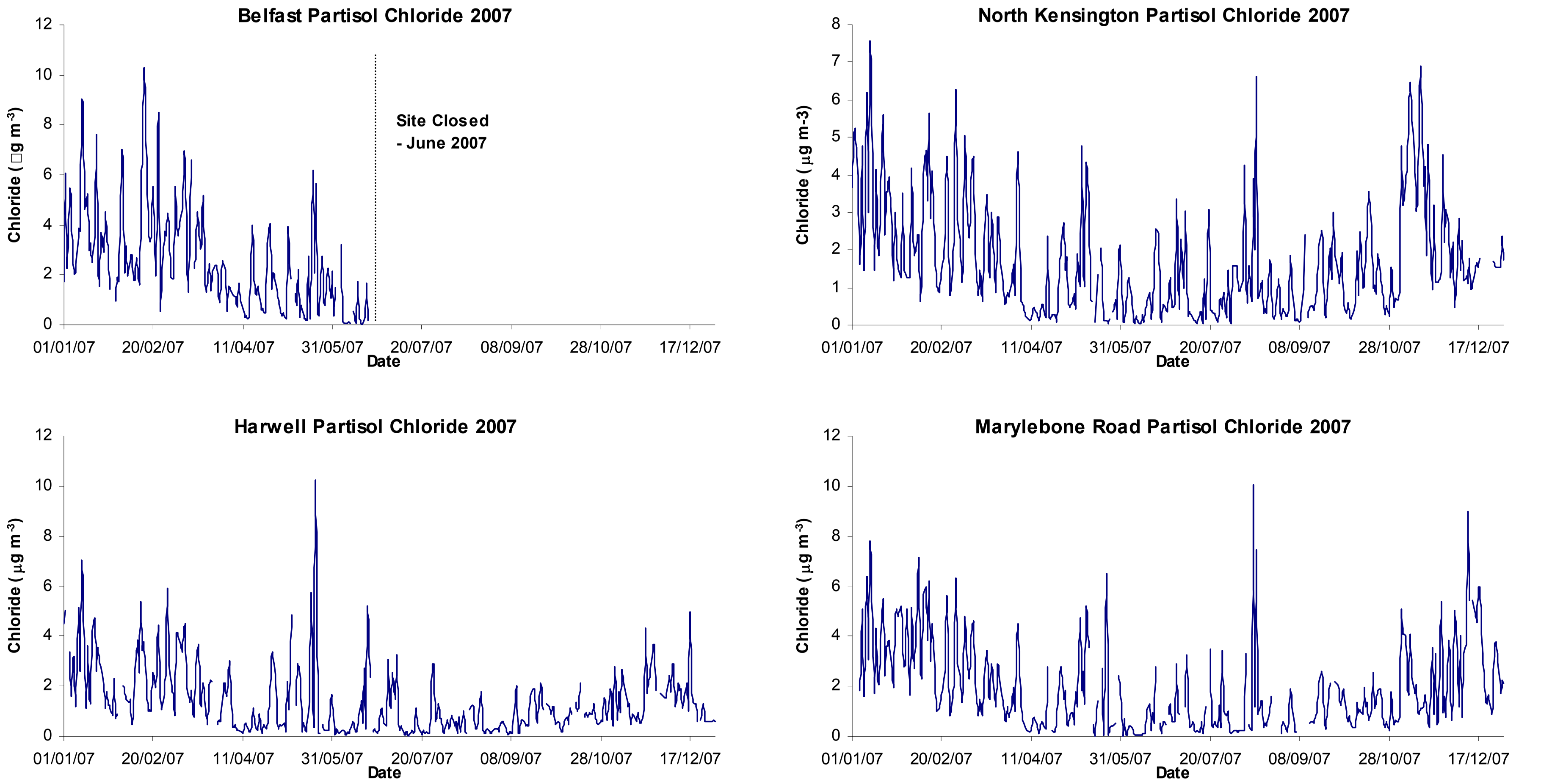


Figure 4-3: Partisol Nitrate Concentrations at Network Sites during 2007.

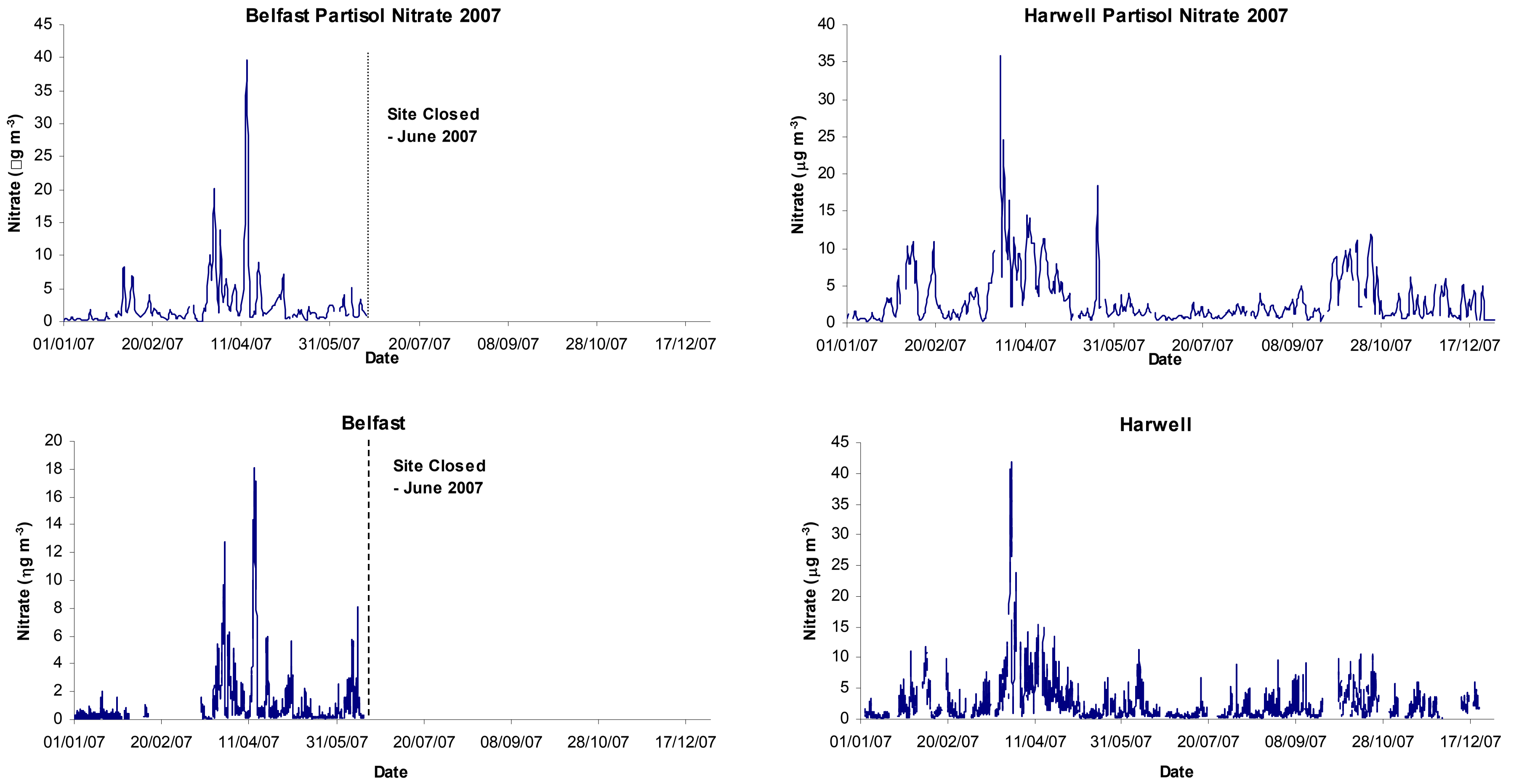


Figure 4-4: Nitrate Concentrations at Network Sites during 2007. Partisol Measurements [Upper Panels] and Automatic Nitrate Analysers [Lower Panels].

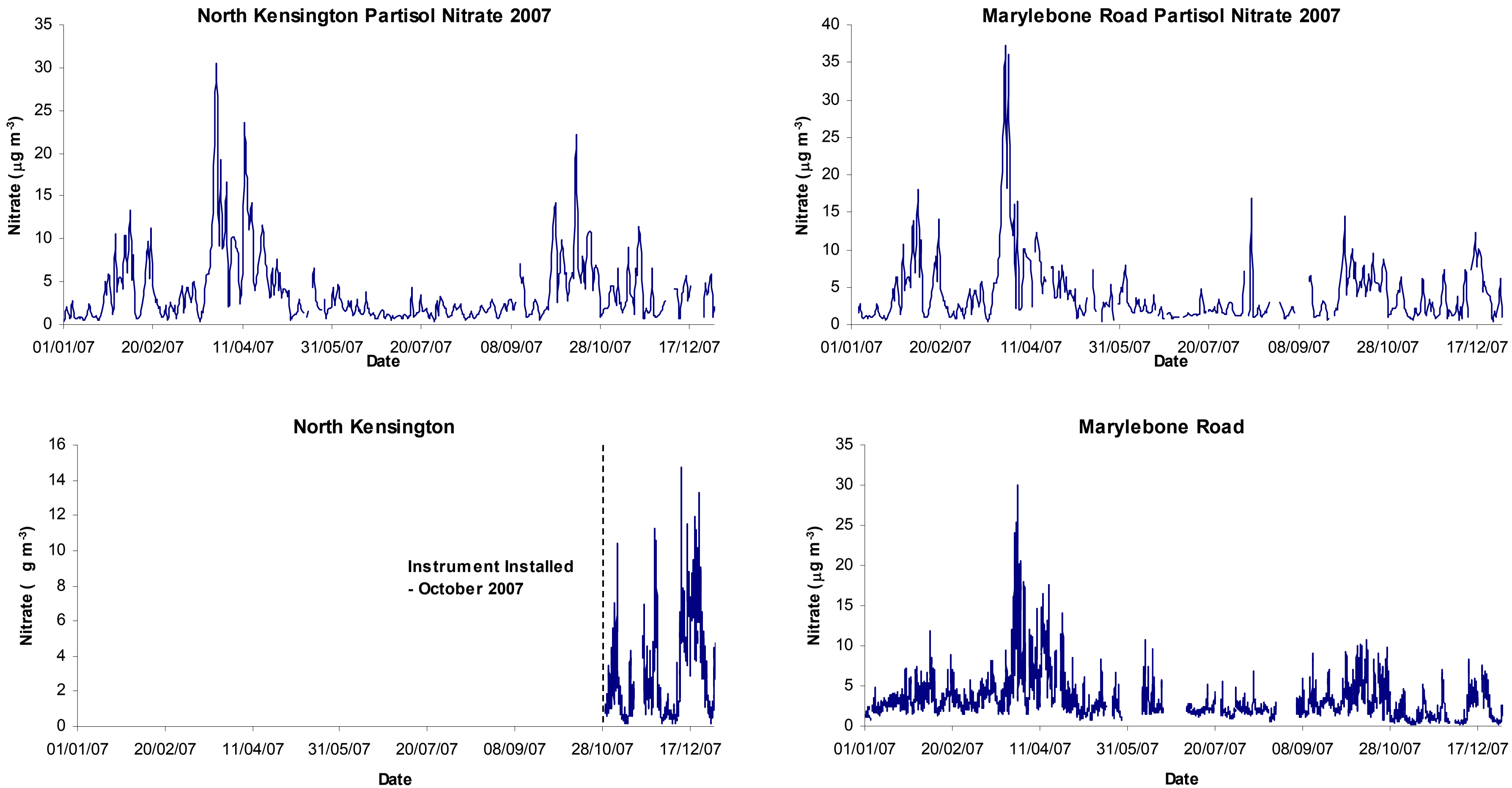


Figure 4-4: Nitrate Concentrations at Network Sites during 2007. Partisol Measurements [Upper Panels] and Automatic Nitrate Analysers [Lower Panels]. (Continued)

Monthly data capture rates for the Partisol 2025 instruments during 2007 are given in Table 4-1.

Table 4-1: Monthly Data Capture for the Partisol 2025 Samplers during 2007

Site	Belfast	Harwell	North Kensington	Marylebone Road
January	94%	97%	100%	90%
February	100%	93%	100%	100%
March	100%*	97%*	100%	100%
April	100%	100%	100%*	93%
May	97%	90%	94%	90%*
June	85%	97%	100%	93%
July	-	100%	100%	90%
August	-	97%	100%	81%
September	-	100%*	97%	77%
October	-	94%	100%*	100%*
November	-	97%	100%	100%
December	-	97%	81%	97%
Average	**96%**	**96%**	**98%**	**93%**

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

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. For Belfast, the average reported data capture is between 1st January and 20th June only. The Partisol was removed from operation on the 21st June 2007.

4.2.2 Automatic Nitrate Analysers

The automatic hourly measurements of particulate nitrate made in 2007 were displayed in the lower panels of Figure 4-4. The upper panels of Figure 4-4 give the partisol nitrate measurements (in the PM_{10} size fraction). There is a good correlation generally between the measurements, which is discussed further in the following section (Section 4.2.3).

Monthly data capture rates for the automatic nitrate instruments during 2007 are presented in Table 4-2. The Equipment Support Unit carries out services and instrument calibrations twice a year. One day has been allowed for each of these service visits and that is reflected in the data capture calculation.

Table 4-2: Monthly Data Capture for the Automatic Nitrate Instruments during 2007.

Site	Belfast	Harwell	Marylebone Road	North Kensington
January	94%	72%	95%	-
February	9%	67%	99%	-
March	59%*	71%*	100%	-
April	100%	78%	88%	-
May	100%	90%	77%*	-
June	100%	85%	38%	-
July	-	80%	80%	-
August	-	96%	71%	-
September	-	74%*	84%	-
October	-	58%	100%*	-
November	-	74%	98%	82%
December	-	21%	82%	99%
Average	**75%**	**72%**	**84%**	**92%**

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

Some data were unfortunately lost from the instrument at Belfast during February and March due to a faulty photo-multiplier tube. This was replaced by Air Monitors at the service visit on the 14th March. The Belfast nitrate instrument was switched off and removed from operation on 15th June so the average data capture in Table 4-2 is for the period 1st January to 15th June only.

The North Kensington nitrate instrument was installed at the site on 31st October, hence the average data capture is calculated from only the last two months of the year.

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 4-5 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.

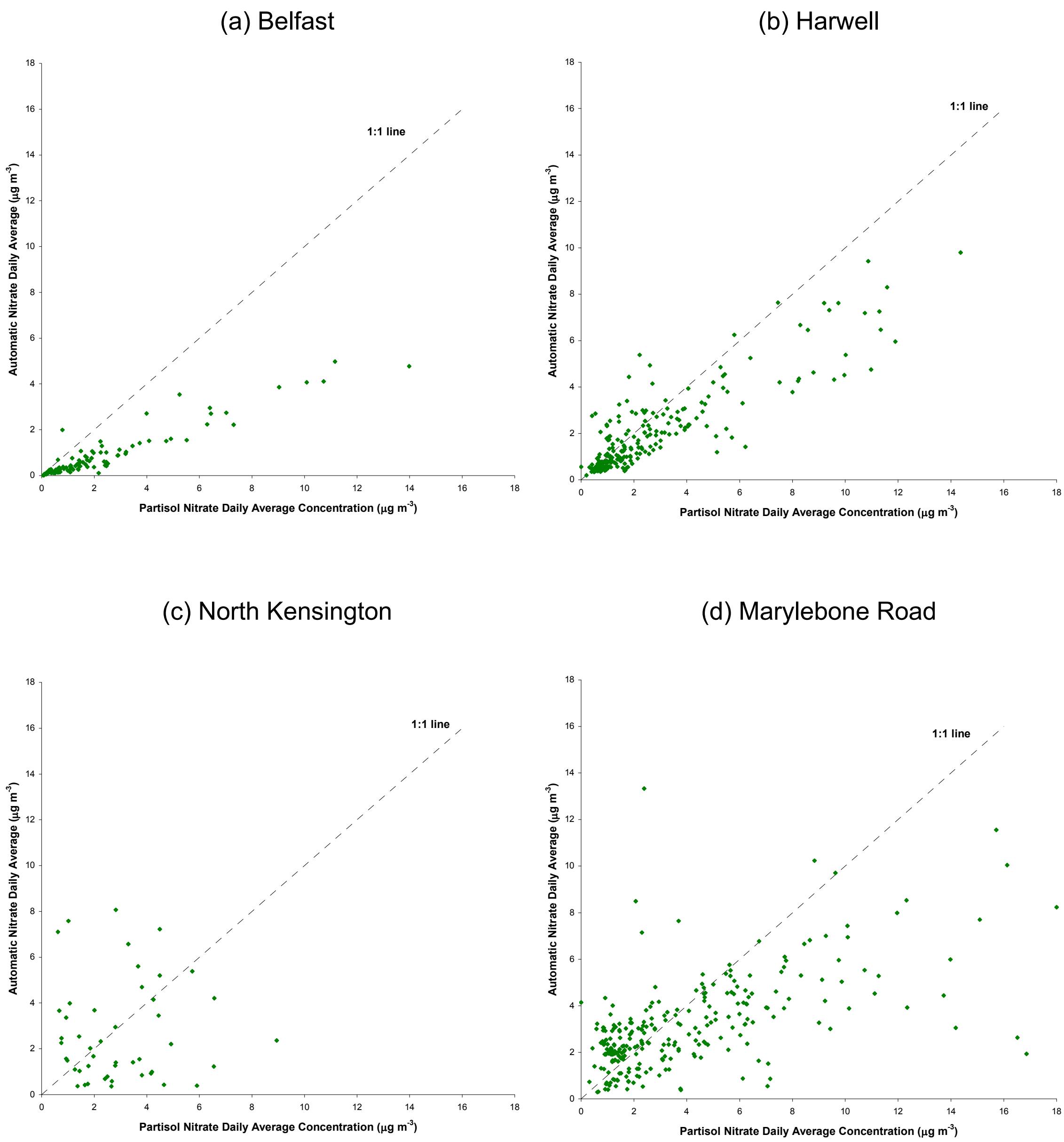


Figure 4-5: Scatter Plots of Nitrate Concentrations at the Network Sites during 2007.

The differences in the two measurement methods gives rise to the discrepancy in the results, and these are described in more detail in the recent NPL uncertainty report [NPL, 2007a]. As the measurements are from different PM size fractions (partisol – PM_{10}, automatic nitrate – $PM_{2.5}$), one would not expect a 1:1 correlation. However, the correlation at Harwell is close to unity, suggesting that the PM nitrate is in the fine fraction and largely composed of NH_4NO_3 (< $PM_{2.5}$). At the other sites, there is presumably a greater contribution of coarse nitrate. The correlations are however consistent with those found in previous years.

4.3 Elemental and Organic Carbon

In March 2007, the manufacturer announced the discontinuation of the automatic 5400 carbon instruments. Previous studies, including the US EPA study [US EPA, 2005], had shown that these instruments do not agree with the manual reference method and that they are prone to technical failures. For these reasons and with Defra's agreement, the automatic carbon analysers were switched off and removed from sites at the end of May 2007. They do not form part of the new network structure. The planned introduction of aethalometers at the sites in 2008 will provide high-resolution temporal measurements of black carbon once more.

Due to the difficulties in calibrating the automatic instruments and the inconsistency of the results in recent years, the data from the automatic instruments are presented as validated only. ***These data are not ratified***.

From May 2007, elemental and organic carbon (EC/OC) concentrations in ambient air have been determined from filters collected at Harwell, Marylebone Road and North Kensington. Between May 2007 and October 2007, the determination has been made from quartz fibre filters provided by Bureau Veritas. These filters had previously been sampled and weighed as part of the Automatic Urban and Rural Network (AURN). At Marylebone Road and North Kensington the sampled particulates were in the PM_{10} size fraction. At Harwell only $PM_{2.5}$ filters were available. There was a significant time delay of several months between the measurement being made in the AURN and the supply of the filter to NPL, a consequence of the AURN ratification process. Further, Bureau Veritas were not able to locate a small number of these filters, leading to gaps in the dataset and hence the poor data capture during this period (see Table 4-4). The data are deemed to be ***validated but not fully ratified.***

From the 25th October 2007, NPL switched the filter type in the 'anion' Partisol samplers from Emfab (PTFE-coated glass fibre) to ultrapure quartz. This has allowed the filters to be used for the analysis of EC/OC in addition to the anions. It is therefore no longer necessary to use AURN filters and, therefore, from 25th October 2007, the EC/OC results from all three sites are from the PM_{10} fraction. ***These data are fully ratified.***

4.3.1 EC/OC Measurements

The automatic and filter measurements of EC, OC and total carbon made in 2007 have been combined and are displayed in Figure 4-6 and Figure 4-7 for the 4 sites. These figures clearly illustrate some of the performance issues with the automatic instruments, most notably at Harwell (see upper right-hand panel of Figure 4-6 and text below).

The following should be noted:

- **Belfast**: During January the site suffered electrical problems with the cabin lights, which caused the automatic carbon instrument to lose configuration every time the lights were turned on. This resulted in some loss of data during the first two weeks of the year (see Figure 4-6), until the lights were repaired on the 10th January.
- **Harwell -** The ratio of organic to elemental carbon at Harwell from the automatic instrument is significantly different to that seen at other sites and from the subsequent filter measurements. There is a suggestion that the EC and OC measurements have been switched but this was checked and was not the case. It is thought that the different ratio was due to the age of the automatic instrument rather than it being a real artefact at the site. Numerous attempts were made to repair the instrument and the data processing procedures were checked thoroughly to ensure no mistakes had been made. This behaviour has been identified in data produced by the 5400 instruments several times during the last few years. Due to the poor quality of the carbon data, ***the automatic measurements for Harwell for 2007 will not be published and are shown here to indicate the issues with the measurements***.

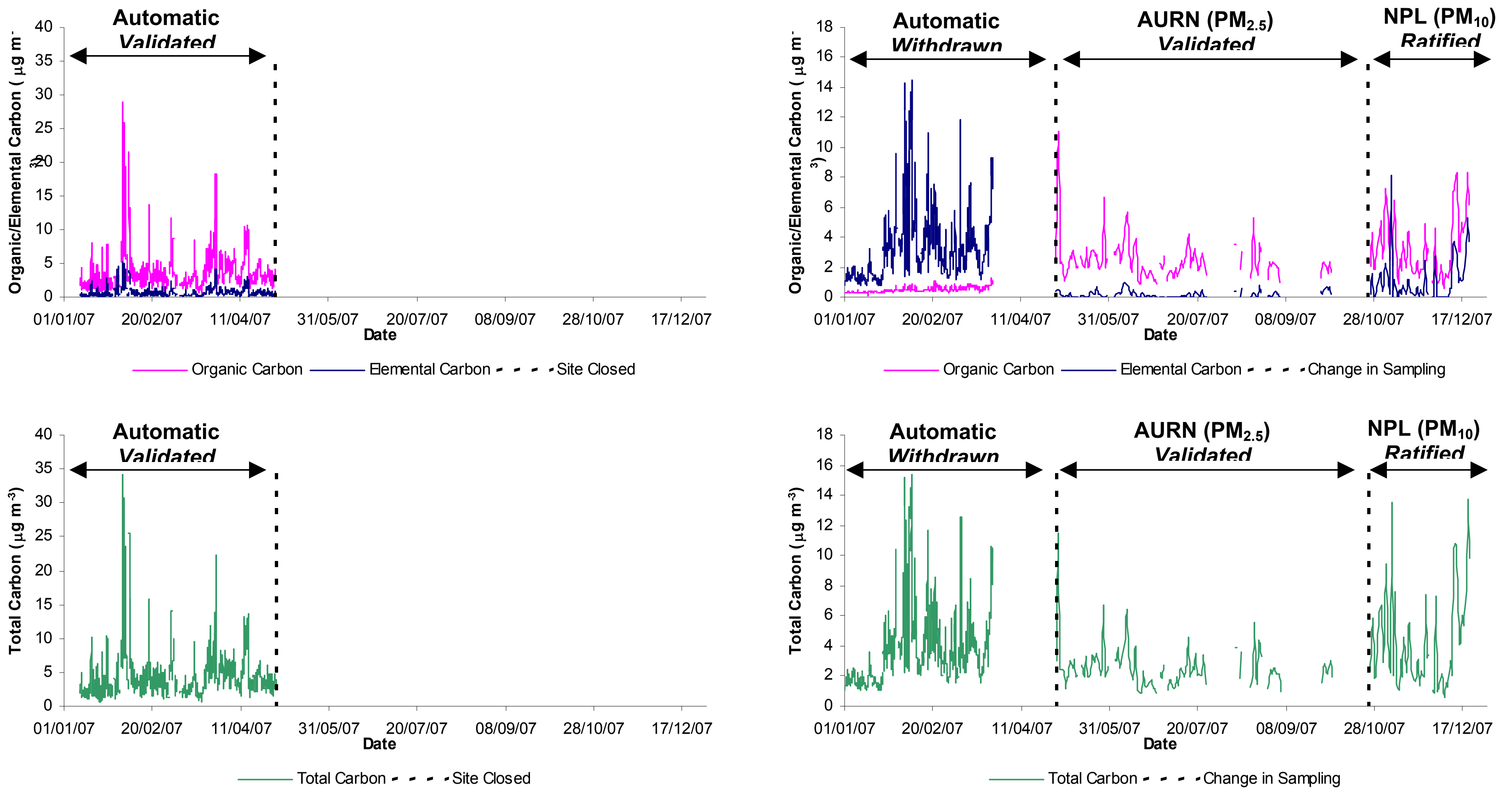


Figure 4-6: Organic, Elemental and Total Carbon Concentrations at Belfast [Left-hand Panels] and Harwell [Right-hand Panels] in 2007. Note the Belfast Site was closed in May 2007 and the Change from Hourly Automatic Measurements to Daily Sampling in May at Harwell.

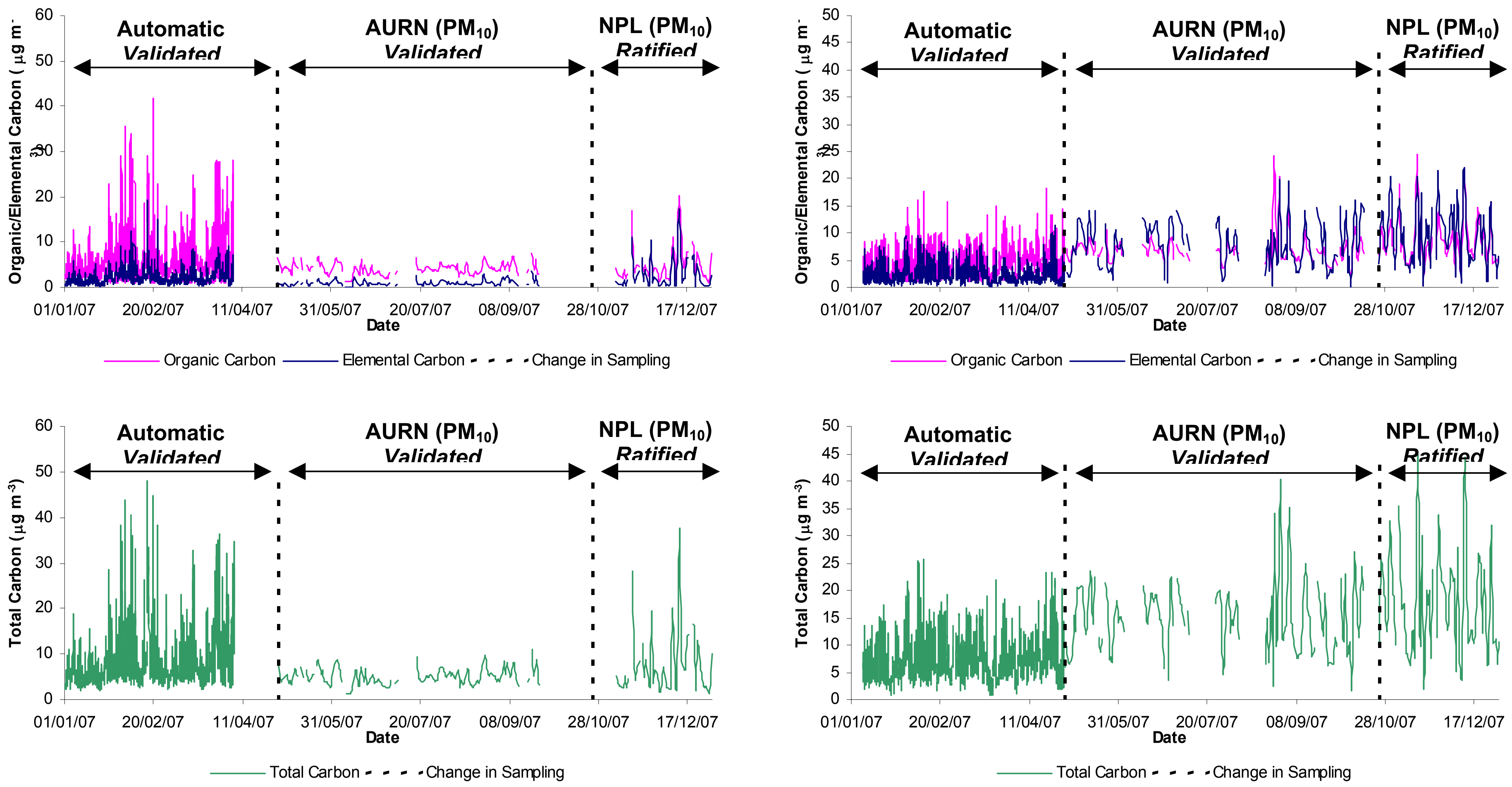


Figure 4-7: Organic, Elemental and Total Carbon Concentrations at North Kensington [Left-hand Panels] and Marylebone Road [Right-hand Panels] in 2007. Note the change from Hourly Automatic Measurements to Daily Sampling in May.

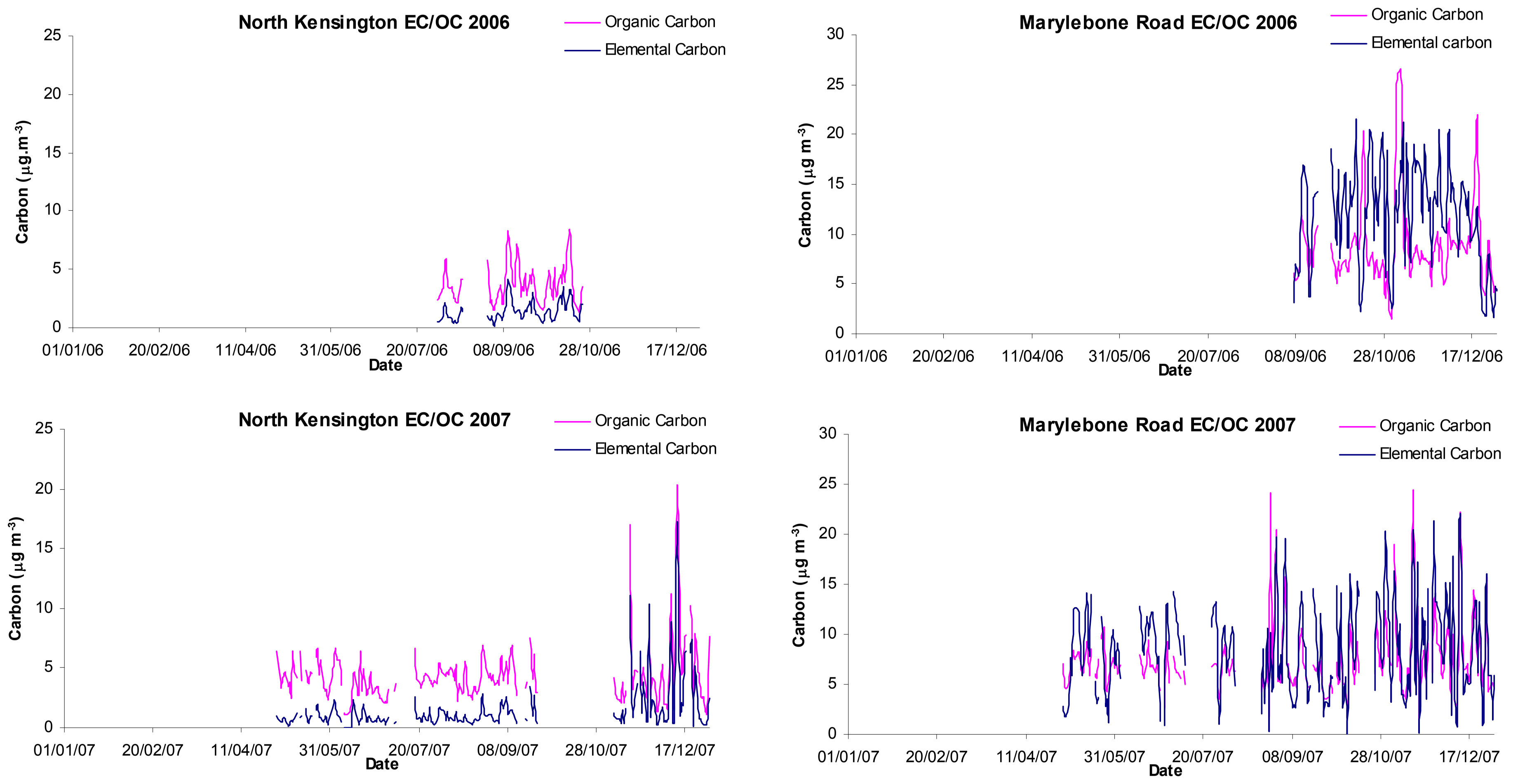


Figure 4-8: Comparison of 2006 and 2007 Organic and Elemental Carbon Measurements from Filter Samples at North Kensington and Marylebone Road.

- **North Kensington** - The average summer concentration for organic carbon was 4.1 µg.m^{-3}, compared with 4.9 µg.m^{-3} in the winter. These concentrations are similar. However, the average elemental carbon concentration more than doubles in the winter, going from 1.0 µg.m^{-3} to 2.7 µg.m^{-3}. This can be explained by an increase in fuel consumption. As the ambient temperature drops, organic carbon concentrations stay relatively constant, while the elemental concentration increases and the OC:EC ratio is gradually reduced. Similar results were seen when a selection of quartz filters (supplied by Bureau Veritas) were analysed in 2006. This can be seen in the left-hand panels of Figure 4-8.
- **Marylebone Road** – The left-hand panels of Figure 4-7 indicate that the spread of carbon concentrations is much increased during the winter months. This is due, in part, to an increase in fuel consumption during the cold weather. Similar results were seen during a short analysis campaign of quartz filters in 2006 [NPL, 2006], as shown in the upper panel Figure 4-8.

For the reasons given previously, there is no further analysis of the automatic carbon data in this Report.

4.3.2 Comparison with Black Smoke

Co-located measurements of black smoke have been made at the North Kensington and Marylebone Road sites. Figure 4-9 shows a time series of the elemental carbon and black smoke measurements at these 2 sites made in 2007 (Note the North Kensington measurements started in March 2007). There is a good correlation between the measurements, most notably at the North Kensington site. Further analysis of these datasets is planned and will be reported elsewhere.

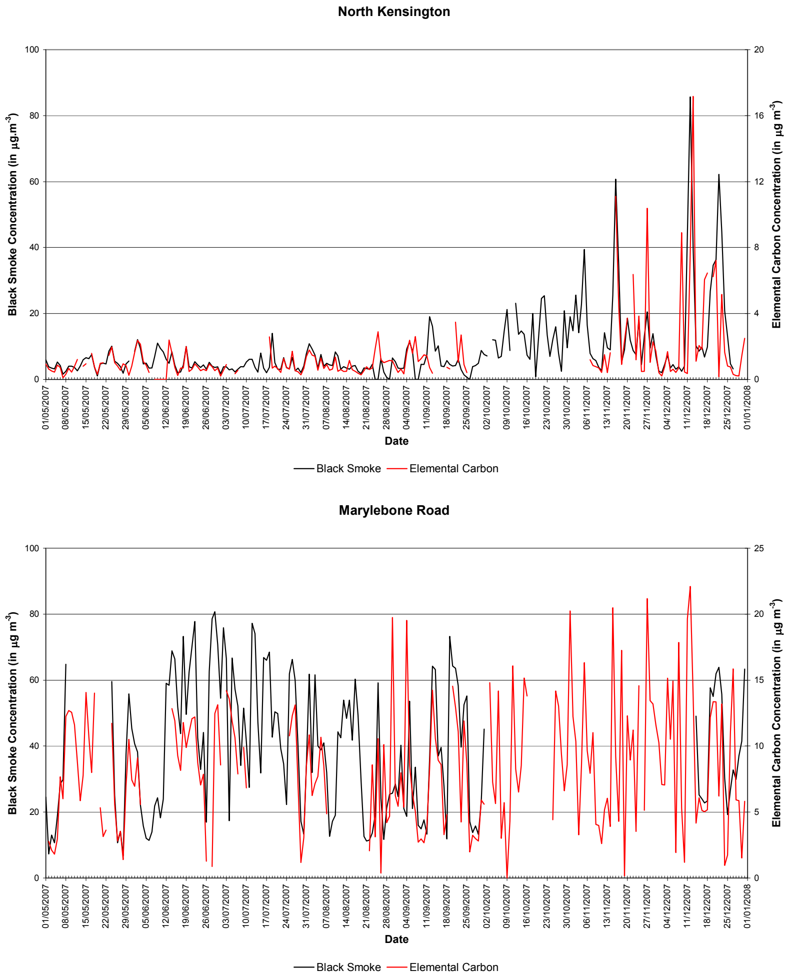


Figure 4-9: Time Series of Black Smoke and Elemental Carbon Measurements at North Kensington [Upper Panel] and Marylebone Road [Lower Panel].

The elevated concentrations of black smoke and elemental carbon at the North Kensington in December 2007 were also seen in the measurements of particle number and oxides of nitrogen (see Figure 4-13 in Section 4.4.1 subsequently).

4.3.3 Data Capture

The automatic carbon instrument were operated from January to April/May. Monthly data capture rates during 2007 are displayed in Table 4-3.

Table 4-3: Monthly Data Capture Statistics for the Automatic EC/OC Instruments during 2007.

Site / Month	Belfast	Harwell	North Kensington	Marylebone Road
January	67%	88%	100%	78%
February	92%	90%	95%	93%
March	89%*	78%*	99%	99%
April	98%	0%	20%*	98%
May	99%	0%	0%	30%*
June	-	-	-	-
July	-	-	-	-
August	-	-	-	-
September	-	-	-	-
October	-	-	-	-
November	-	-	-	-
December	-	-	-	-
Average	**89%**	**51%**	**62%**	**79%**

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

The Equipment Support Unit carried out a service and instrument calibration once between January and May. One day has been allowed for each of these service visits and this is reflected in the data capture calculation.

From May 2007, the EC/OC measurements were made using filters. Monthly data capture rates for the filter measurements during 2007 are displayed in Table 4-4.

Table 4-4: Monthly Data Capture Statistics for the Filter EC/OC Instruments during 2007.

Site / Month	Harwell	North Kensington	Marylebone Road
January	-	-	-
February	-	-	-
March	-	-	-
April	-	-	-
May	94%	90%	90%
June	93%	97%	63%
July	77%	61%	48%
August	48%	100%	55%
September	30%	70%	97%
October	32%	-	71%
November	97%	73%	93%
December	68%	97%	100%
Average	**67%**	**74%**	**77%**

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

As indicated earlier, between May 2007 and October 2007, EC/OC concentrations have been made from quartz fibre filters provided by Bureau Veritas. Bureau Veritas were not able to locate a small number of these filters, leading to gaps in the dataset during this period and reduced data capture.

4.4 Particle Number and Size Distributions

4.4.1 Particle Number Concentrations (CPC)

Time series of the particle number concentrations (between 7nm and several microns in diameter) measured at network sites during 2007 are shown Figure 4-10 for the discontinued sites and in Figure 4-11 for the new and retained sites.

Due to network restructuring, the CPCs at Belfast, Glasgow, Manchester and Port Talbot were taken out of operation during June 2007. Following a service and calibration, the instrument from the Manchester site was redeployed to Harwell.

The following should be noted:

Discontinued Sites

- **Belfast** – The instrument was at TSI for its annual service and calibration during part of February and March 2007. The instrument was removed from operation on the 22nd June 2007.
- **Glasgow** – The instrument was removed from operation on the 30th June 2007.
- **Manchester** – The Instrument was removed from operation on the 6th June 2007.
- **Port Talbot** – The instrument was removed from operation on the 27th June 2007.

New/Retained Sites

- **Birmingham** - The CPC was removed from site on the 22nd January to allow for site refurbishment including laying a new floor (by Enviro Technology). The instrument was reinstalled in February and resumed normal operation on the 16th February. The instrument was serviced and calibrated in October.
- **Harwell** – The instrument was installed at the site on the 1st October 2007, following a full service and repair at TSI in September.
- **Marylebone Road** – The LSO reported unstable flow on the 29th March and the CPC was returned to TSI for repair. The fault was found to be oil in the pump and flow capillary. This was rectified and the instrument reinstalled on 2nd May. It was serviced during October and November.
- **North Kensington** – The instrument was serviced and calibrated during March and April 2007.

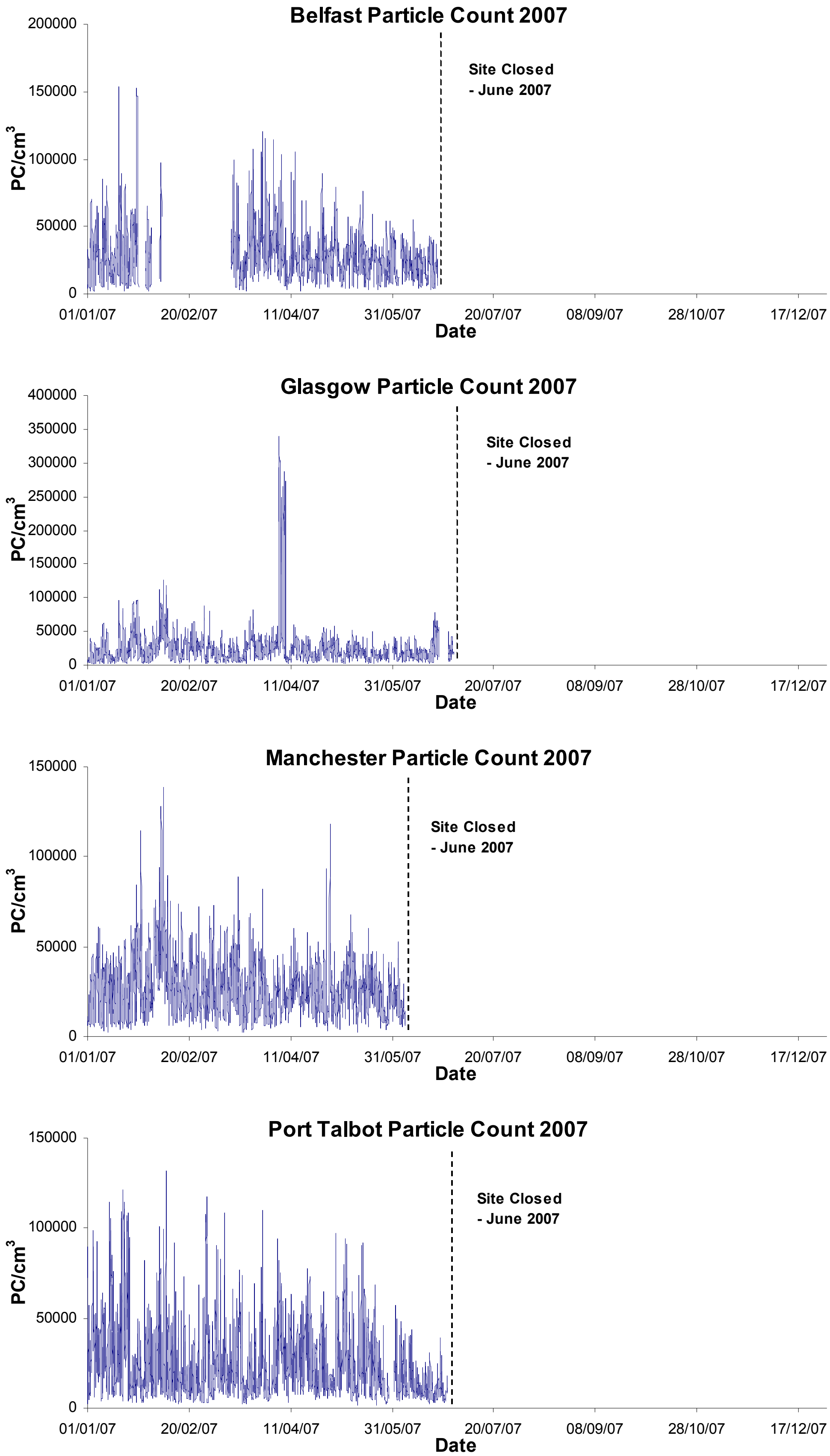


Figure 4-10 CPC Particle Count at the Discontinued Sites (Belfast, Glasgow, Manchester and Port Talbot) during 2007.

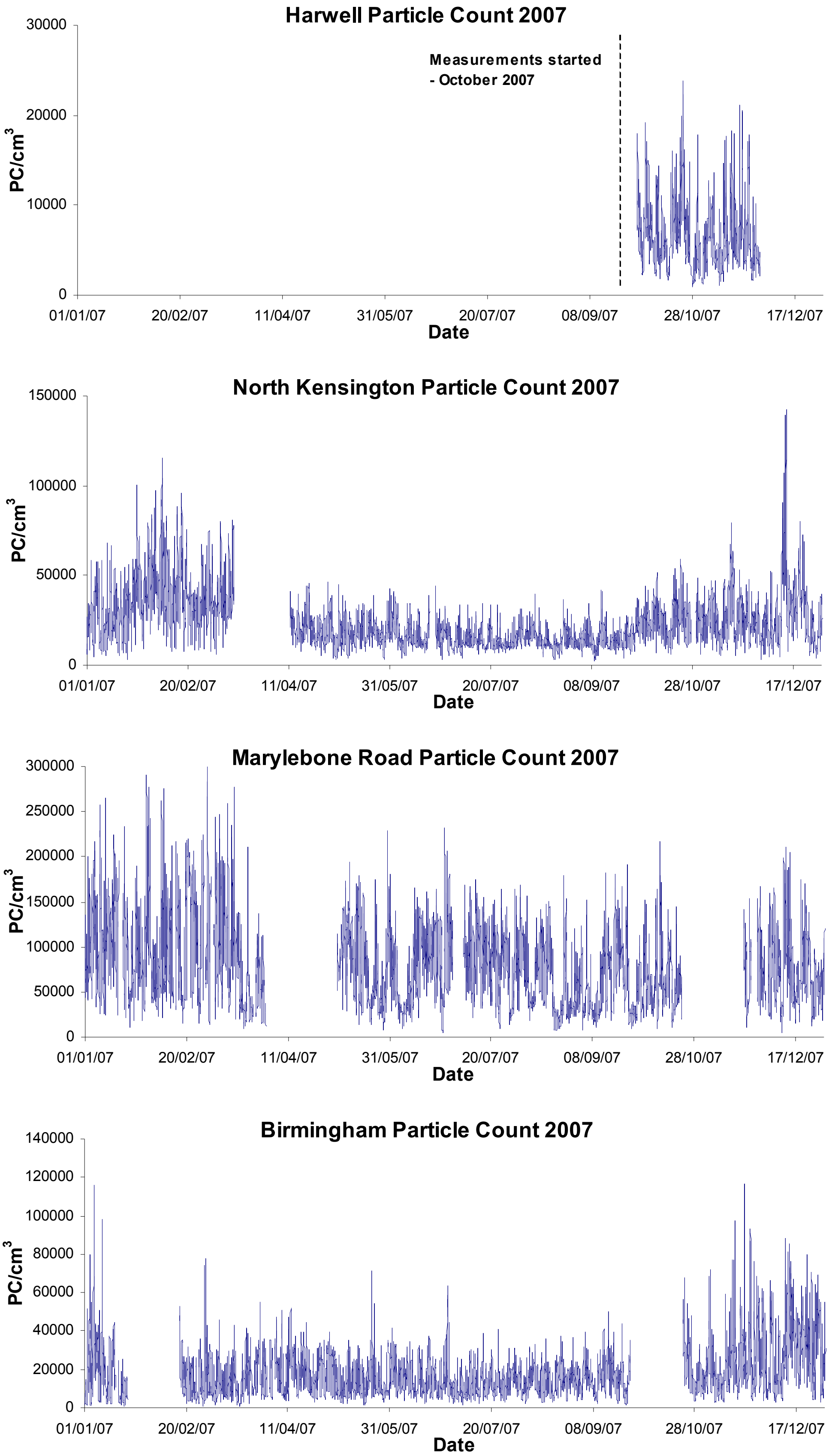


Figure 4-11 CPC Particle Count at the New and Retained Network Sites during 2007.

There was a major peak in the number concentration of ambient particles at Glasgow during the period 5th-8th April. This could be attributed to a local farmers' market held near to the site in St Enoch's Square. The measurements made during period are shown in Figure 4-12 and are compared to the nitric oxide and nitrogen oxides concentrations for the same period. Markets like these are regularly held in the Square and have often resulted in enhanced levels of particulates, which have been noted in the Annual Reports of previous years.

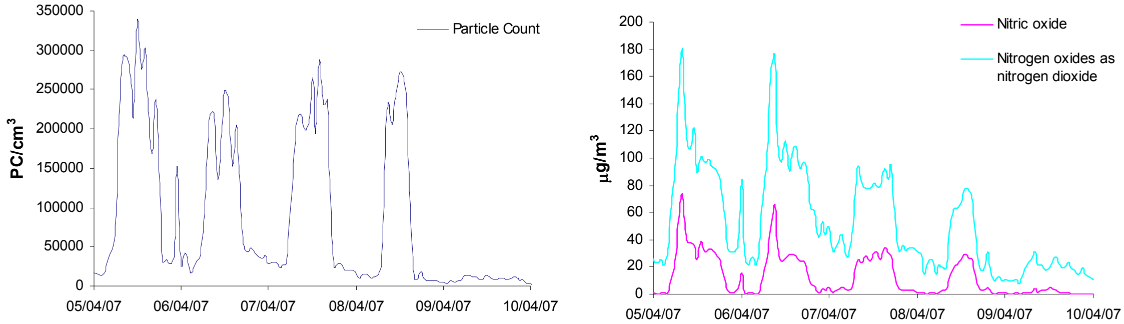


Figure 4-12: Correlation between the High Concentrations of Particle Numbers [Left-hand Panel] and those of Nitric Oxide and Oxides of Nitrogen [Right-hand Panel] at Glasgow during April 2007.

There was also a major peak in the number concentration of ambient particles seen at North Kensington between the 11th and 13th of December, as illustrated in Figure 4-11. Figure 4-13 presents the particle number measurements for December on an expanded scale (upper left-hand panel). The peak in the particle number concentration was mirrored in the NO_x concentrations at this site during the same period (lower left-hand panel of Figure 4-13) and the black smoke measurements (see Figure 4-9). The particle number and NO_x concentrations at North Kensington approached those measured at Marylebone Road, as shown in the right-hand panels of Figure 4-13, indicating that this was part of a more extensive winter-time episode in London during this period.

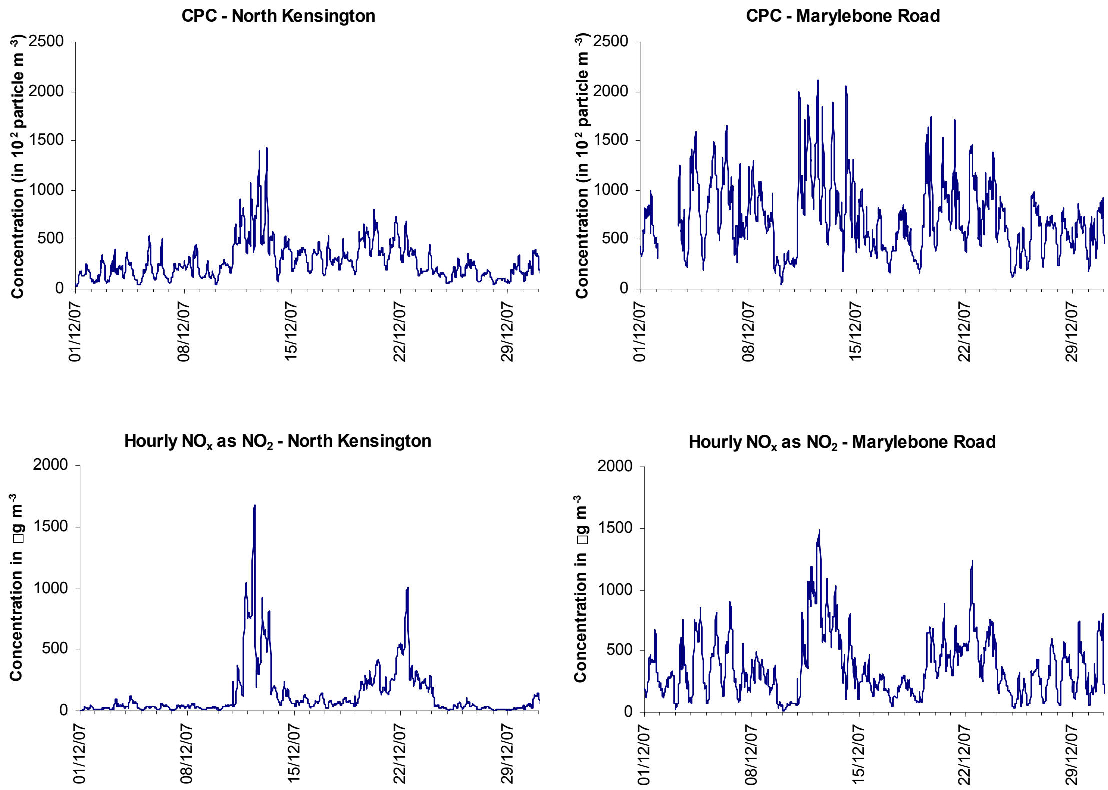


Figure 4-13: Elevated Concentrations of Particle Numbers and of Oxides of Nitrogen Observed at North Kensington [Left-hand Panels] and Marylebone Road during December 2007 [Right-hand Panels].

Monthly data capture rates for the CPC instruments during 2007 are displayed in Table 4-5. 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 4-5 Monthly Data Capture for CPC Instruments during 2007.

Site	Belfast	Birmingham	Glasgow	Harwell
January	89%	64%	100%	
February	80%*	43%	100%	
March	63%*	100%	100%	
April	100%	93%	100%	
May	100%	100%	94%	
June	95%	97%	85%	
July		98%		
August		100%		
September		85%		
October		99%*		100%
November		100%		93%
December		100%		68%*
Average	**87%**	**90%**	**96%**	**87%**

Site	North Kensington	Marylebone Road	Manchester	Port Talbot
January	100%	93%	100%	100%
February	100%	91%	100%	100%
March	91%*	85%	99%	100%
April	86%*	0%	100%	98%
May	100%	82%	100%	91%
June	87%	97%	100%	99%
July	100%	83%		
August	100%	100%		
September	100%	97%		
October	93%	81%*		
November	100%	78%*		
December	100%	96%		
Average	**97%**	**82%**	**100%**	**98%**

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

Due to the network restructuring, the CPCs at Belfast, Glasgow, Manchester and Port Talbot were taken out of operation during June 2007. The data capture for these sites in June, and the average data capture, takes into account the reduced number of available days.

4.4.2 Particle Number and Size Distributions (SMPS)

Following an NPL intercomparison of two commercially available SMPS analysers in 2006, the TSI analyser (model 3936L75) was judged to be most suitable for the network. Three new systems were installed at Bloomsbury, Harwell and Marylebone Road at the end of March 2007. The Bloomsbury system was later moved to North Kensington as part of the network restructuring.

Total particulate counts (between 16 nm and 605 nm aerodynamic diameter[1]) have been plotted in Figure 4-14. 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 SMPS at Bloomsbury suffered a flow fault in May 2007 and was returned to TSI for repair. It was removed from the site on 25th June 2007 and taken into storage before reinstalling at North Kensington.

[1] The previous SMPS instruments covered the size range from 12 and 450 nm aerodynamic diameter.

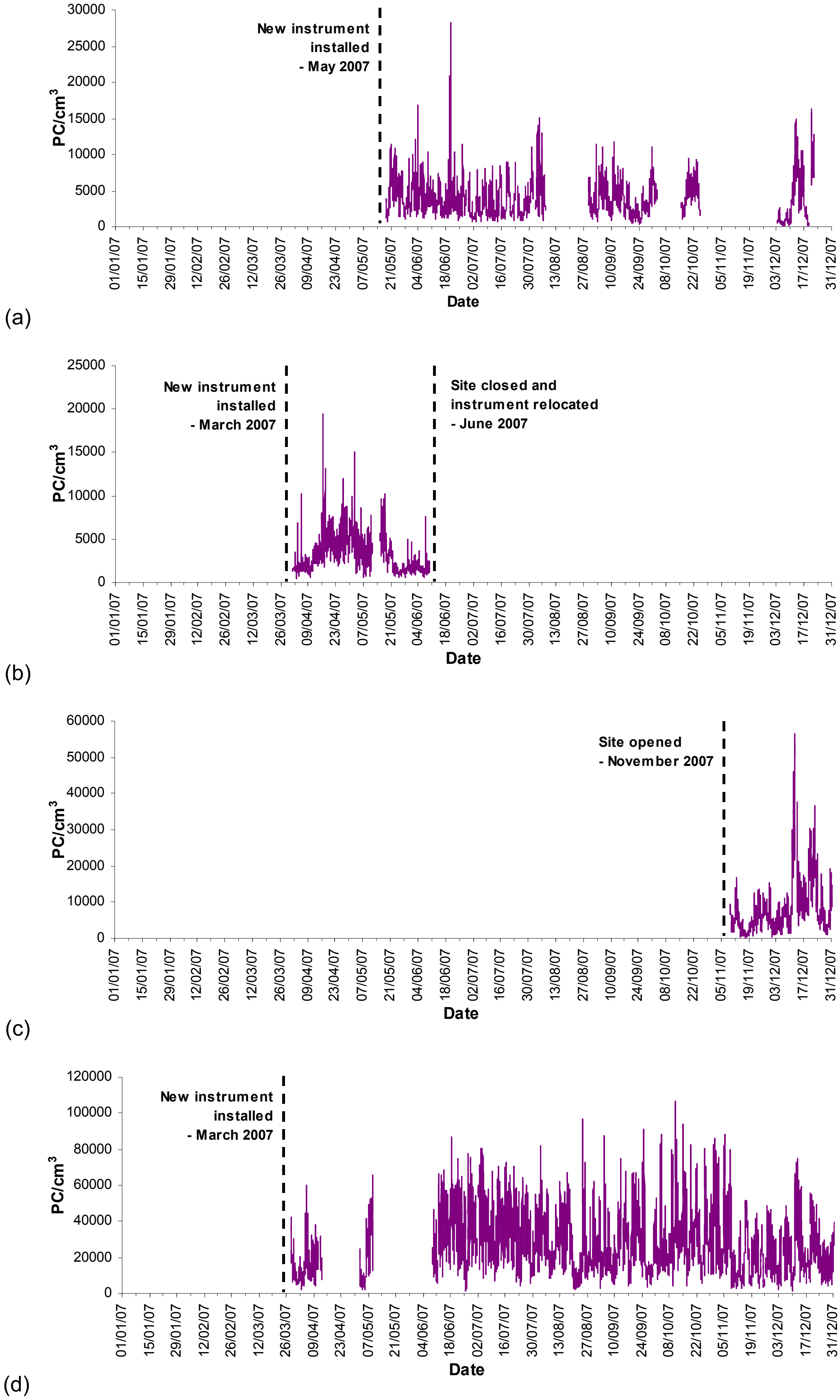


Figure 4-14: SMPS Total Particle Number Concentrations at Network Sites during 2007: (a) Harwell, (b) Bloomsbury, (c) North Kensington and (d) Marylebone Road.

The counts in each particle size bin measured during 2007 are presented as monthly averages in the left-hand panels of Figure 4-15 and as an annual average in the right-hand panels.

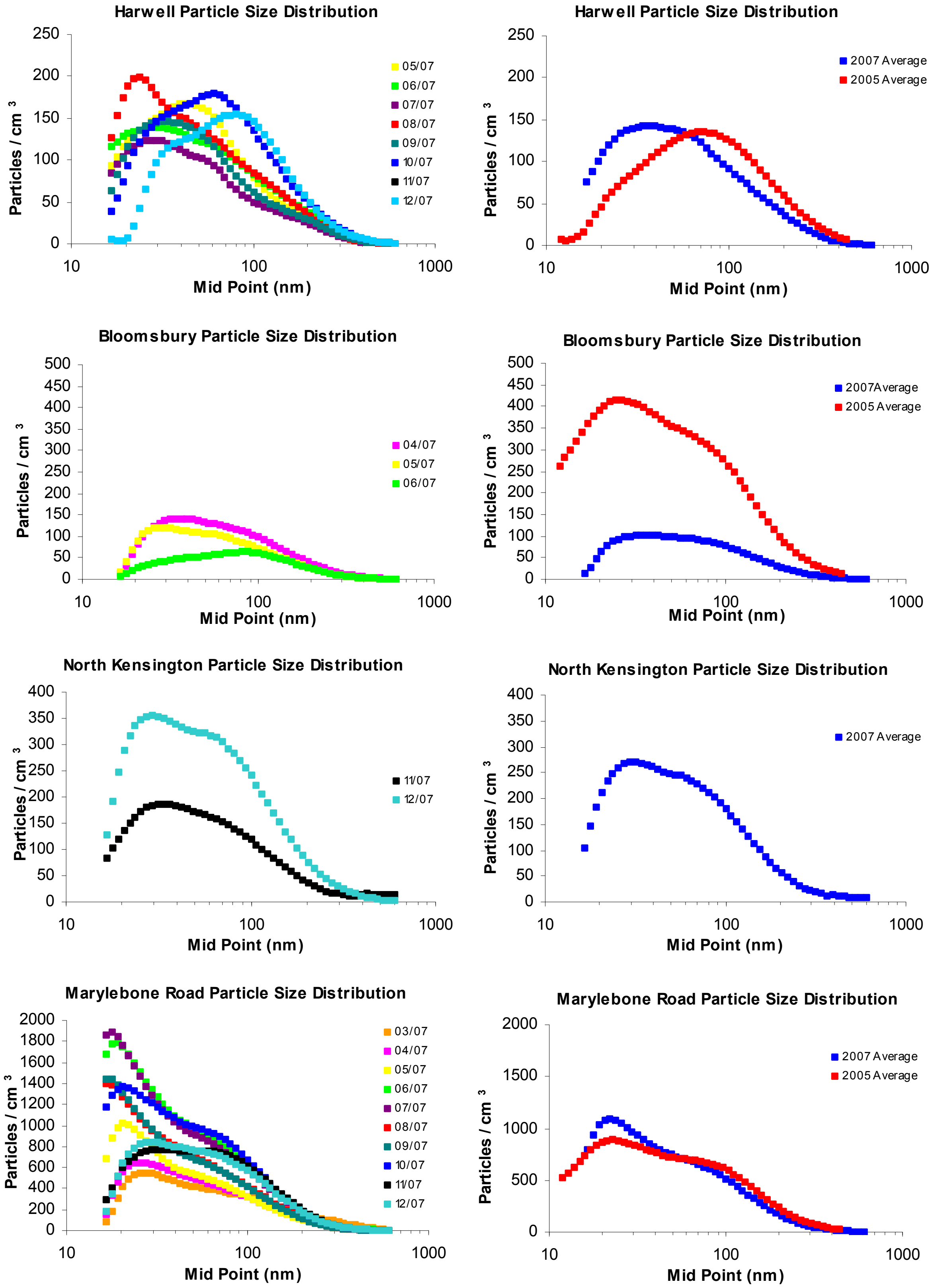


Figure 4-15 Monthly-averaged Particle Size Distributions at Network Sites during 2007 [Left-hand Panels] and Comparison of the 2005 and 2007 Annual-averged Size Distributions [Right-hand Panels].

The average size distributions for 2005 have also been included in Figure 4-15 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 lower number concentrations at Bloomsbury is striking. Figure 4-16 compares the monthly-averaged particle number counts by size bin in 2005 and 2007. Although the 2007 annual averages are based on data from a three month period in the spring, it is not simply that the measurements were lower during this period in 2007 than the corresponding period in 2005. Further work is needed to confirm the measurements and to see if external factors, such as changes in the vicinity of the monitoring site, meteorology, could explain the difference.

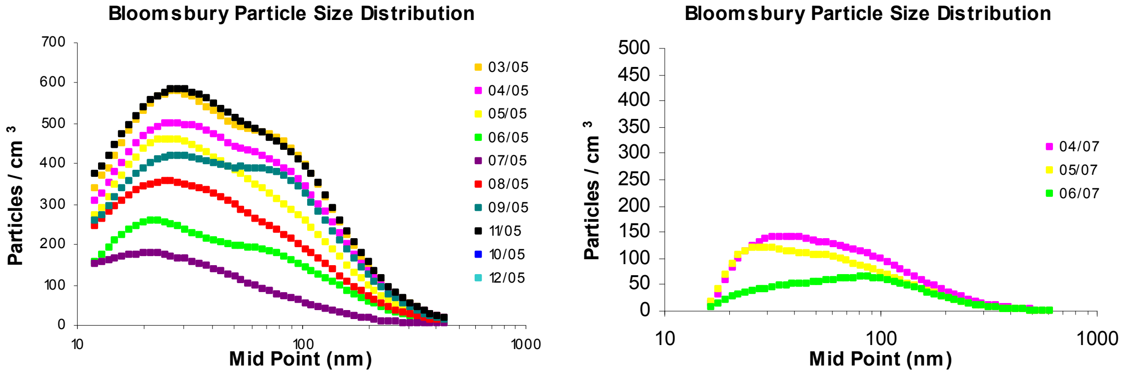


Figure 4-16: Comparison of the Monthly-averaged Particle Counts by Size Bin at Bloomsbury in 2005 [Left-hand Panel] and 2007 [Right-hand Panel].

Monthly data capture rates for the SMPS instruments during 2007 are displayed in Table 4-6.

Table 4-6: Monthly Data Capture for SMPS Instruments during 2007.

Site / Month	Harwell	London Bloomsbury	North Kensington	Marylebone Road
January	-	-	-	-
February	-	-	-	-
March	-	-	-	12%
April	-	100%	-	38%
May	44%	86%	-	23%
June	93%	100%*	-	69%
July	97%	-	-	98%
August	26%	-	-	100%
September	100%	-	-	97%
October	38%	-	-	99%
November	0%	-	71%	96%
December	57%	-	95%	97%
Average				

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

The SMPS was removed from Bloomsbury during June 2007, therefore the data capture given in this table reflects the reduced available time.

The production of data from SMPS instruments is a complicated process, summarised schematically in Figure 4-17. 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.

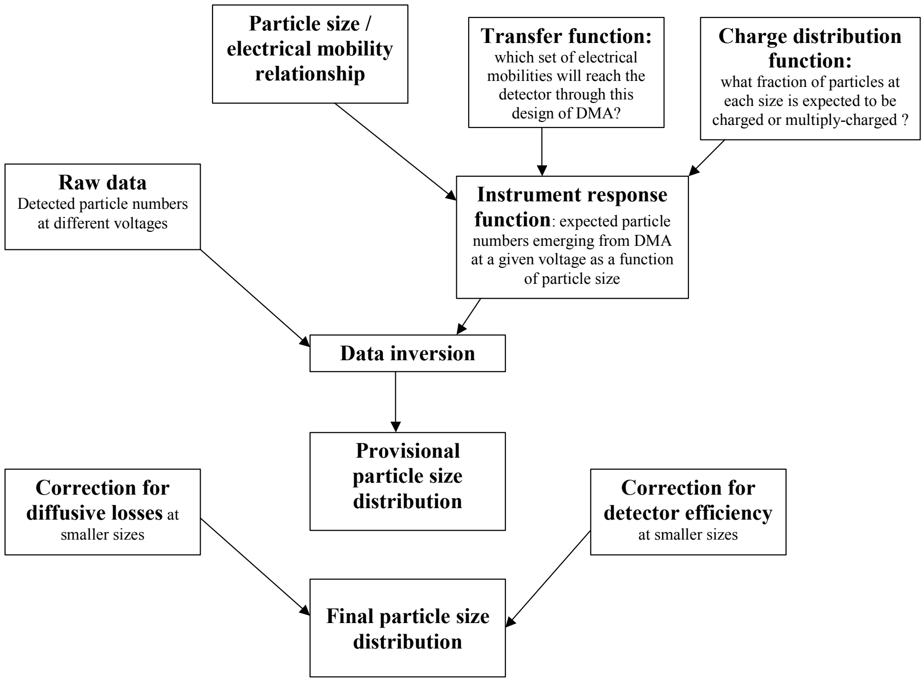


Figure 4-17: Schematic of the Internal Data Processing of the Current SMPS Instrument in the Network.

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 4-18. 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.

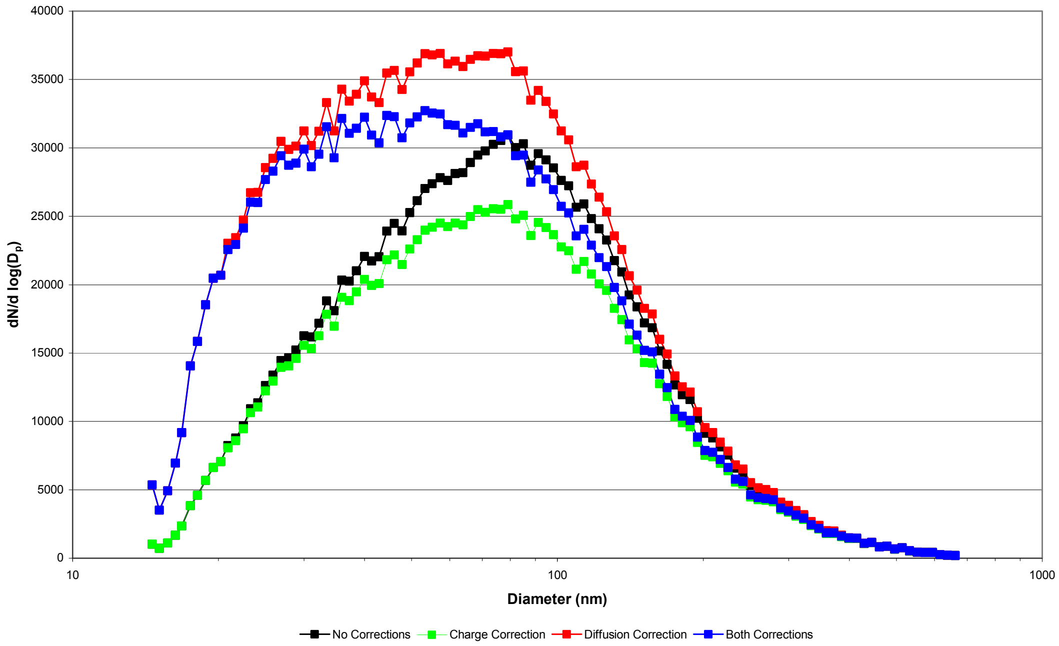


Figure 4-18: Effect of (i) the Multiple Charge, (ii) the Diffusion Loss and (iii) the Combined Corrections on the SMPS Size Spectra.

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.

Comparability of SMPS instruments is an active field of research being addressed, among others, by the EUSAAR project, ISO TC 24, and work at NPL (as discussed further in Sections 5.2.2-5.2.4 and 6.3). One of the Network instruments took part in a EUSAAR comparison with other European instruments at Leipzig in March 2008. The results of this are not yet available.

4.4.3 SMPS versus CPC data

A scatter plot between the CPC particle counts and total SMPS particle counts (all size fractions) at Marylebone Road in 2007 is presented in Figure 4-19.

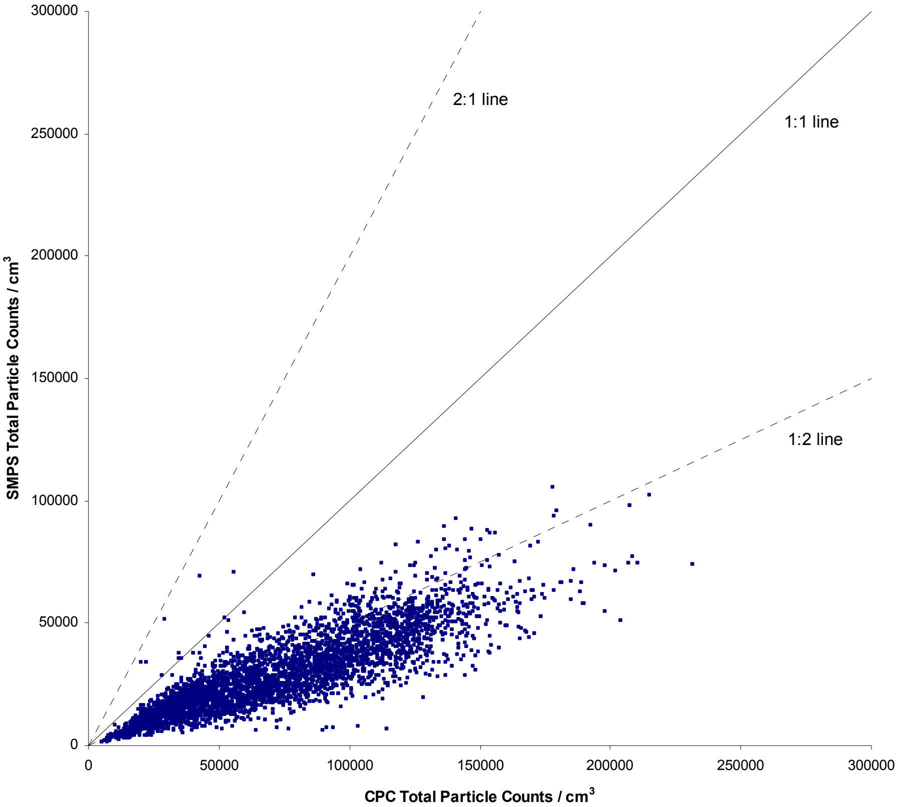


Figure 4-19: Scatter plot showing the relationship between CPC particle counts and total SMPS particle counts (all size fractions)

However, historically there has been a relatively stable relationship between the two sets of data at Marylebone Road (until March 2007, this was the only site with collocated SMPS and CPC instruments). An example of the historical relationship of the ratios of the CPC to SMPS total counts is shown in Table 4-7.

Table 4-7: 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

Since new collocated instruments were installed at Harwell, North Kensington and Marylebone Road in 2007, this relationship has changed very little. CPC to SMPS particle count ratios for these three sites in 2007 are shown in Table 4-8.

Table 4-8 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

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, but the effect is expected to be much smaller than the observed difference.

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 2007 are displayed in Table 4-9.

Table 4-9: Monthly Data Capture for Meteorological Instruments during 2007.

Site	**Harwell**	**Rochester**
January	99%	99%
February	98%	100%
March	98%	96%
April	99%	100%
May	96%	100%
June	100%	97%
July	100%	100%
August	100%	99%
September	100%	100%
October	84%	100%
November	95%	100%
December	92%	100%
Average	97%	99%

Wind roses have been derived for Harwell and Rochester for each month in 2007. These can be found in Annex 4.

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 4-10. The table also includes the annual mean concentrations for the years 2003 to 2006 for comparison.

Table 4-10: Annual Mean Concentrations of Inorganic Anions, 2003–2007.

Component	2003 Mean	2004 Mean	2005 Mean	2006 Mean	2007 Mean	Units
Belfast Nitrate ($PM_{2.5}$)	0.70	0.52	0.44	0.48	-	$\mu g.m^{-3}$
Harwell Nitrate ($PM_{2.5}$)	2.66	4.27	1.94	1.61	2.26	$\mu g.m^{-3}$
Marylebone Road Nitrate ($PM_{2.5}$)	-	-	3.33	3.18	3.25	$\mu g.m^{-3}$
North Kensington Nitrate ($PM_{2.5}$)	-	-	-	-	-	$\mu g.m^{-3}$
Belfast Daily Nitrate (PM_{10})	3.24	1.52	2.15	2.21	2.54	$\mu g.m^{-3}$
Harwell Daily Nitrate (PM_{10})	3.90	2.76	3.17	3.21	3.06	$\mu g.m^{-3}$
Marylebone Road Daily Nitrate (PM_{10})	5.06	3.93	3.97	4.39	4.05	$\mu g.m^{-3}$
North Kensington Daily Nitrate (PM_{10})	4.32	3.38	3.91	3.74	3.76	$\mu g.m^{-3}$
Belfast Daily Sulphate (PM_{10})	1.87	1.78	2.18	2.38	2.30	$\mu g\ m^{-3}$
Harwell Daily Sulphate (PM_{10})	2.44	2.29	2.40	3.01	2.40	$\mu g\ m^{-3}$
Marylebone Road Daily Sulphate	3.18	3.16	3.21	4.00	3.15	$\mu g\ m^{-3}$
North Kensington Daily Sulphate (PM_{10})	2.61	2.95	3.02	3.51	2.79	$\mu g\ m^{-3}$
Belfast Daily Chloride (PM_{10})	1.82	1.96	1.98	2.30	2.54	$\mu g\ m^{-3}$
Harwell Daily Chloride (PM_{10})	0.91	1.04	1.19	1.32	1.38	$\mu g\ m^{-3}$
Marylebone Road Daily Chloride (PM_{10})	1.45	1.54	1.64	2.01	1.91	$\mu g\ m^{-3}$
North Kensington Daily Chloride (PM_{10})	1.11	1.24	1.33	1.57	1.66	$\mu g\ m^{-3}$

4.6.2 Monthly Trends

Using data from the contract CPEA 28, 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 4-20 to Figure 4-25). All available data has been used, regardless of the data capture in any particular month. Monthly averages are, however, not shown for

- the automatic carbon measurements, because of the lack of confidence in the recent data and the discontinuation of the equipment (Section 4.3.1).
- the SMPS measurements, because of the changes in the instruments and data processing software (see Section 4.4.2)

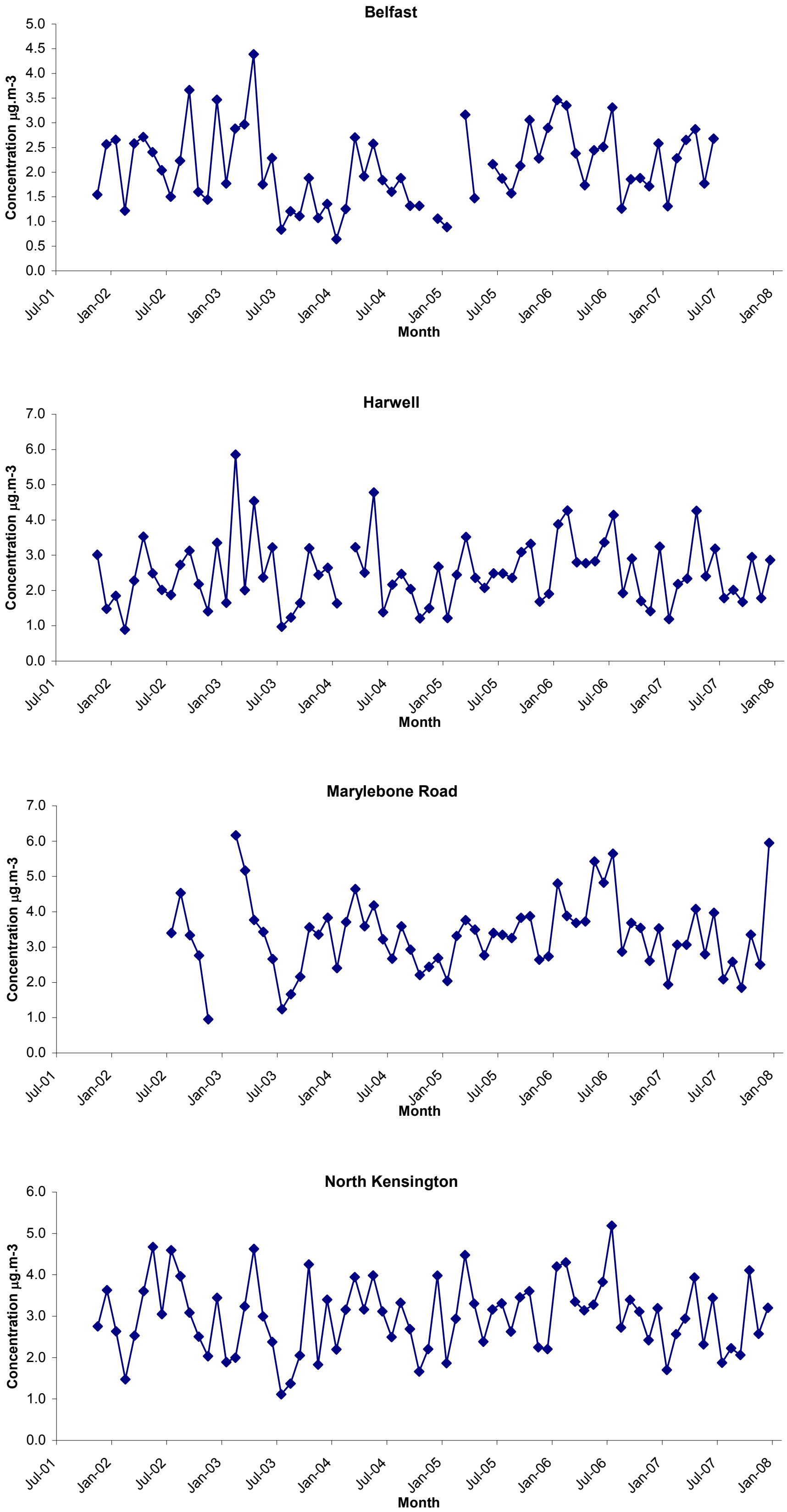


Figure 4-20: Monthly Averaged Sulphate Concentrations (Filter).

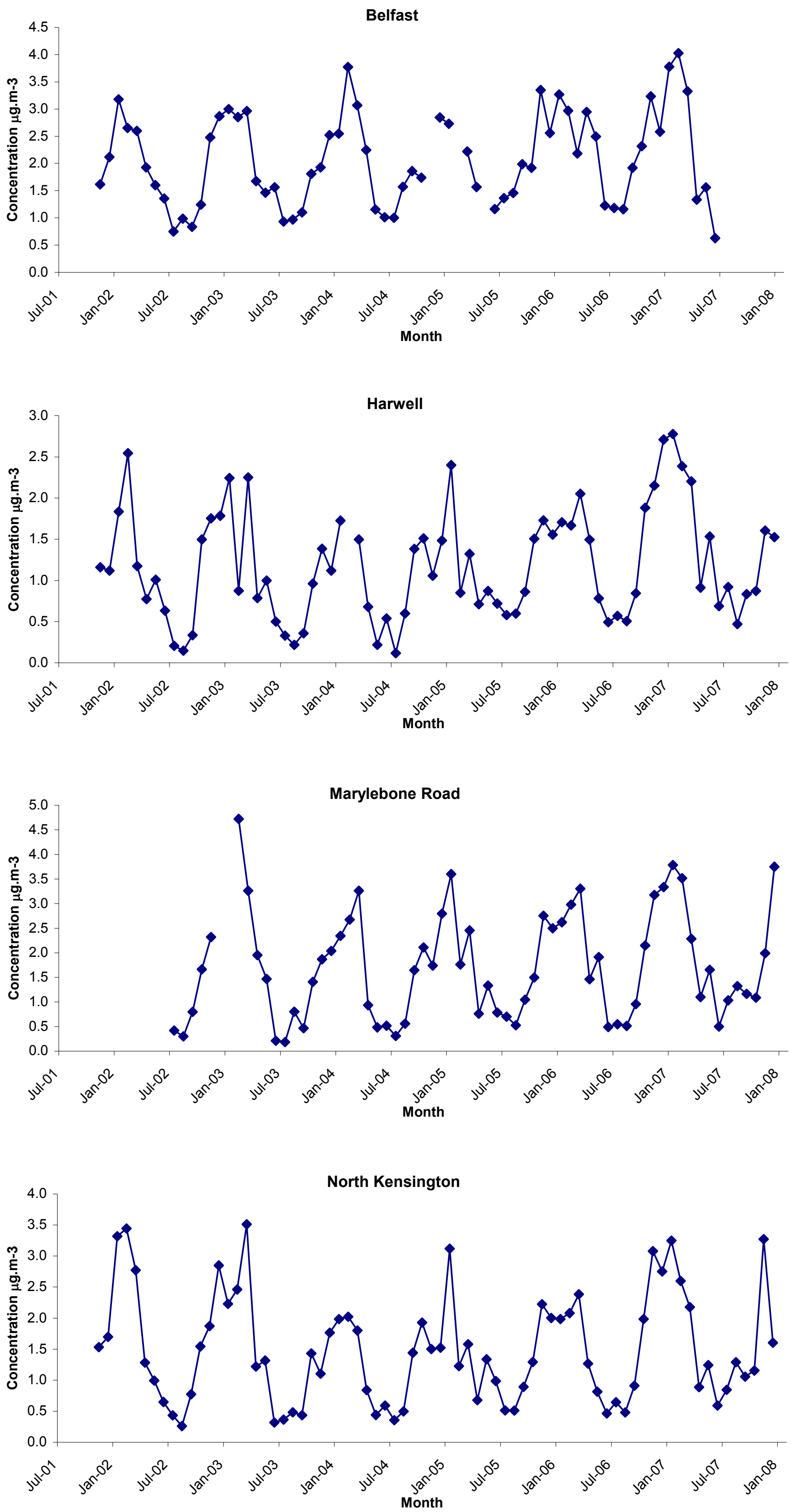


Figure 4-21: Monthly Averaged Chloride Concentrations (Filter).

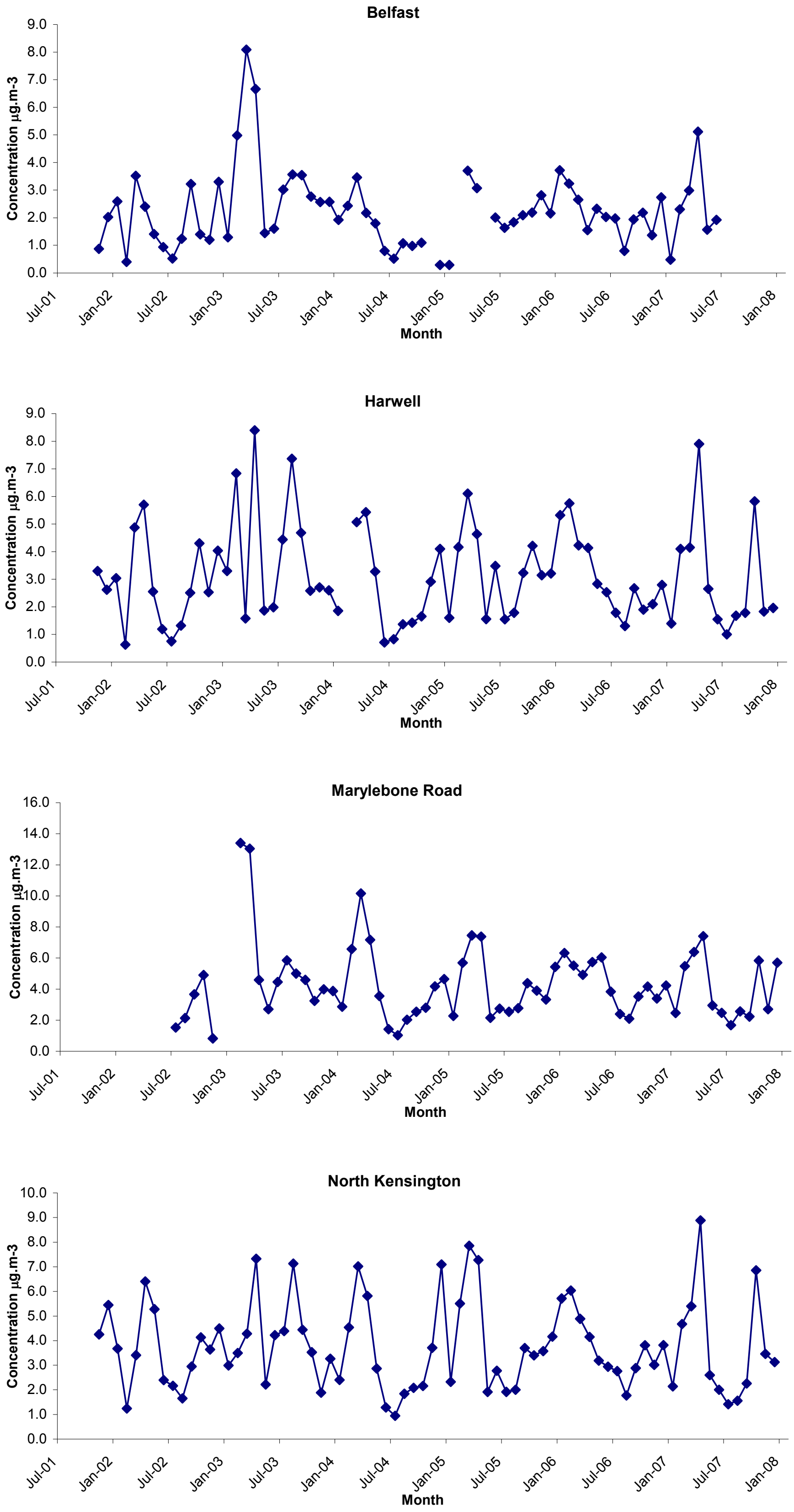


Figure 4-22: Monthly Averaged Nitrate Concentrations (Filter).

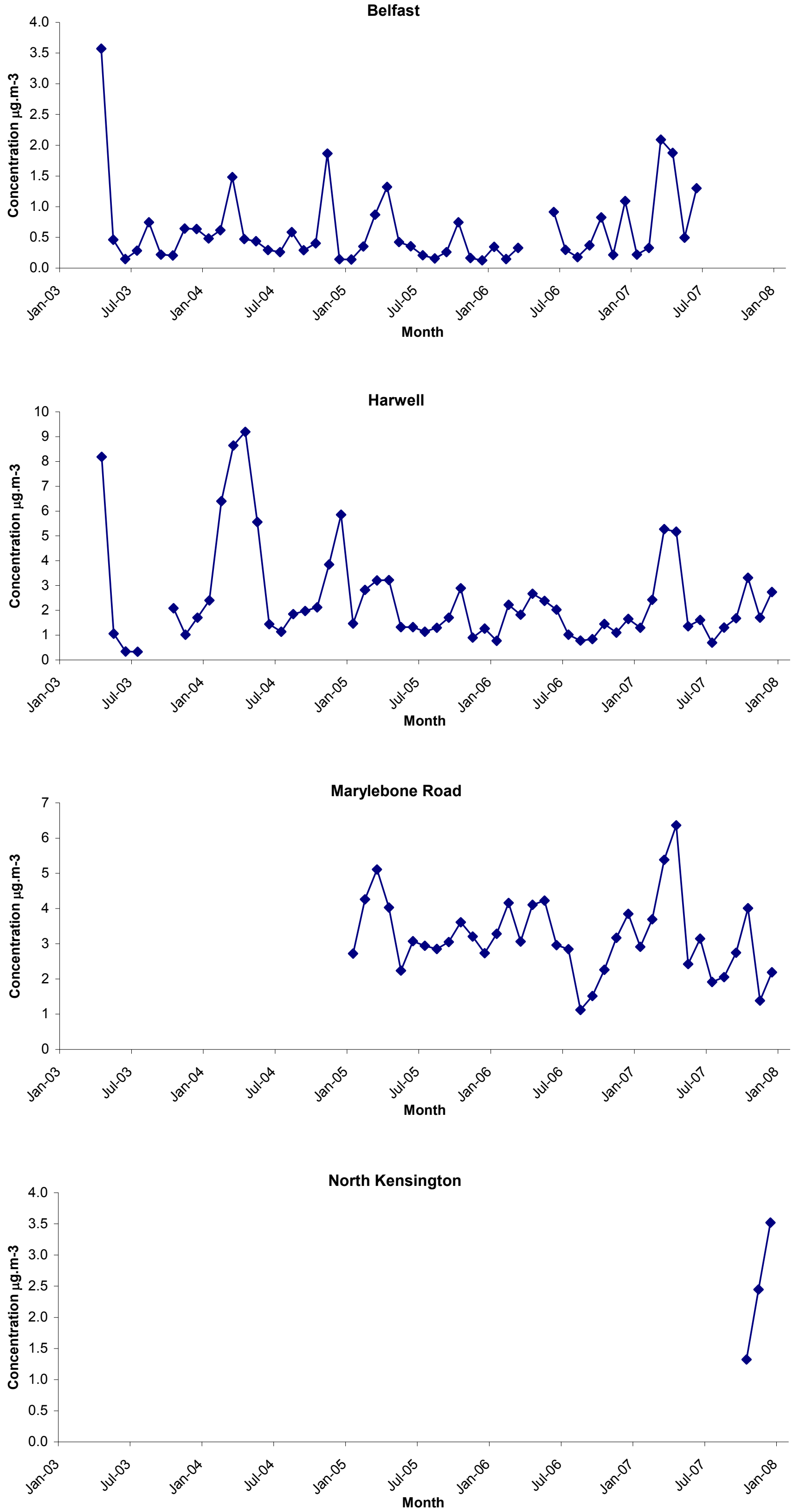


Figure 4-23: Monthly Averaged Nitrate Concentrations (Automatic).

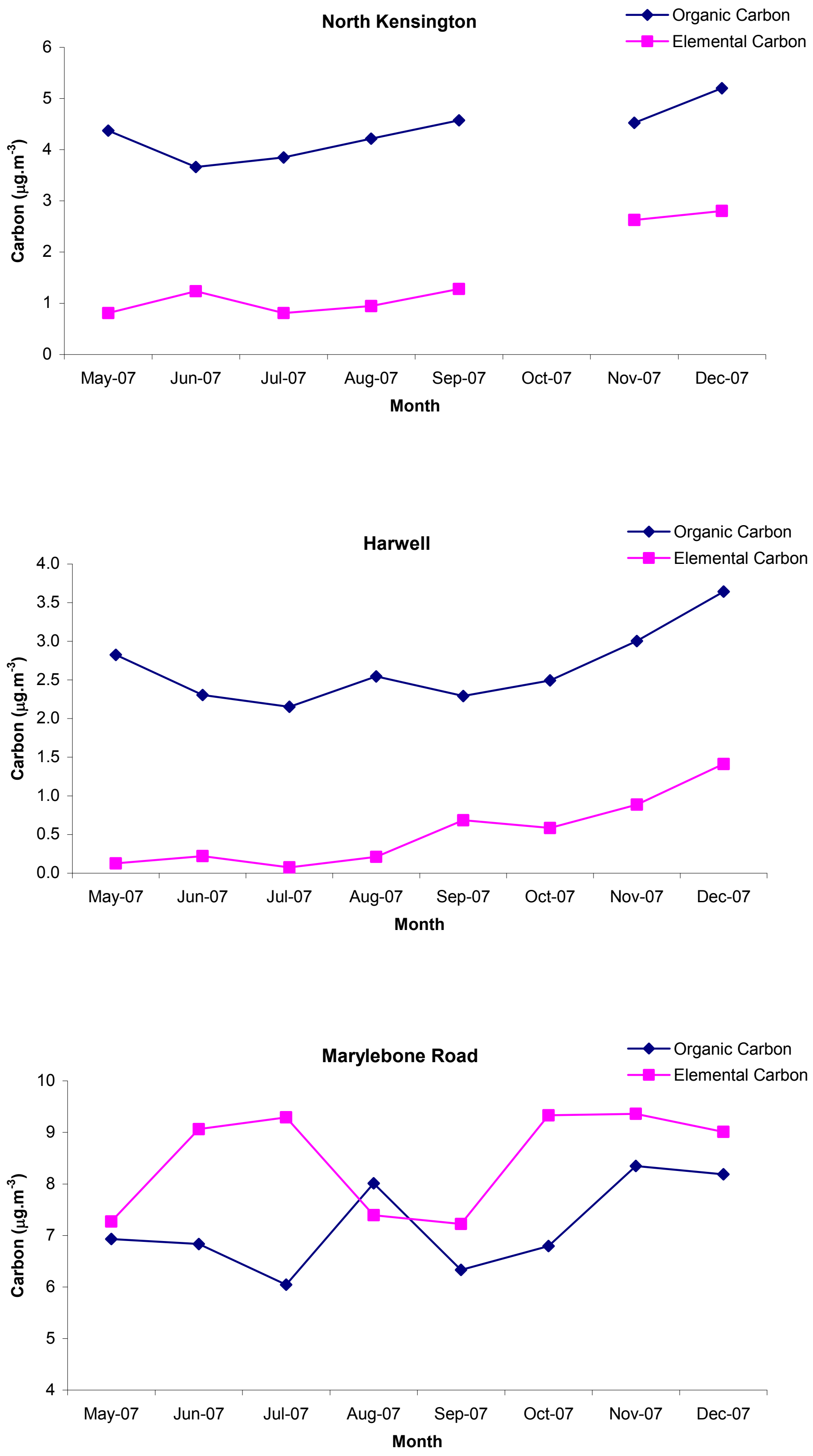


Figure 4-24: Monthly Averages – Daily Elemental and Organic Carbon

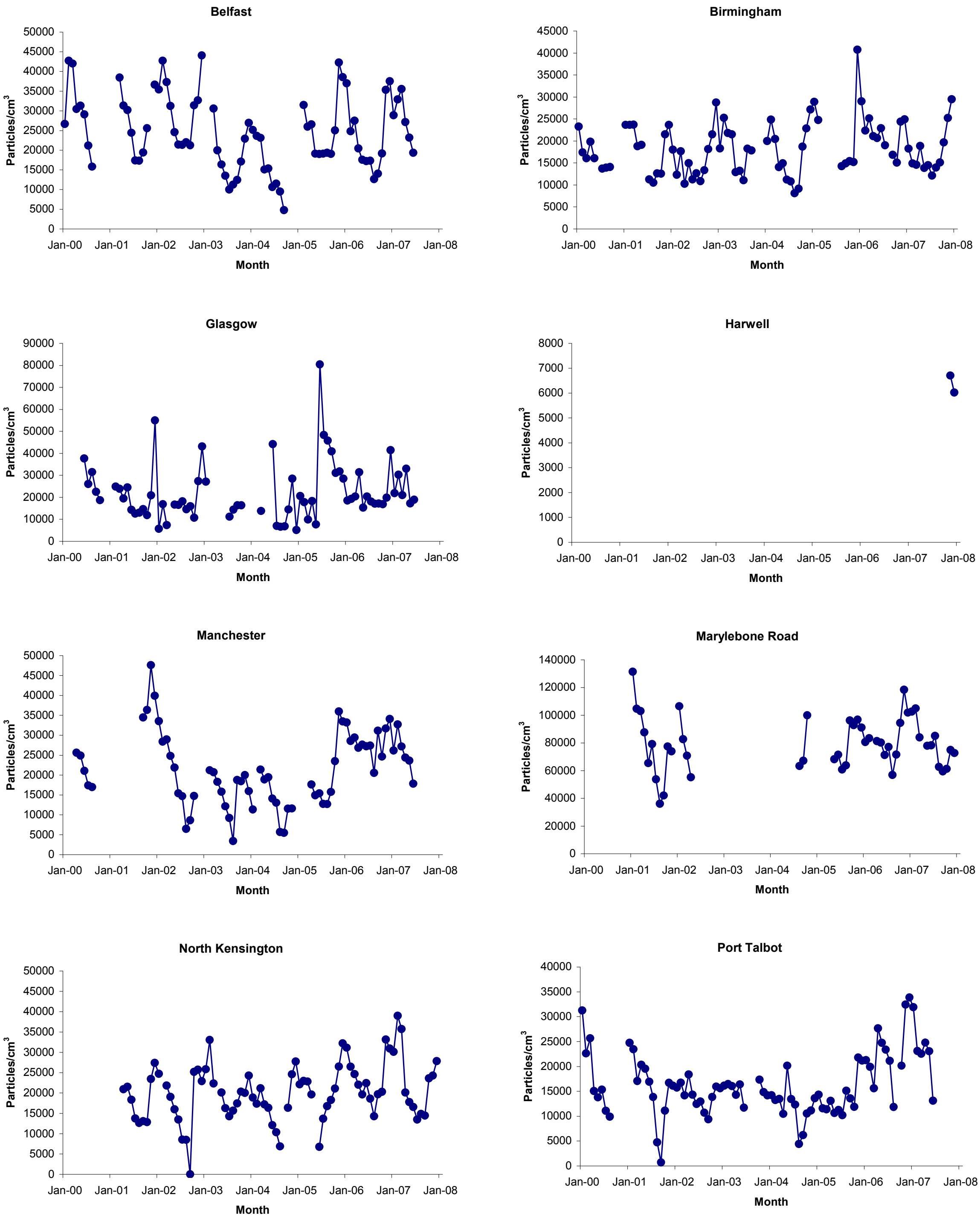


Figure 4-25: Monthly Averages –Particle Counts from CPC.

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 4-26 for the nitrate and in Figure 4-27 for the CPC measurements.

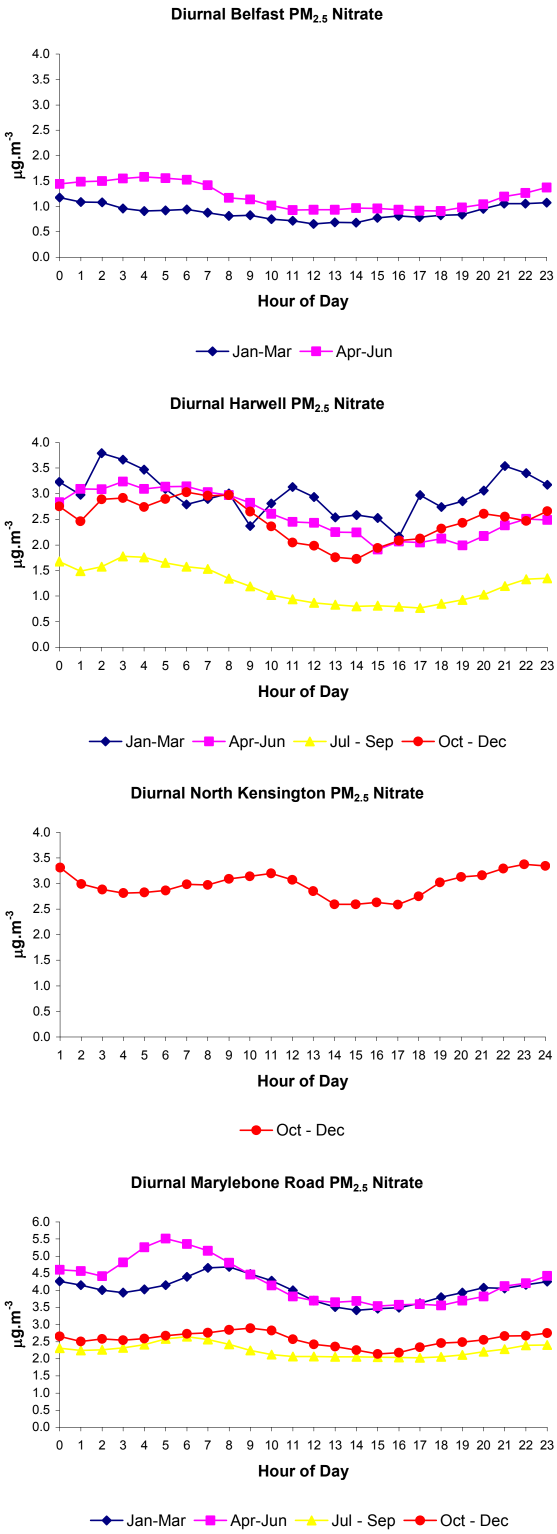
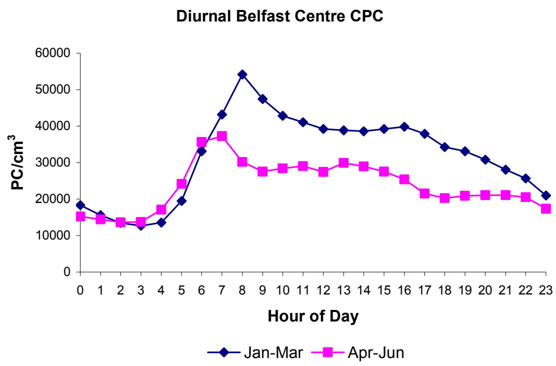
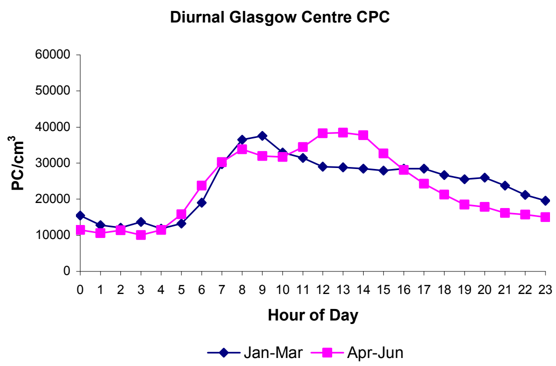
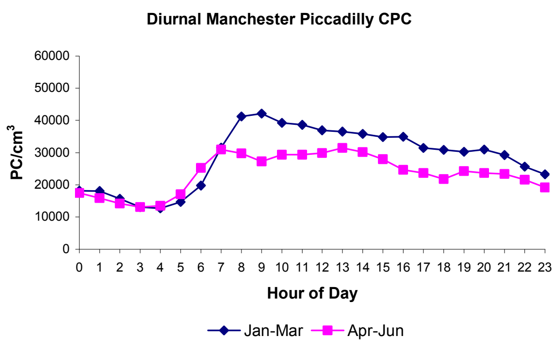


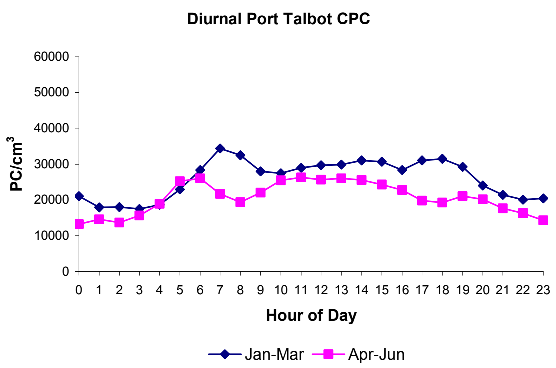
Figure 4-26: Diurnal Profiles of the Automatic Nitrate Concentrations at Network Sites during 2007 by Season.

(A) DISCONTINUED SITES

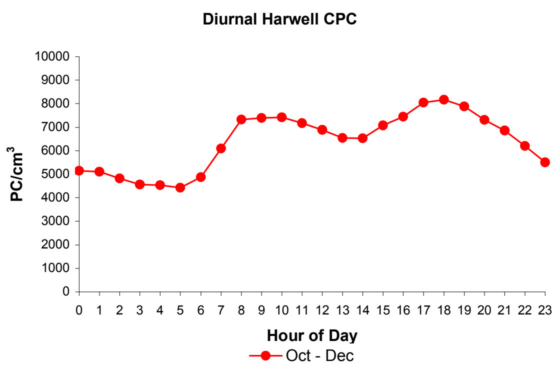


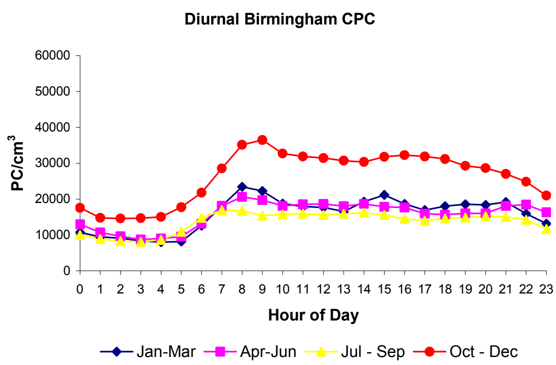


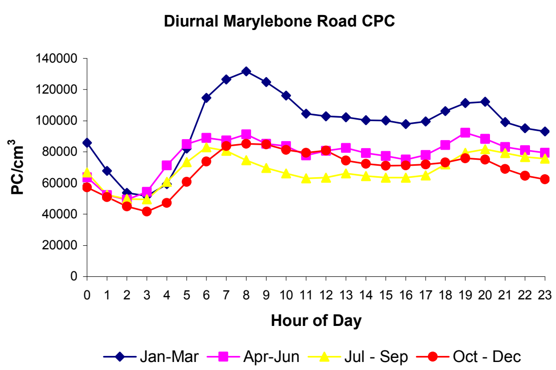




(B) NEW/RETAINED SITES







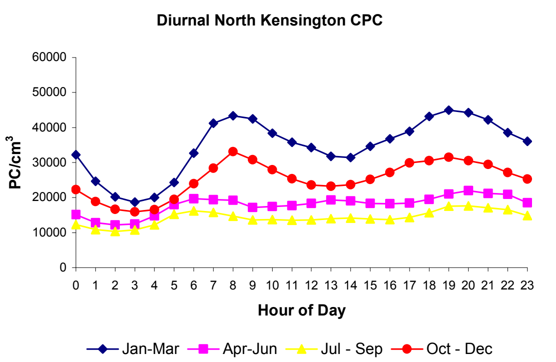


Figure 4-27: CPC Diurnal Profiles by Quarter in 2007.

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

<u>AURN measurements</u>

Any investigation of PM must be linked to the officially reported PM10 and PM2.5 measurements. The discrepancies between the reference gravimetric method and the standard TEOM instrument are well known, and it has also become more 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.

<u>Black Smoke Measurements</u>

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 µg 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 are being replaced with aethalometers, 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).

<u>Rural Monitoring</u>

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. The 2006 have been obtained but the 2007 data were not available for comparison during the writing of this report.

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 two intensive monitoring campaigns in June 2006 and January 2007 with a focus on gas-particle partitioning and particulate matter. CEH Edinburgh deployed steam-jet aerosol collectors at both Auchencorth Moss and Harwell during these periods. The measurements made at Harwell from the June 2006 monitoring campaign have been supplied to NPL.

NPL was funded to analyse the EC/OC filter measurements made at Auchencorth Moss. There is a clear need for NPL to work closely with CEH on the measurements of inorganic anions to ensure consistency of measurements across different Defra monitoring programmes and to avoid unnecessary duplication of measurements (e.g. at Harwell).

5.2 Update on European Activities

5.2.1 Proposal for revised EU Air Quality Directive

In December 2007, the European Parliament agreed text for the new Air Quality Directive. The Directive has now been formally approved, and is expected to be in place by May 2008. The directive aims to revise and combine 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. Firstly, 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. Secondly, there is more explicit allowance for pollution arising from “natural sources” to be excluded. Again, research-led measurements should make the determination of the “natural” fraction of PM a clear aim.

Lastly, 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 a need to clarify what is meant in practice by EC and OC.

5.2.2 CEN standards

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.

The working group is also in the early stages of drafting a CEN standard for automatic PM_{10} measurement. There are no CEN standards planned for ambient particle number or size. There is now, however, a proposal from Germany to CEN TC 264 to produce standard(s) for EC/OC particulate measurements , based on EUSAAR practices.

5.2.3 ISO Standards

There are many standards for particle sizing being prepared within ISO TC24 SC4, though they are mainly not applicable to measuring particles in air. The most relevant is ISO/DIS 15900 “Determination of Particle Size Distribution – Differential Electrical Mobility Analysis for Aerosol Particles” – i.e. measurements using SMPS. This is close to the final voting stage.

This standard does not include requirements for calibrating the number concentration part of the measurement – i.e. CPCs. This will form the topic of a new standard (ISO 27891), on which work has recently started.

5.2.4 EMEP

EMEP published its assessment report on Particulate Matter in August 2007. The conclusions of relevance to this monitoring programme can be summarised from statements such as “There is still a great lack of understanding of some of the major PM components” and “Current knowledge on PM levels and speciation are hampered by shortcomings in monitoring and modelling. Measurements of

PM mass concentrations may not necessarily be comparable across Europe because of the comparability of the different methods, because of differences in correction factors applied to the measurements to make them comparable with reference methods and because of a number of specific analytical issues that may hamper the comparison of PM composition measurements."

Within the EMEP Task Force on Measurements and Modelling, discussions have been initiated on the next phase of the EMEP monitoring strategy. It is likely that the strategy will retain a focus on particulate matter and its composition.

6 Update on Instrumentation

6.1 Discontinued Instruments

In March 2007, Thermo Fisher announced the discontinuation of the following instruments:

- Series 8400N Particulate Nitrate Monitor
- Series 8400S Particulate Sulphate Monitor
- Series 5400 Carbon Particulate Monitor

There are currently five 8400N automatic nitrate analysers in this network. Three are deployed at sites, Harwell, Marylebone Road and North Kensington, and there are two hot spares. Spare parts were available until March 2008 and consumables are expected to be made available until March 2009. The equipment service unit, Air Monitors, has sufficient parts and consumables in stock to run these three deployed instruments until at least the end of the current contract.

There is one 8400S automatic sulphate analyser owned by this network, but it is not deployed.

There are five automatic carbon analysers. Four of these were deployed at sites, Belfast, Harwell, Marylebone Road and North Kensington, until May 2007. Following the discontinuation notice and poor data quality demonstrated in recent studies, these analysers were removed from sites at the end of May 2007.

6.2 Replacement Instruments

Nitrate

Alternative instrumentation 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. In order to assess the suitability of these instruments for integration into a network, NPL will be coordinating a short comparison trial at Teddington in 2008. A detailed schedule and list of participating instruments will be produced before the trial begins.

Carbon

During 2007, King’s College London conducted a trial at Marylebone Road, which compared seven different instruments that measured either black smoke, black carbon or elemental carbon [ERG, 2007]. The measurements of elemental carbon undertaken by NPL using the Sunset Laboratories instrument provided a reference against which the other instruments could be measured. The Magee AE-21 provided the closest agreement to the elemental carbon measurement over a long time period. To provide time-resolved carbon data, three aethalometers are to be installed at Harwell, Marylebone Road and North Kensington between May 2008 and October 2008.

6.3 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. The other proposals are being investigated and costed for Defra's consideration.

6.4 Update on Chemistry and Biology Metrology Programme

The Chemistry and Biology Metrology (CB) programme forms part of the activities in the UK's National Measurement System (NMS), funded by the Department for Innovation, Universities and Skills (DIUS). The CB Programme was launched on 1st April 2007 with the strategic integration of the Valid Analytical Measurements programme and the Measurements for Biotechnology programme. It includes funding for research into particulates and trace chemical analysis, and has allowed continued investment and development of NPL's nanoparticles measurement facilities.

The programme has so far looked into practical metrology that has future implications for ambient nanoparticle monitoring. The outcome of most direct relevance to the particle counting network is the development of a capability to calibrate Condensation Particle Counters by comparison to an aerosol electrometer. The electrometer itself is calibrated using direct current injection, using a traceable current source, meaning that traceability to the SI can be realised. This procedure is due to be submitted for UKAS assessment in 2008.

The investigation of alternatives to radioactive neutralisers in the SMPS has shown that a dual corona discharge method yields very similar results to the conventional neutraliser. Although the design used introduces a dilution of approximately 10:1 of the particles present, resulting in additional calibration steps, the loss of the administrative overhead associated with the use of radioactive sources will undoubtedly increase the desirability of the SMPS as a field instrument.

Future research is focused on the topics of airborne particulate surface area and distinguishing engineered nanoparticles from those of an environmental background. The former will initially centre on the comparison of different measurement techniques including SMPS and diffusion charging, helping increase the relevance of the already deployed SMPS instruments to the current nanotoxicology debate.

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, NPL Report xx, this report.

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).

Estimation of the Emission Factors of Particle Number and Mass Fractions from Traffic at a Site Where Mean Vehicle Speeds Vary Over Short Distances, A.M. Jones and R.M. Harrison, Atmospheric Environment, **40**, 7125-7137 (2006).

Assessment of Natural Components of PM_{10} at UK Urban and Rural Sites, A.M. Jones and R.M. Harrison, Atmospheric Environment, **40**, 7733-7741 (2006).

What are the Sources and Conditions Responsible for Exceedences of the 24 h PM_{10} Limit Value (50 µg m^{-3}) at a heavily trafficked London site? A. Charron, R.M. Harrison and P.G. Quincey, Atmospheric Environment, **41**, 1960-1975 (2007).

Particulate Matter at a Rural Location in Southern England during 2006: Model Sensitivities to Precursor Emissions, R. Derwent, C. Witham, A. Redington, M Jenkin, J. Stedman, R. Yardley and G Hayman, submitted to Atmospheric Environment, March 2008.

8 References

ERG (2007) **Marylebone Road Aethalometer Trial Report**, King's College London, May 2007.

NPL (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 2006.

NPL (2007a) **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.

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

Paul Quincey (2007) **A relationship between Black Smoke Index and Black Carbon Concentration**, Atmospheric Environment, Volume 41, Issue 36, Pages 7964-7968.

US EPA (2005) **Comparison of Integrated Filter and Semi-Continuous Measurements of $PM_{2.5}$ Nitrate, Sulfate, and Carbon Aerosols in the Speciation Trends Network (STN)**, US Environmental Protection Agency EPA 454/R-05-004, 2005.

9 Acknowledgements

We wish to acknowledge the support provided by the Department for Environment, Food and Rural Affairs (Defra) and the Devolved Administrations (the Scottish Executive, Welsh Assembly Government and the Department of the Environment Northern Ireland) for this work under contract CPEA 28.

Annex 1. Network Instruments

(a) Network Structure, January to May 2007.

Site	Hourly $PM_{2.5}$ nitrate	Daily PM_{10} (anions)	Hourly Carbon	CPC	SMPS
Belfast Centre (Urban centre)	x	x	x	x	
Birmingham Centre (Urban centre)				x	
Glasgow Centre (Urban centre)				x	
Harwell (Rural)	x	x	x		x
Bloomsbury (Urban centre)					x
North Kensington (Urban background)		x	x	x	
Marylebone Road (Roadside)	x	x	x	x	x
Manchester Piccadilly (Urban centre)				x	
Port Talbot (Urban background)				x	

(b) Network Structure, June to December 2007.

Site	Hourly $PM_{2.5}$ nitrate	Daily PM_{10} (anions)	Daily 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
Hourly carbon	Thermo 5400
Daily PM_{10} filter	Thermo Partisol 2025
CPC	TSI model 3022A
SMPS	TSI model 3936
Daily OC/EC	Thermo Partisol 2025

Annex 2. Map showing Location of Network Sites (January to May 2007)

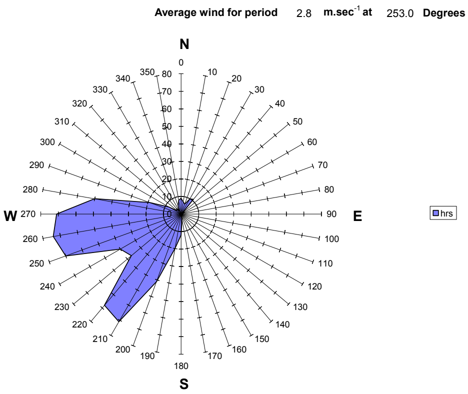
Annex 3. Instrument Repairs

Site	Instrument	Date	Fault
Belfast	Carbon	01/02/07	Power trip at site – instrument needed manually restarting. Multiple lamp failure
		05/03/07	Filter temperature warning
	Nitrate	01/02/07	Faulty PMT unit
Harwell	Carbon	11/04/07	Leaking pinch valve replaced.
	Nitrate	08/01/07	Reaction cell pressure too high – pump was rebuilt and NOx analyser recalibrated
		18/05/07	NOx analyser warning. Pulse analyser fitted with new circuit board. All recalibrated.
		03/07/07	Sample flow out of range
		06/11/07	PMT assembly replaced (removed to workshop due to lack of space at site)
		19/12/07	High and erratic flow
		03/01/08	Analyser communication failure. CPU replaced.
Marylebone Road	Nitrate	20/06/07	Communication failure.
		15/11/07	NOx analyser flow fault. Solenoid valve assembly replaced.
		06/12/07	NOx reaction cell changed.
North Kensington	Carbon	16/02/07	Afterburner lamps replaced.

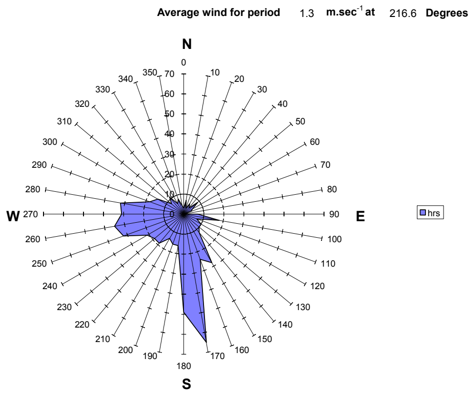
Annex 4. Wind Roses at Harwell and Rochester

Wind Roses – Harwell, January-June 2007

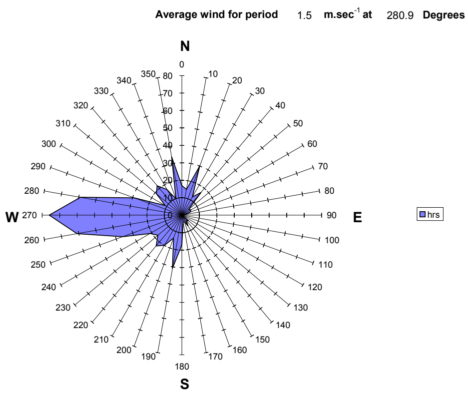
January 2007



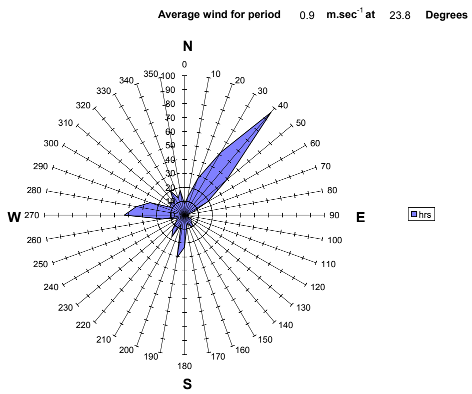
February 2007



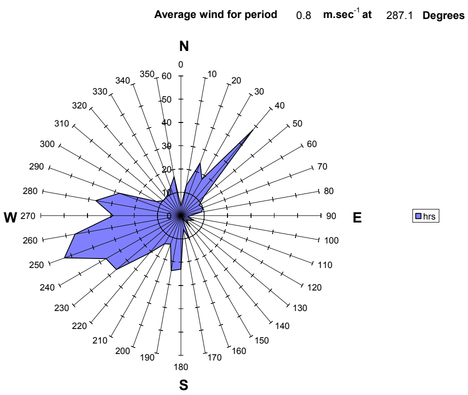
March 2007



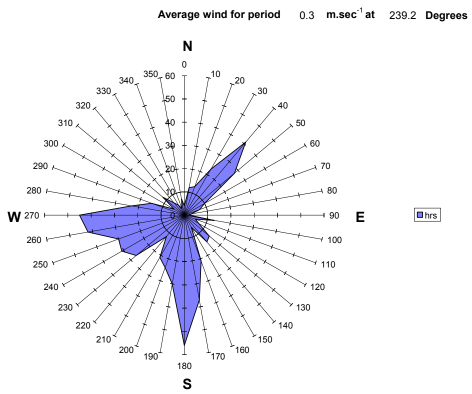
April 2007



May 2007

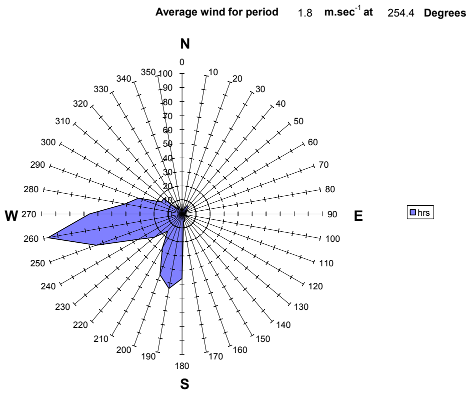


June 2007

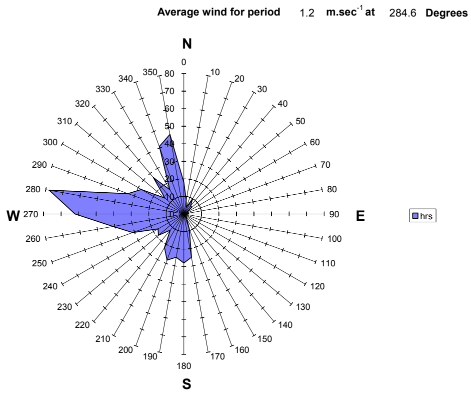


Wind Roses – Harwell, July-December 2007

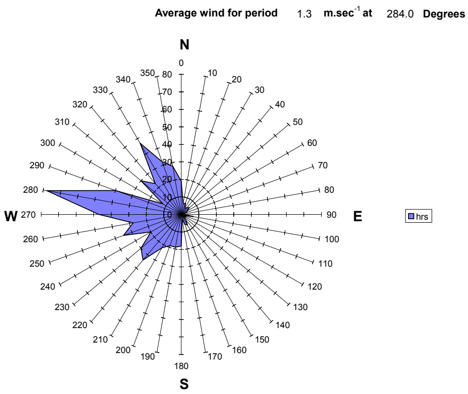
July 2007



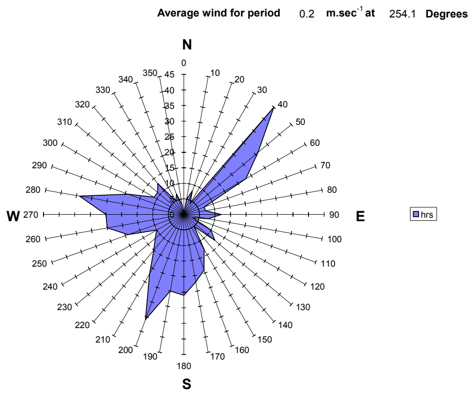
August 2007



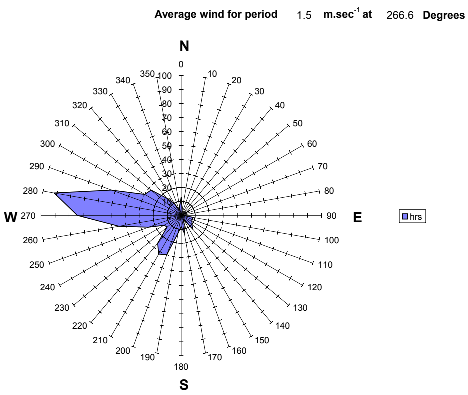
September 2007



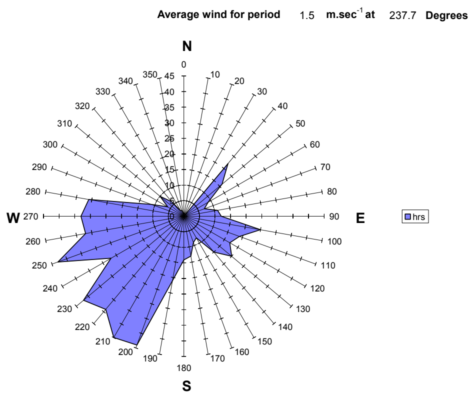
October 2007



November 2007

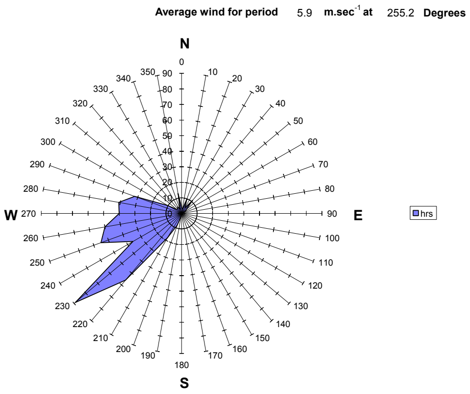


December 2007

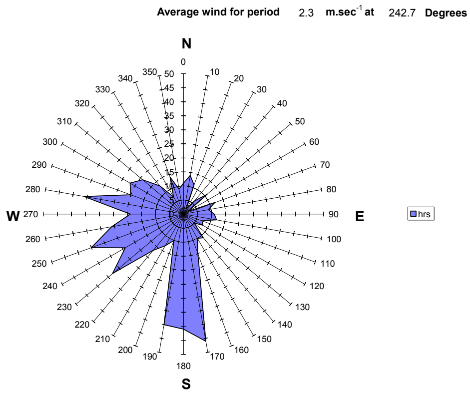


Wind Roses – Rochester, January-June 2007

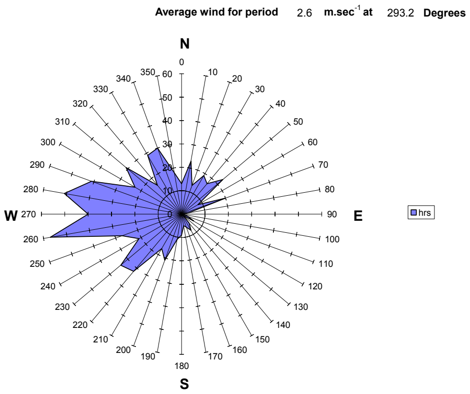
January 2007



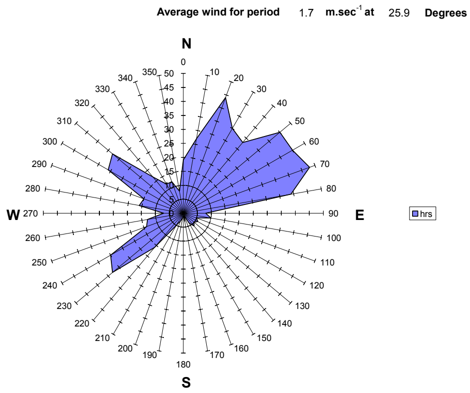
February 2007



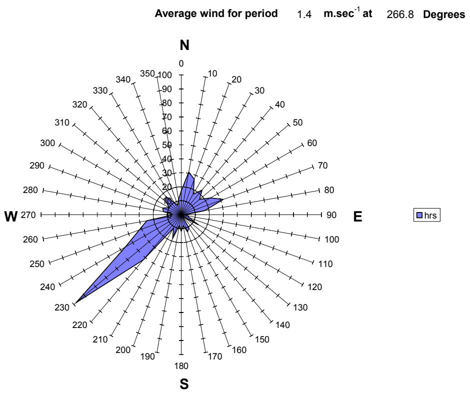
March 2007



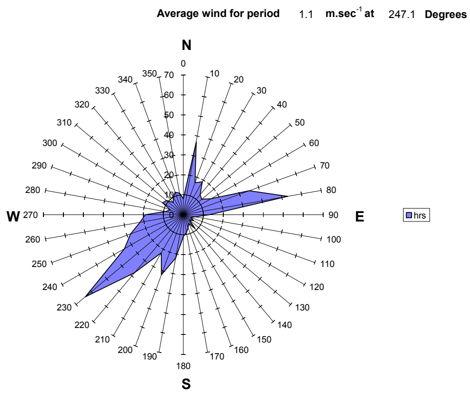
April 2007



May 2007

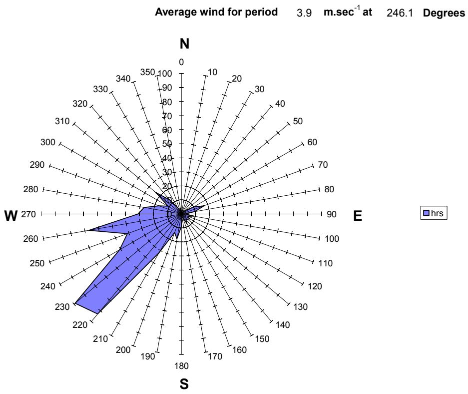


June 2007

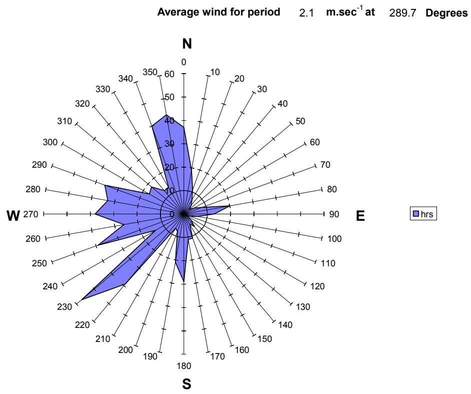


Wind Roses – Rochester, July-December 2007

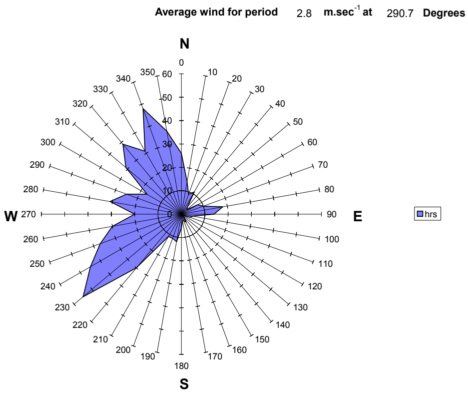
July 2007



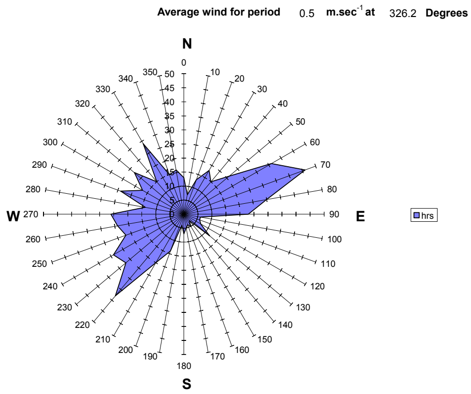
August 2007



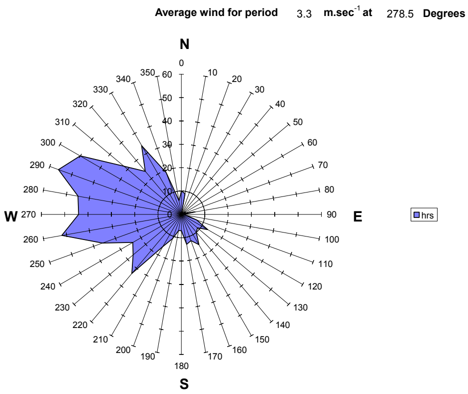
September 2007



October 2007



November 2007



December 2007