NPL REPORT AS 74

Airborne Particulate Concentrations and Numbers in the United Kingdom (phase 3)
Annual report 2011

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MAY 2013

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ISSN 1754-2928

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Approved on behalf of NPLML by Martyn Sené, Operations Directors

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EXECUTIVE SUMMARY

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

This is the Annual Summary Report for 2011 and contains:

- A summary of network operation and quality procedures.
- A graphical presentation of all ratified network data from 2011.
- Data capture per instrument per month.
- Comparison of 2011 data with data from 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 and all instruments have been serviced and calibrated by the instrument manufacturer or Equipment Service Unit or NPL.

In addition to the measurement programme, research reports have been commissioned on specific topics related to the measurement programme. As part of the contract, 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. A list of topic reports in the year is given, together with their main findings.

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1 INTRODUCTION

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All equipment was audited during the annual audit round and all instruments have been serviced and calibrated by the instrument manufacturer or Equipment Service Unit or NPL.

In addition to the measurement programme, short-term research projects have been commissioned on specific topics related to the measurement programme. As part of the contract, 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. A list of topic reports in the year is given in Section 6 together with their main findings.

2 NETWORK OPERATION

2.1 OVERVIEW

The operation of the network in 2011 was structured in the same way as previous years. King's College London (KCL) has continued its role as the Central Management and Control Unit (CMCU). It has carried out activities including routine collection of data from site, initial data validation and instrument fault finding, routine liaison with the Local Site Operator (LSO) and the Equipment Support Unit (ESU). The QA/QC activities were performed by NPL and included site audits, instrument calibrations, data ratification and reporting.

2.2 NETWORK STRUCTURE

The measurement programme during 2011 is shown in Table 2-1. Wind speed and direction are reported for the Rochester site. Site details are available through http://aurn.defra.gov.uk/stations/index.htm.

In early February 2011, two URG-9000B Ambient Ion Monitors (AIM) were installed at the two sites in London to measure PM_{10} anion and cation concentrations with high time resolution.

To comply with the European Directive 2008/50/EC, which requires $PM_{2.5}$ composition measurements at rural sites to ensure adequate information on background levels, a Leckel Sequential Sampler SEQ47/50 has been installed at Harwell and Auchencorth Moss respectively in September and November 2011 to sample $PM_{2.5}$ for subsequent analysis for Organic Carbon and Elemental Carbon (OC/EC).

Table 2-1 Network structure during 2011

SITE	Hourly PM_{10} Anions/cations	Daily PM_{10} OC/EC	Weekly $PM_{2.5}$ OC/EC	Hourly $PM_{2.5}$ Black Carbon	CPC	SMPS
Birmingham Tyburn (Urban background site)					X	
Harwell (Rural site)		X	X	X	X	X
Auchencorth Moss (Rural site)			X			
London North Kensington (Urban background site)	X	X			X	X
London Marylebone Road (Roadside site)	X	X			X	X

2.3 INSTRUMENTATION

A brief summary of the operation of the network instruments 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[1].

2.3.1 Particle counting and sizing analysers

Particle number concentrations are measured using a Condensation Particle Counter (CPC) TSI model 3022A. This works by passing the sample through a heated tube saturated with butanol, and then cooling the airstream to set up supersaturated conditions. The butanol vapour then condenses on particles down to very small size, enabling them to be counted optically. CPCs are sensitive to particles from 7 nm up to several microns in size, and have a concentration range from zero to 10^7 cm^{-3}. At lower concentrations, each particle is individually counted, and at higher concentrations an optical integrating mode is used.

Particle size distributions are measured using a Scanning Mobility Particle Sizer (SMPS). This consists of a CPC (TSI model 3775) combined with an electrostatic classifier (TSI model 3080). The electrostatic classifier consists of a charge neutraliser (incorporating a Kr-85 radioactive source) and a Differential Mobility Analyser (DMA – TSI model 3081). The former brings the particles in the sample to a known steady state charge distribution and the latter allows particles of a single electrical mobility (a quantity related to particle diameter) to pass to the CPC. By varying the operating voltage of the DMA, the size of particles sent to the CPC can be varied and a size distribution obtained.

2.3.2 NPL drying units

The EU funded EUSAAR project (European Supersites for Atmospheric Aerosol Research) aimed at, amongst other things, improving the harmonisation of the monitoring of many of the pollutants

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[1] NPL report DQL – AS 037“ CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2) Estimation of Measurements Uncertainty in Network Data”, R. Yardley, B. Sweeney, D. Butterfield, Q. Quincey, G. Fuller, D. Green, March 2007

covered by this network. Harwell was a EUSAAR site. The EUSAAR project finished in March 2011 and many of its activities are continued in the project ACTRIS.

The Harwell site was audited by a group from EUSAAR in November 2007 and a number of recommendations were made, most notably on the sampling inlet and regulating the humidity of the inlet air. New manifolds with PM$_1$ size selective cyclones were installed for the SMPS and CPC at Harwell and the other Network sites in late 2009 to meet these recommendations. The humidity of the sample air going to both the CPC and SMPS instruments is now controlled and monitored through drying units designed by NPL, which use Nafion driers (see Figure 2-1). Humidity sensors have been installed and are logged by the computers.

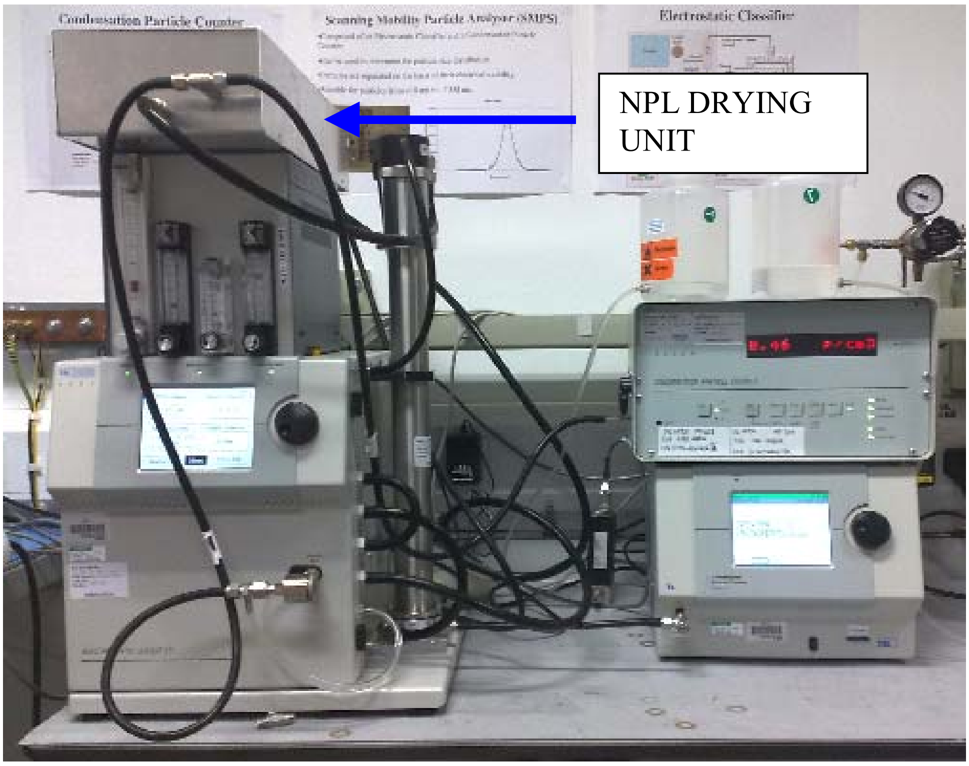

Figure 2-1 Typical configuration of CPC, SMPS and NPL drying unit at the Network sites

2.3.3 Organic Carbon and Elemental Carbon (PM$_{10}$ and PM$_{2.5}$)

Sampling for daily measurements of OC/EC components of PM$_{10}$ were made using a Thermo Partisol 2025 sequential air sampler and weekly measurements of PM$_{2.5}$ using a Leckel SEQ47/50 sequential sampler. Ultrapure quartz filters (Pallflex Tissuquartz 2500QAT-UP) were used for the analysis.

The analysis is carried out using the Sunset Laboratory Inc. thermal/optical carbon analyser. In the laboratory, a 1.5 cm^2 punch is taken from each filter and analysed for elemental and organic carbon in a procedure based on the NIOSH protocol[2]. It involves heating the sample to remove the PM from the filter, conversion of carbonaceous material 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 and reflection 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. The protocol used is termed Quartz, a close variation of the NIOSH protocol. Correction can be made

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[2] PD CEN/TR 16243:2011 Ambient air quality — Guide for the measurement of elemental carbon (EC) and organic carbon (OC) deposited on filters.

using either the transmitted or reflected signal, often giving significantly different results. As the European standardisation process is at an early stage, as described in Section 5, and data from different methods is being evaluated, the results from both methods are presented in this report.

For some of the $PM_{2.5}$ samples, analysis is performed using both Quartz and EUSAAR_2 protocols.

(a) (b)

Figure 2-2 (a) Thermo Partisol 2025 sampler. (b) Leckel SEQ47/50 sampler

Figure 2-3 Sunset Laboratory Inc. thermal/optical carbon analyser

2.3.4 URG – 9000B Ambient Ion Measurements (PM_{10} anion and cation measurements)

The URG – 9000B AIM (Figure 2-4) draws a volumetric flow by measuring the pressure drop across an orifice, along with the orifice temperature, ambient temperature and pressure. The sample is drawn through a Liquid Diffusion Denuder where interfering acidic and basic gases are removed. In order to achieve high collection efficiencies, the particle-laden air stream next enters the Aerosol Super Saturation Chamber to enhance particle growth. An Inertial Particle Separator collects these enlarged particles, which it then stores in an Aerosol Sample Collector until the particles can be injected into the Ion Chromatograph.

The instrument samples for 55 minutes during each hour then analyses the collected sample. The analysis takes 15 minutes. It is a two-stage instrument, analysing the previous sample while it is collecting the current sample. Hence the instrument allows the production of hourly averages for all relevant anions and cations, dramatically improving the science outputs. The two instruments in this Network are supplied with a size selective PM_{10} monitoring head for consistency with the previous anions sampling equipment.
The sampler is used in the field together with the 2000 Dionex Ion chromatograph (IC), which has its own eluent re-generator and makes automated running simpler. The eluent used for anion measurements is 20 mM Methanesulphonic acid and the eluent used for anion measurement is potassium hydroxide. The 2000 series IC also allows ramps in eluent concentration to speed up analysis for the longer retention time species.

A comparison between the daily averages of chloride, sulphate and nitrate measurements produced by the URG analyser and daily filter-based measurements using the quartz filters described above was carried at North Kensington to test the performance of the automatic analyser. The filters were analysed in the lab by Ion Chromatography. 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.

Details of the comparison are reported in Section 4.4.2.

Figure 2-4 URG – 9000B Ambient Ion Measurements

2.3.5 Aethalometer ($PM_{2.5}$ Black Carbon)

Aethalometers quantify Black Carbon on filter samples based on the transmission of light through a sample. The sample is collected onto a quartz tape, and the change in absorption coefficient of the sample is measured by a single pass transmission of light through the sample, measured relative to a clean piece of filter. The system evaluates changes in two optical sensors (sample and reference), with the light source both on and off, such that independent measurements of the change in attenuation of the sample are produced for averaging periods of typically five minutes. The absorption coefficient for material added during the period, α [m^{-1}], is calculated from the attenuation change, and the area and volume of the sample, and converted to a Black Carbon concentration for the period, as a first approximation, using a mass extinction coefficient [16.6 m^2 g^{-1}] chosen by the manufacturer to give a good match to Elemental Carbon. In practice this mass extinction coefficient will vary with factors such as particle size, sample composition and quantity of material already on the filter, as discussed below.

The Aethalometers Magee Scientific (Figure 4-5) run on the Network operate at 2 wavelengths, 880nm and 370 nm. The 880nm wavelength is used to measure the Black Carbon (BC) concentration of the aerosol, while the 370nm wavelength gives a measure of the “UV component” of the aerosol. At wavelengths shorter than about 400 nm, certain classes of organic compounds (such as polycyclic aromatic hydrocarbons, and also certain compounds present in tobacco smoke and fresh diesel exhaust) start to show strong UV absorbance. The UV component can therefore in principle be used as an indicator of oil and solid fuel emissions.

The UV component concentration is obtained by subtracting the measured BC concentration from the concentration measured by the 370nm source. The UV component is not a real physical or chemical material, but a parameter based on UV absorption due to the mix of organic compounds measured at this wavelength. This ‘UVPM’ is expressed in units of ‘BC Equivalent’.

It is well known that the assumption of constant mass extinction coefficient does not hold as the filter spot darkens, leading to nonlinearity in the Aethalometer response. The effect of this nonlinearity results is that the Aethalometer under-reads at high filter tape loadings. To correct for this nonlinearity, the model developed by A Virkkula[3] has been used to correct for increased attenuation due to spot darkening during sampling. This uses a simple equation $BC_{corrected} = (1+k.ATN) BC_{uncorrected}$, where ATN is the light attenuation by the filter spot, and k is a parameter determined for each filter spot such that continuity between adjacent filter spots is greatly improved. All of the Black Carbon and UV component results in this report have been corrected by this method.

In this Network ambient air is drawn into the sampling system through a standard stainless steel rain cap mounted on the end of a vertical stainless steel tube. Size selection of the sampled aerosol is made by a $PM_{2.5}$ cyclone placed close to the inlet of the aethalometer. All of the tubing before the cyclone is constructed from stainless steel.

Data from the Harwell aethalometer are shown in more detail in the 2011 Black Carbon Network report[4].

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[3] A Simple Procedure for Correcting Loading Effects of Aethalometer Data, A Virkkula *et al*, *Journal of Air and Waste Management Association, 57:1214-1222, 2007.*

[4] NPL report “2011 Annual Report for the UK Black Carbon Network” May 2012

Figure 2-5 Magee Scientific aethalometer

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.
- An annual audit of all sites and instruments conducted by NPL.
- Calibration data produced at audit by the Equipment Support Unit (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.
- Field blank filters have been analysed to evaluate the contamination due to the transport of the filters to the sites and back to the laboratory.
- Routine maintenance is carried out on all instruments according to manufacturers' instructions.
- The 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 Business Innovation and Skills (BIS) 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.

3.1 SCHEDULED INSTRUMENT SERVICE AND CALIBRATION

The 2025 Partisol at North Kensington was serviced twice by the ESU, Air Monitors on 15th June and 26th October. The service procedure includes replacing old or worn parts, temperature and flow calibrations, leak tests and pump refurbishment. The Partisols at Harwell and Marylebone Road were not serviced in 2011 due to planned changes to the sampling arrangements (which did not take place). They will be serviced on 2012.

Since January 2009, the 3022A and 3775 CPCs have been serviced and calibrated at NPL. NPL received ISO 17025 accreditation for this calibration in 2008. Since January 2010 the SMPS instruments have also been serviced and calibrated at NPL.

Table 3-1 Annual CPC/SMPS service and calibration dates. (*) Only 'as found' calibration.

Site	2009 service	2010 service	2011 service	2012 service
Birmingham	March 09	January 10	March 11	February/March 12
North Kensington	March 09	February 10	January 11	February/March 12
Marylebone Road	January 09(*)	February 10	February 11	February/March 12
Harwell	March 09	January 10	March 11	February/March 12

The two URG analysers were serviced on 3rd and 4th October 2011. The service includes flow measurement at the by-pass flow on the top of the sampler, replacing sample lines and peristaltic pump tubes, and cleaning the sample syringes.

4 NETWORK DATA

The following sections discuss the different measurements made in the monitoring programme. The concentration data are also presented in a graphical format and unusual or interesting occurrences are noted and discussed.

Annual ratified data from 2011 will be provided to Defra's UK-AIR (http://uk-air.defra.gov.uk/) and will be used to form the basis of future topic reports, produced in collaboration with the University of Birmingham.

4.1 POLLUTION EPISODES

In 2011 a few pollution episodes were identified, which involved mainly London and the South East of England. A list of the episodes which affected the network measurements with a brief description is given below.

- **Late February 2011.** Widespread "moderate" PM_{10} particulate levels were recorded at many roadside sites across the South East on 18th and into the morning on 19th February as a result of light easterly winds bringing in an influx of particulate matter from continental Europe. "Moderate" PM_{10} levels were also recorded at background sites in central London. The elevated levels dropped rapidly on the afternoon of the 19th due to a short term change in wind direction and bands of rain crossing the UK. The episodic conditions were resumed again on the 20th when a return to drier conditions and easterly winds bought in a second polluted continental air mass and particulate levels increased and remained elevated on the two following days.

- **Mid/late March 2011.** Widespread 'moderate' PM_{10} particulate was recorded across London and south-east England following a large flux of particulate from Europe.

- **Smog mid-April 2011.** A widespread PM_{10} and O_3 episode affected most of the UK at the end between the 17th and 24th of April. PM_{10} concentrations reached the highest levels of the year. Warmer temperatures and stronger sun also led to widespread 'moderate' O_3. The pollution episode was caused by a combination of both UK pollution sources and pollution from continental Europe brought into south east England on an easterly air flow.

- **End of September – early October 2011.** Unseasonably warm and sunny weather brought about unusually elevated levels of O_3, PM_{10} and NO_2 across London and the South East. The elevated pollution levels were caused by high pressure over Europe. London and South East England basked in warm air which had circulated over some of the most densely populated and industrial areas of North West Europe where it gathered substantial concentrations of air pollution. The highest concentrations of primary air pollution in the South East of England were measured in London where air pollution from the capital added to that imported from Europe.

- **Guy Fawkes.** Elevated concentrations of PM_{10} particulate were measured in several areas on the evening of 5th November. However, the damp and breezy weather in southern England dispersed smoke rapidly and air pollution remained ‘low’.

- **Smog November 2011.** Calm foggy conditions combined with a polluted continental air mass caused ‘moderate’ PM_{10} particulates were recorded at a number of busy roadside locations throughout London on 20th, 21st and 22nd November 2011.

- **December 2011.** All measurements show a drop in concentration at almost all the network sites, probably due to warm temperatures and Christmas break.

(Source: London Air Quality Network - www.londonair.org.uk/)

It should also be noted that demolition work was carried in the vicinity of the Harwell site from mid-June until October. The demolition works and the associated increased traffic might have affected the measurements at the site.

4.2 OC/EC MEASUREMENTS (PM_{10})

Monthly data capture rates for the Partisol 2025 instruments in 2011 are given in Table 4-1. The data capture in March was low at Harwell because of repeated filter exchange failures. The instrument was eventually fixed by the ESU.

Table 4-1 Monthly data capture for the Partisol 2025 Samplers during 2011

Site	Harwell	North Kensington	Marylebone Road
January	55%	84%	94%
February	68%	86%	96%
March	55%	94%	100%
April	90%	100%	100%
May	97%	97%	100%
June	100%	77%	90%
July	100%	100%	100%
August	94%	94%	100%
September	100%	100%	100%
October	94%	84%	100%
November	93%	100%	100%
December	81%	94%	94%
Average	**85%**	**92%**	**98%**

The filter measurements of OC, EC and TC (Total Carbon – the sum of OC and EC) made in 2011 are displayed in Figures 4-1 to 4-4 for the three sites. Concentrations for EC and OC are shown for thermal/optical transmission (TOT) and thermal/optical reflectance (TOR) methods. Because the optical correction simply determines the split of TC into EC and OC, TC is the same for both methods. Data are reported as the mass of carbon atoms per unit volume of air.

The PM pollution episodes are highlighted in each graph for each site. These are less notable in the EC concentrations at Marylebone Road, where local traffic is the main source of elemental carbon.

The concentrations dropped dramatically at all sites in December. This is consistent with the CPC and SMPS measurements in this network and NOx and PM_{10} from AURN measurements.

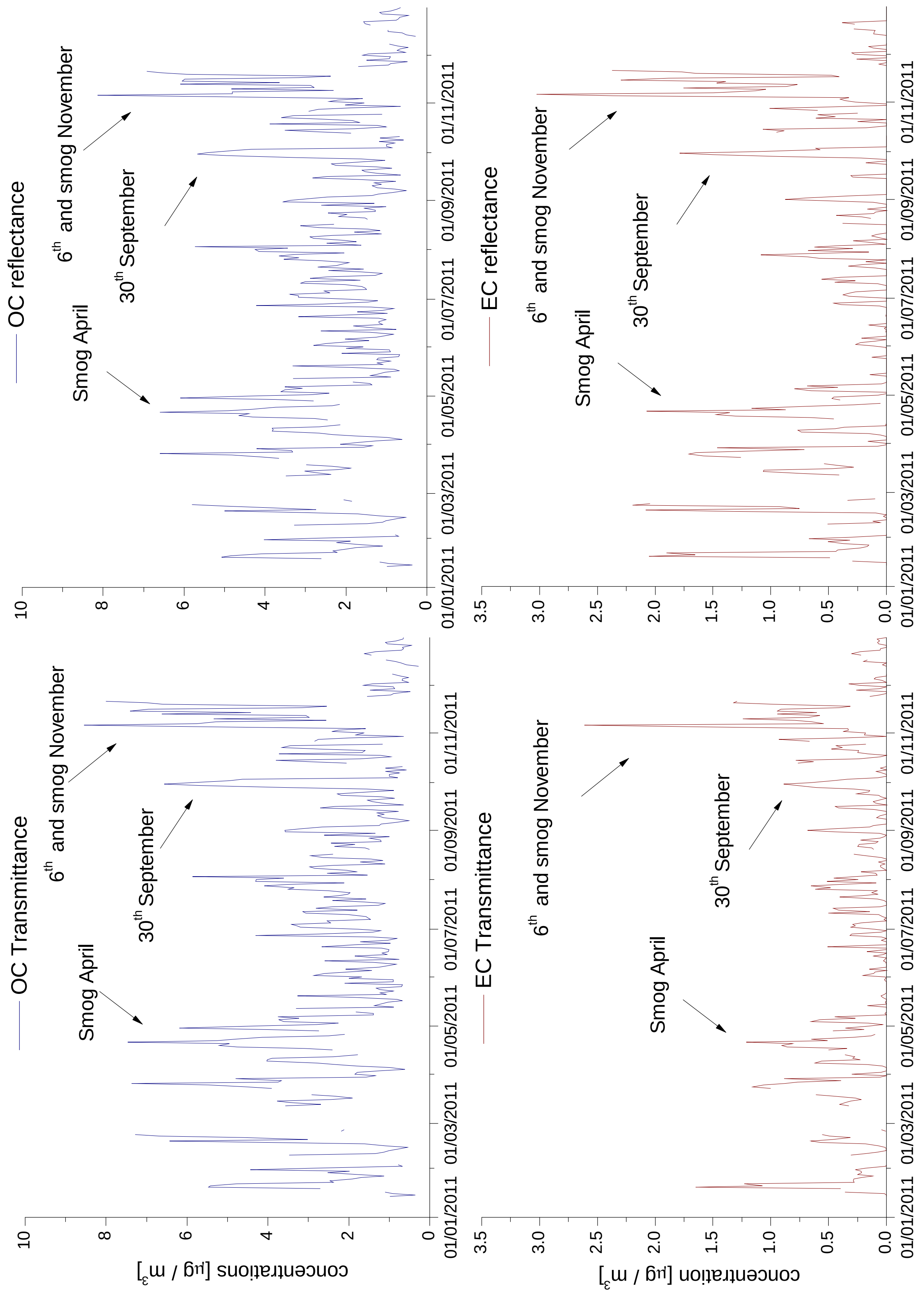


Figure 4-1 PM$_{10}$ OC/EC concentrations at the Harwell site during 2011

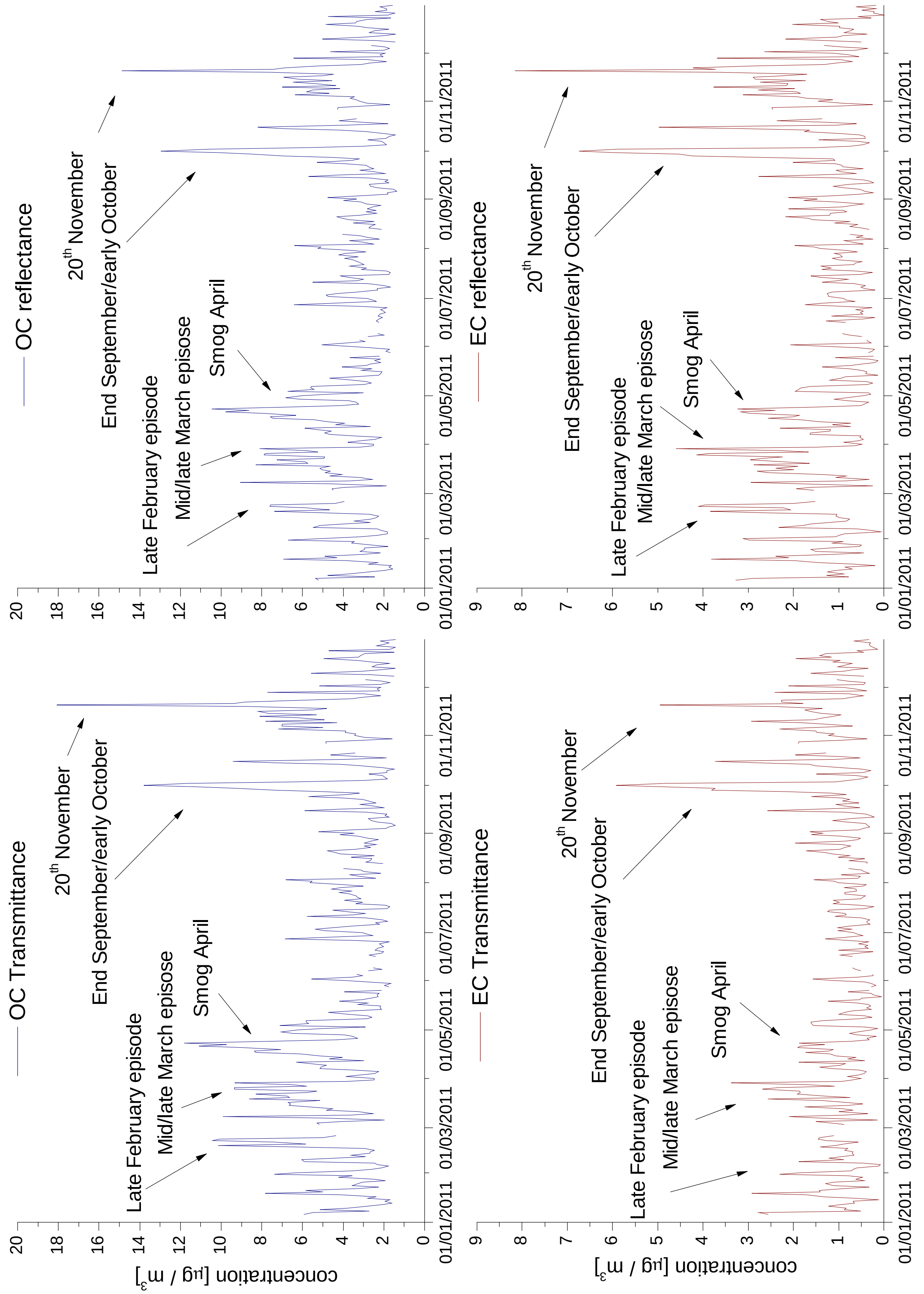


Figure 4-2 OC/EC concentrations at the North Kensington site during 2011

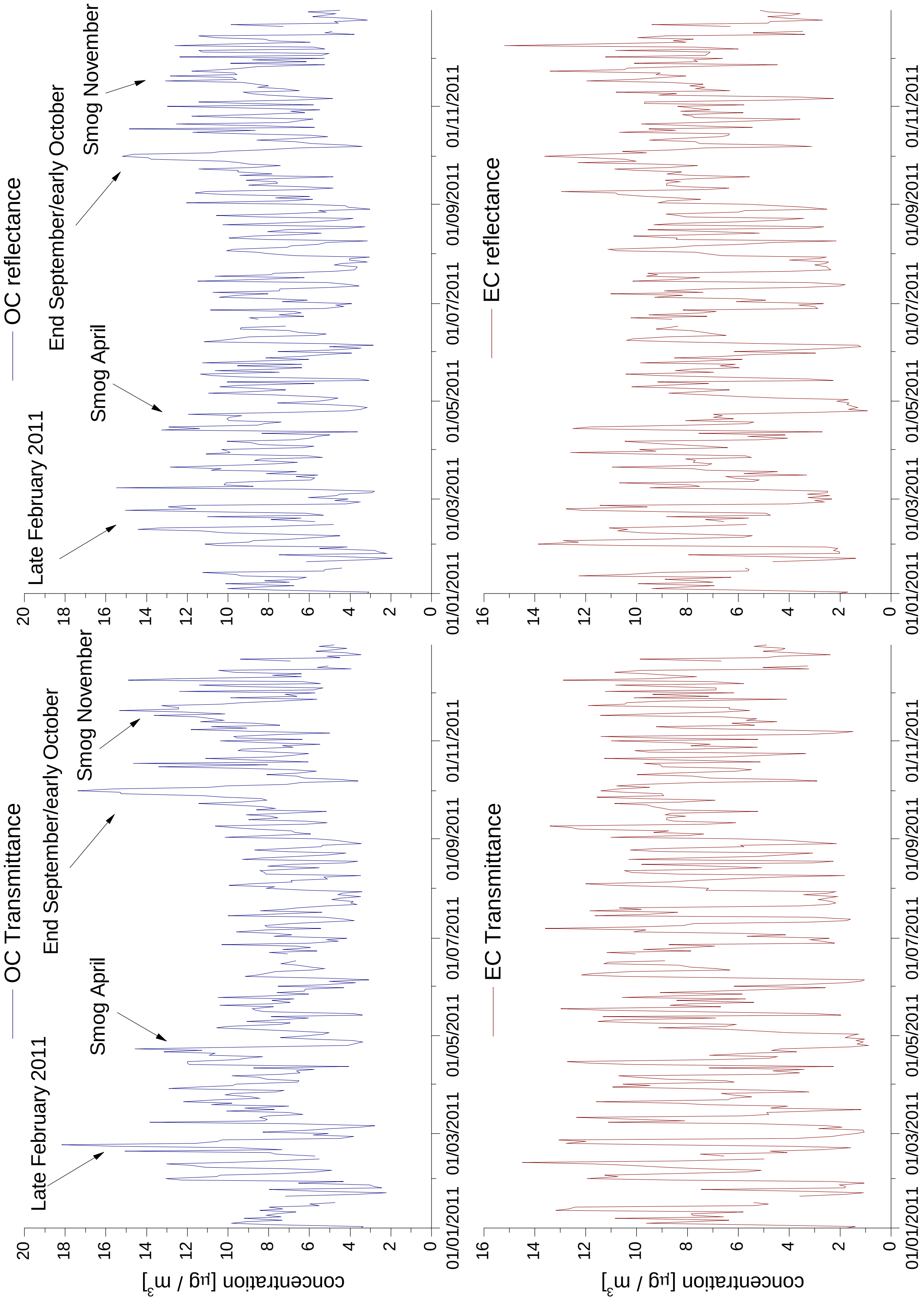


Figure 4-3 OC/EC concentrations at the Marylebone site during 2011

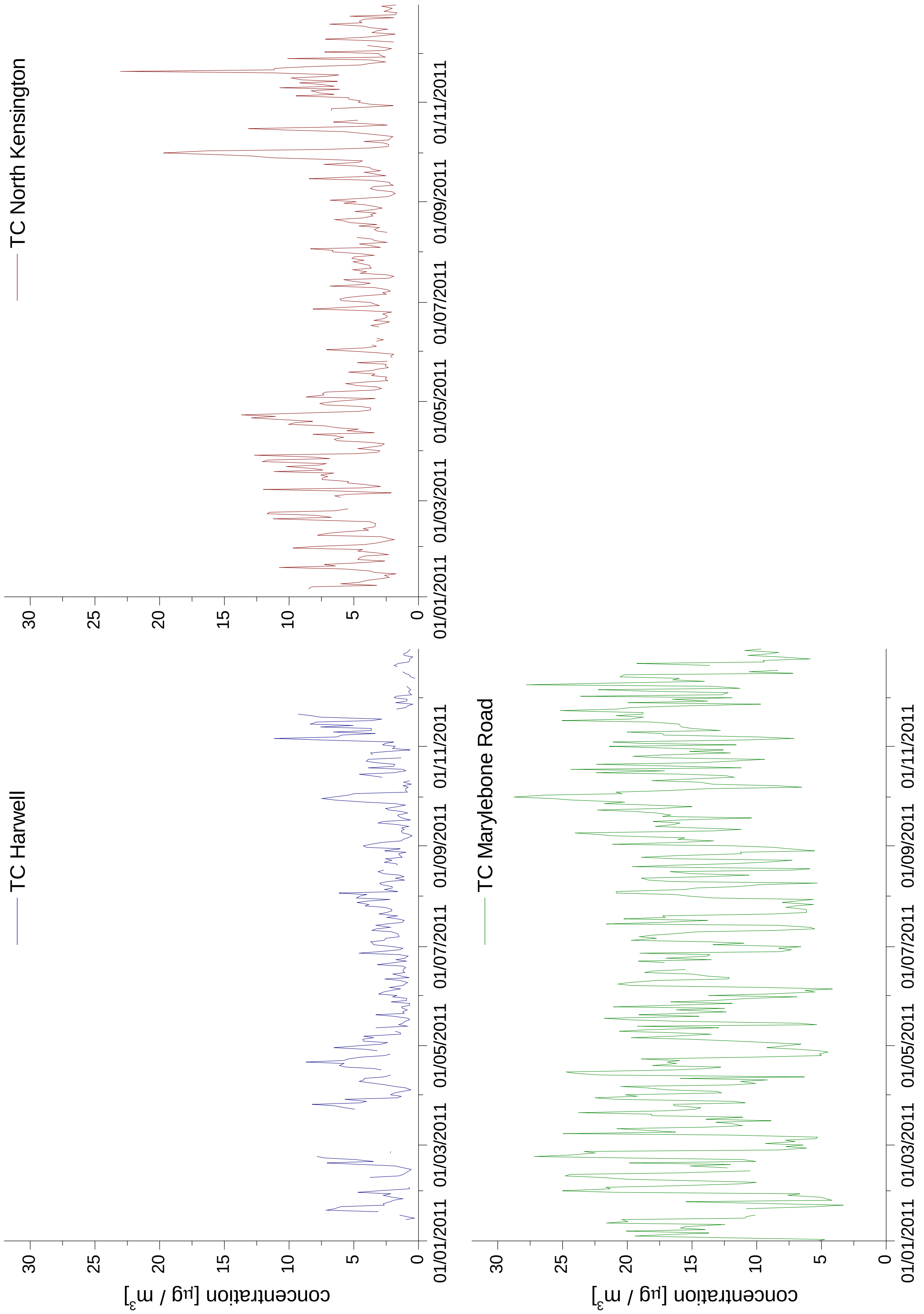


Figure 4-4 TC concentrations at the three sites during 2011

Figure 4-5 to 4-7 show scatter plots between the Reflectance and the Transmittance concentrations. The results are consistent with previous years.

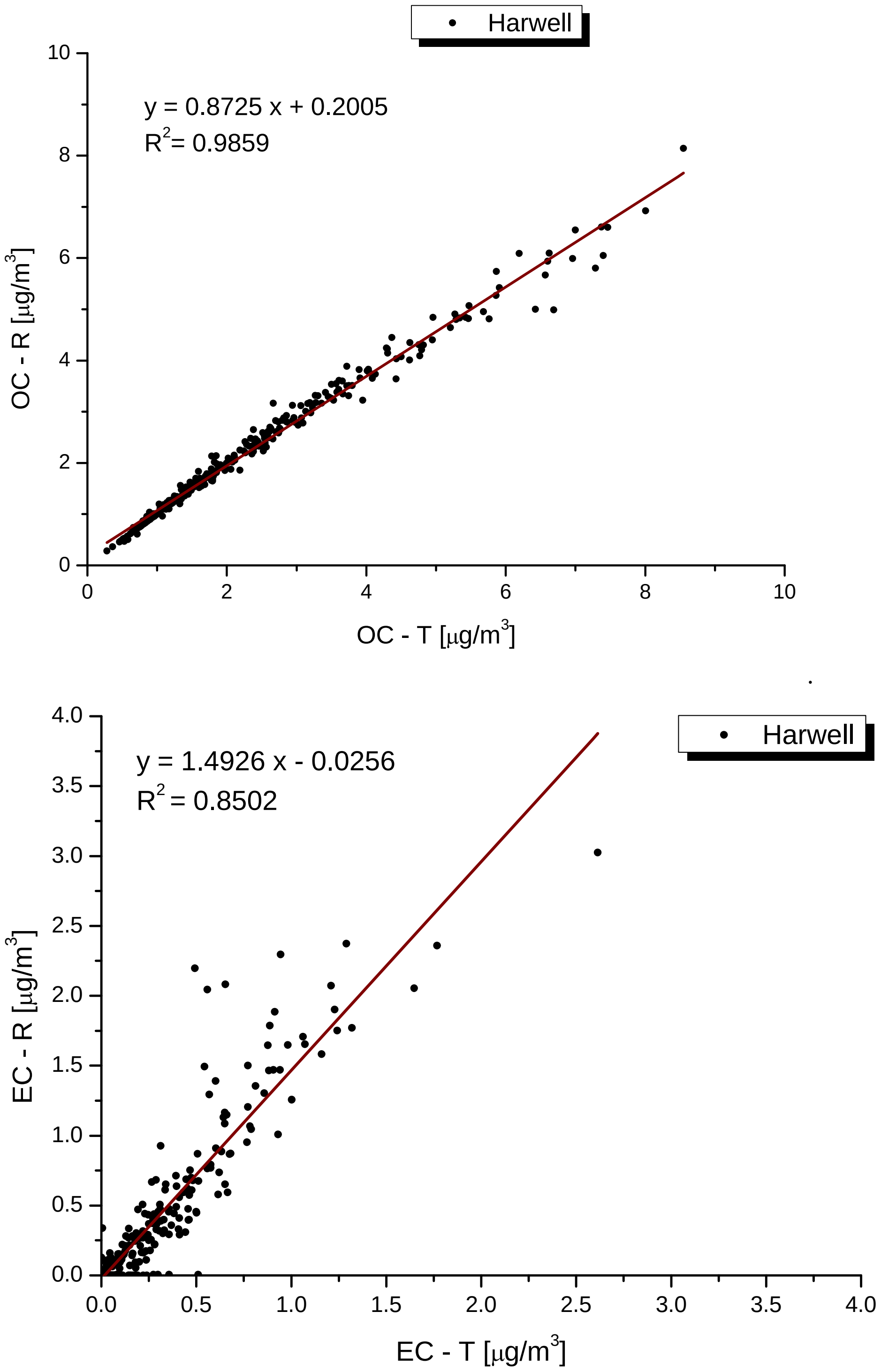
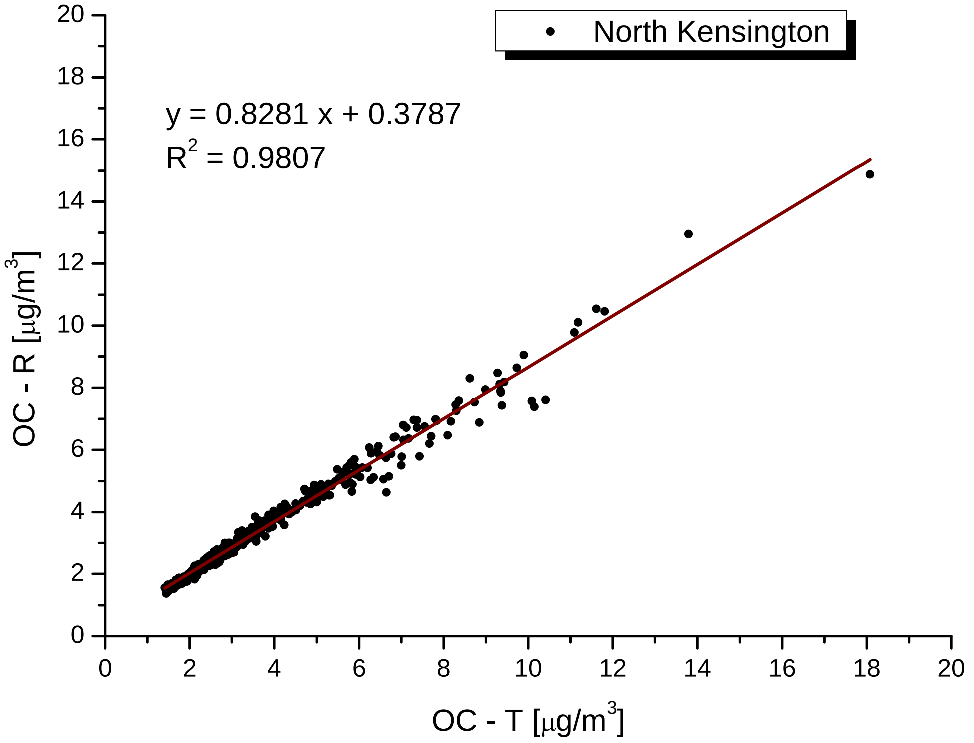


Figure 4-5 Scatter plots of OC and EC measurements for TOT and TOR methods at Harwell



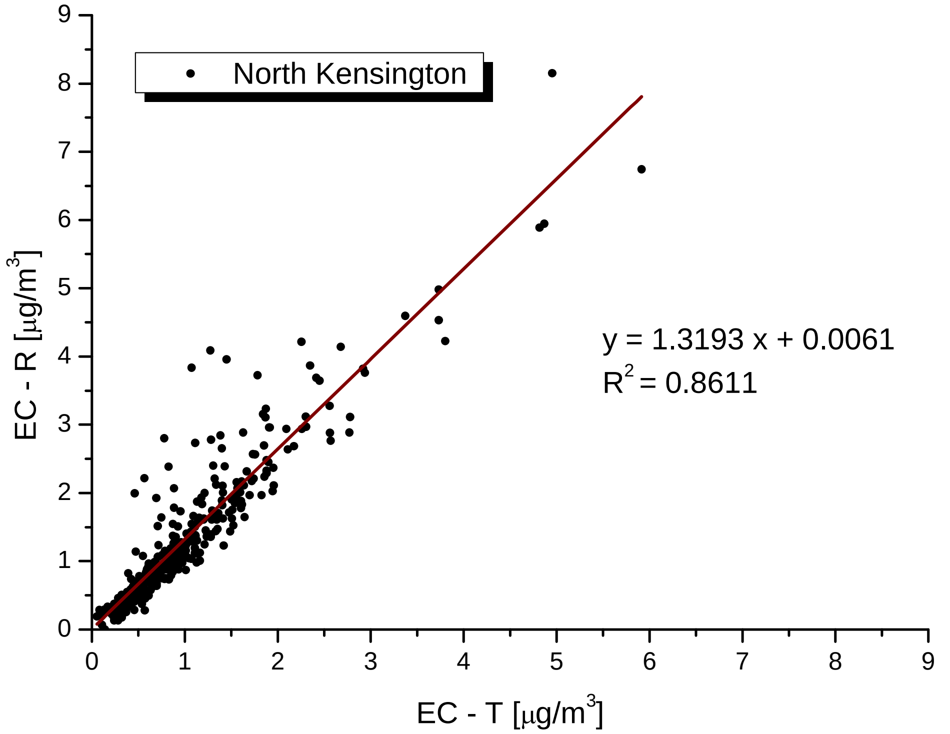
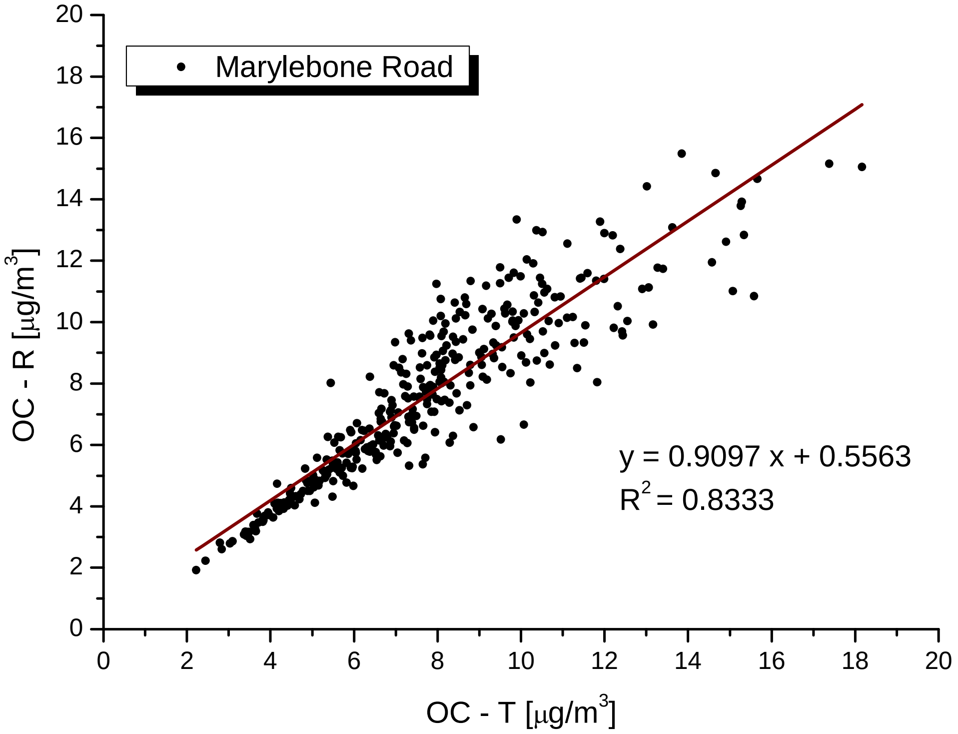


Figure 4-6 Scatter plots of OC and EC measurements for TOT and TOR methods at North Kensington



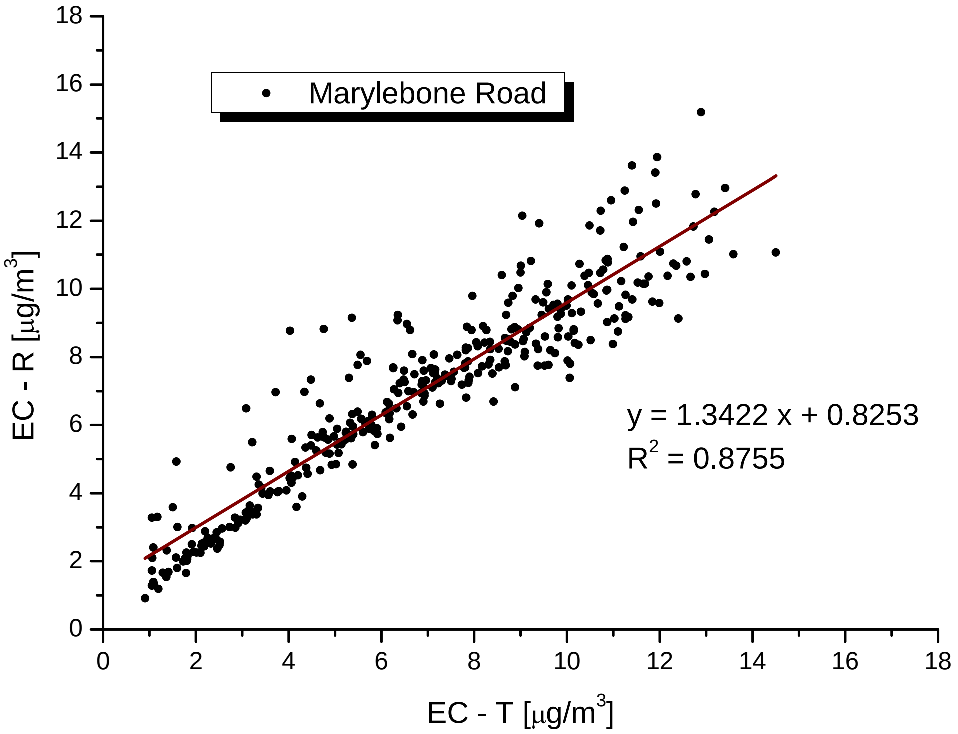


Figure 4-7 Scatter plots of OC and EC measurements for TOT and TOR methods at Marylebone Road

4.2.1 Comparison between Elemental Carbon and Black Carbon

In principle, the chemically based Elemental Carbon metric and the optically based Black Carbon metric both quantify the "soot" component of airborne particles. Co-located measurements of Black Carbon ($PM_{2.5}$) have been made at North Kensington and Marylebone Road, using aethalometers, as part of the Defra Black Carbon Network, and at Harwell as part of this Network. The different size fraction is not expected to have a large effect, as soot from combustion processes is expected to be below 2.5 µm in size.

The time series of the elemental carbon (EC), obtained by using TOT method, and black carbon (BC) measurements, by using aethalometers, have been compared and are shown in Figures 4-8, 4-9 and 4-10 as well as scatter plots.

The comparison at all sites shows a good agreement, although the BC measurements are generally higher than the EC measurements by 15-25%. This is consistent with the observation that thermo-optical OC/EC measurements using the Quartz protocol tend to under-read EC (and hence over-read OC), whether either transmittance or reflectance is used for the pyrolysis correction, and this effect is significant at rural sites like Harwell[5].

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[5] An evaluation of measurement methods for organic, elemental and black carbon in ambient air monitoring sites¸ P. Quincey, D. Butterfield, D. Green, M. Coyle, J. Neil Cape, *Atmospheric Environment, 43 (32) 5085 – 5091, 2009*

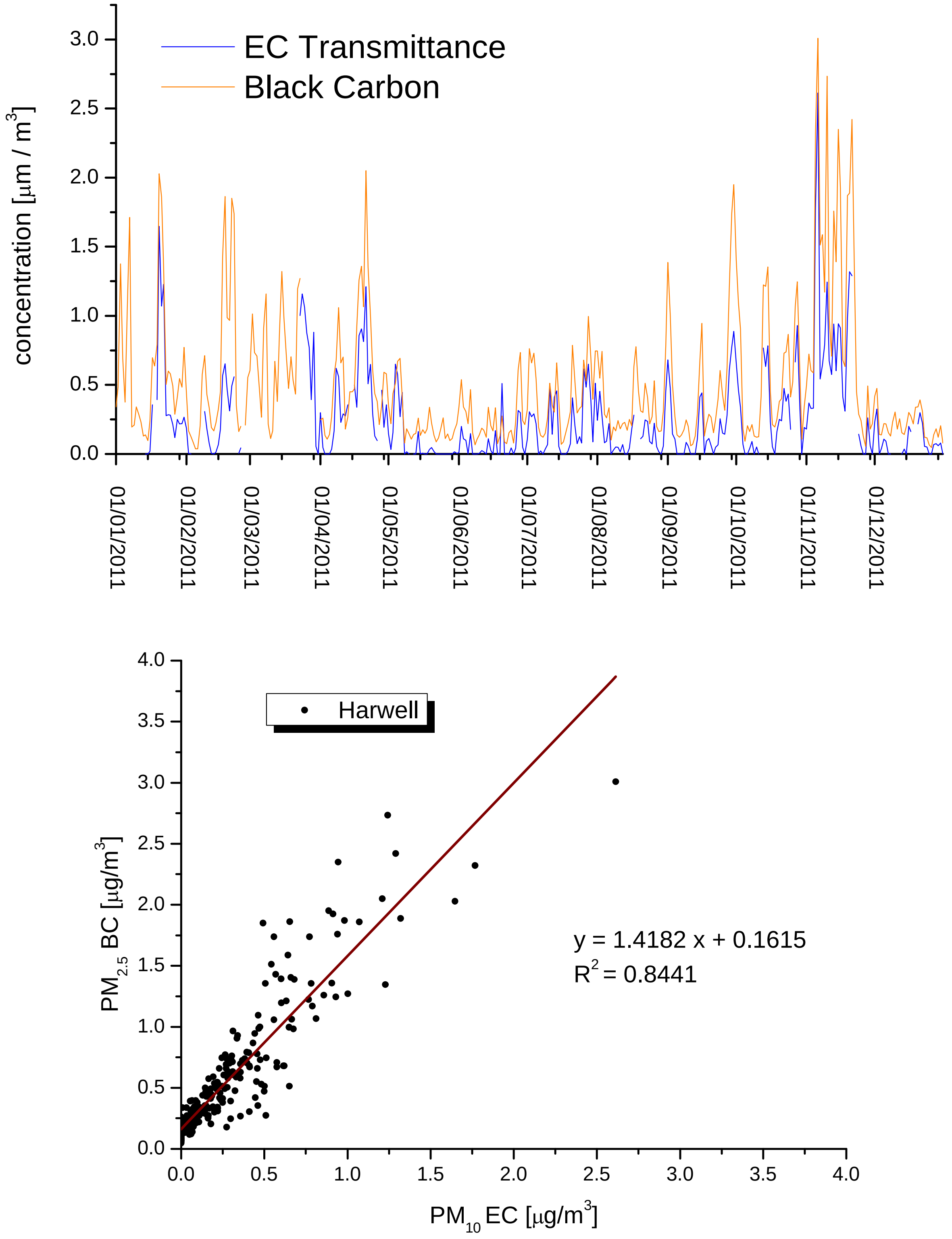
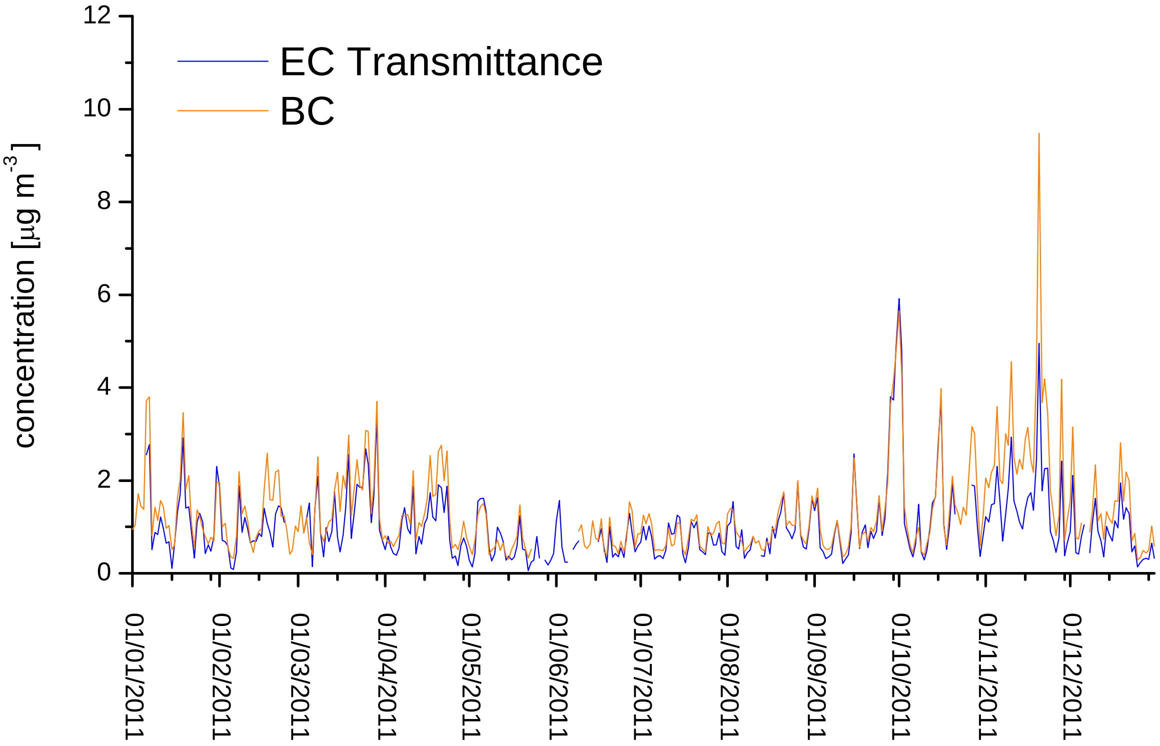


Figure 4-8 Comparison between $PM_{2.5}$ BC and PM_{10} EC (T) at Harwell in 2011



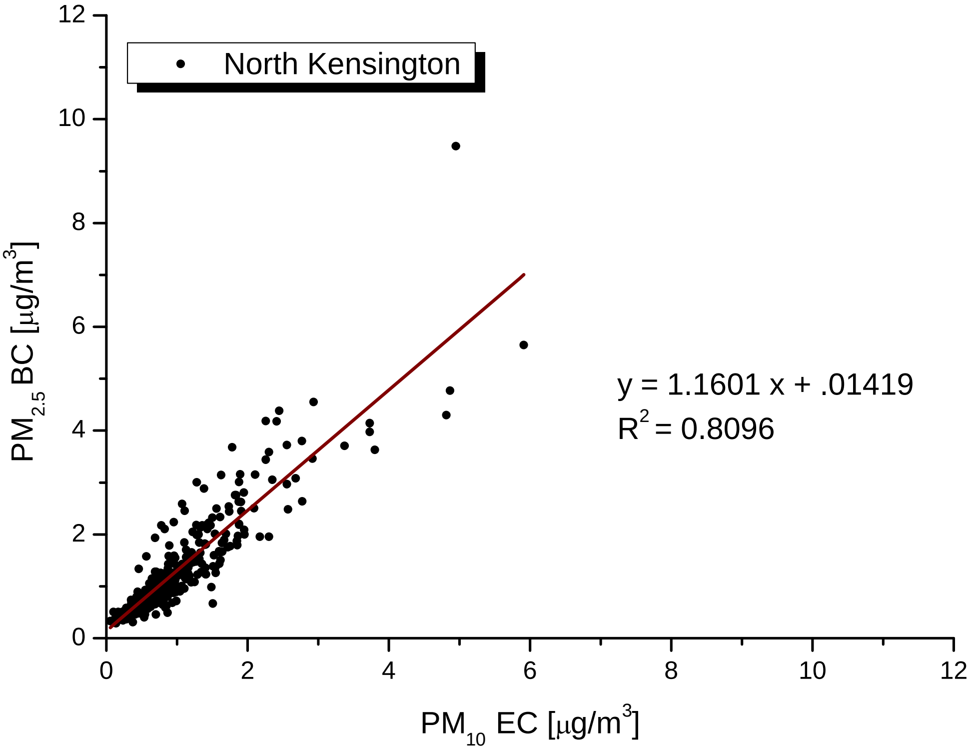


Figure 4-9 Comparison between $PM_{2.5}$ BC and PM_{10} EC (T) at North Kensington in 2011

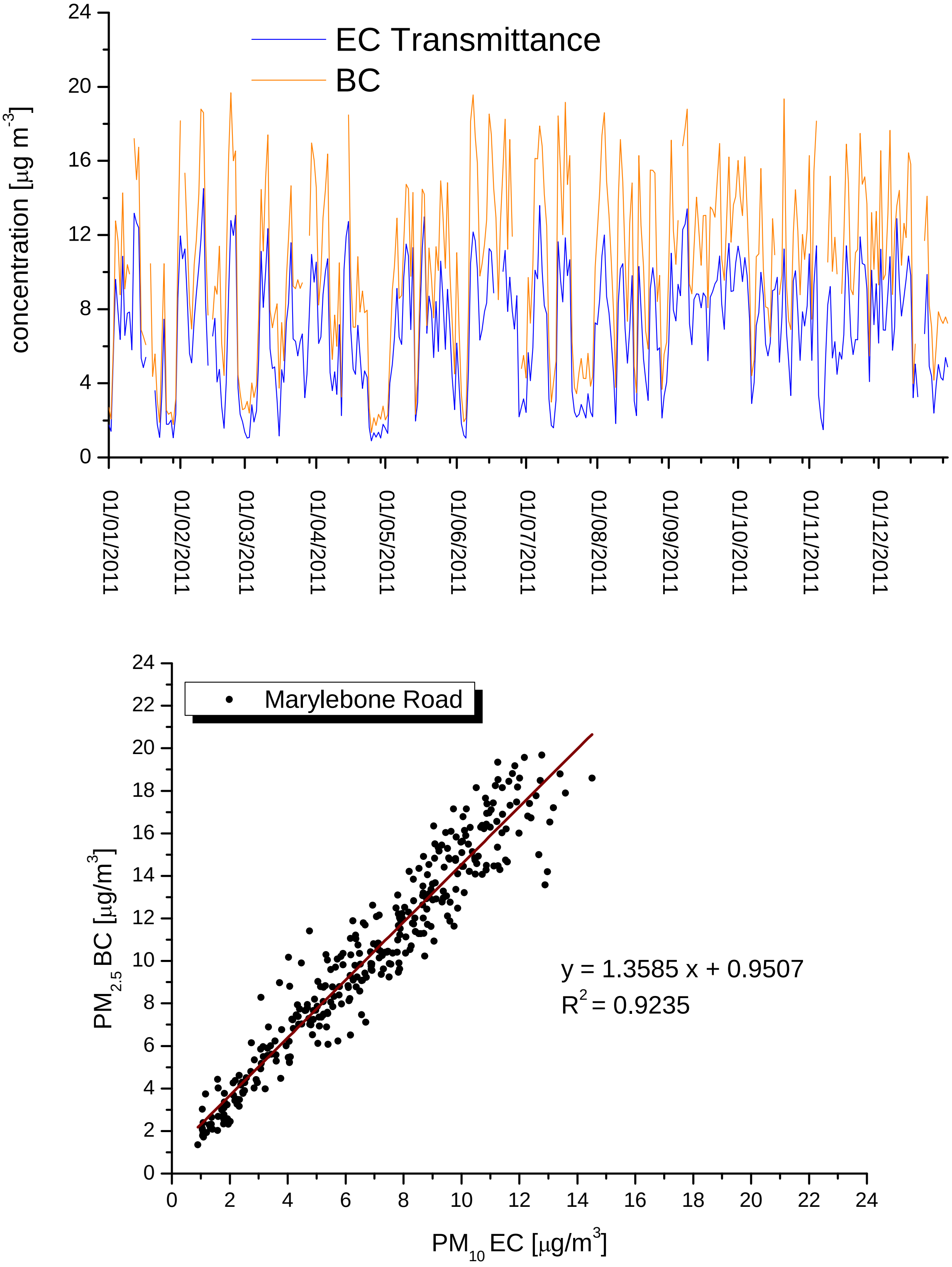


Figure 4-10 Comparison between $PM_{2.5}$ BC and PM_{10} EC (T) at Marylebone Road in 2011

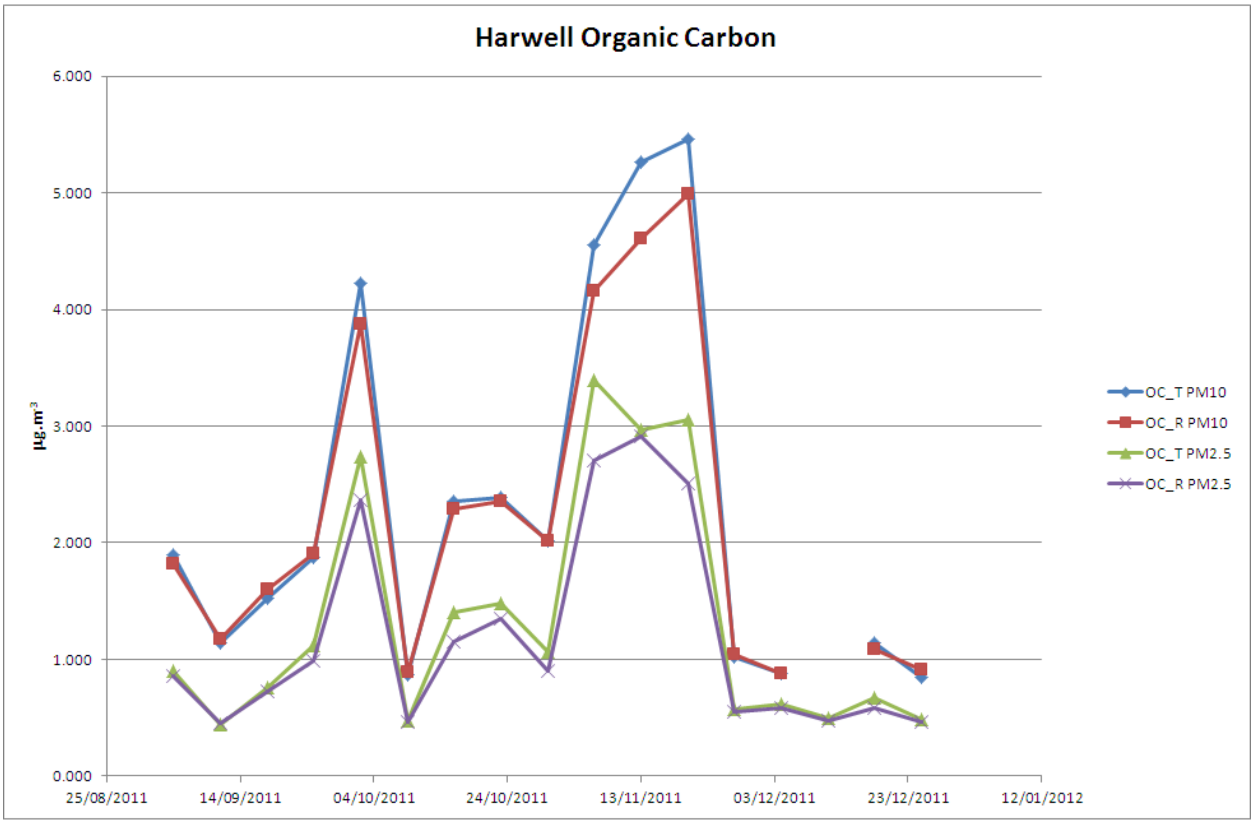
4.3 OC/EC MEASUREMENTS ($PM_{2.5}$)

$PM_{2.5}$ weekly filters were sampled at Harwell and Auchencorth Moss to comply with the European Directive 2008/50/EC (see Section 5.2.1).

The sampler at Harwell has been in operation since 1st September 2011. The sampler at Auchencorth Moss was damaged during transport to the site and was eventually installed on 17th November. Data capture until the end of the year was 100% for both sites.

The results from Harwell are reported in Figures 4-11 and 4-12. The concentrations were compared with weekly averages from the PM_{10} filters from the Partisol. The correlation between the two measurements is good, with $PM_{2.5}$ total carbon being on average about 60% of the PM_{10} total carbon, with most of the difference being in the OC. This may be due to losses of semi-volatile OC during the longer (weekly) sampling period of the $PM_{2.5}$ fraction rather than coarse OC.

Some of the weekly $PM_{2.5}$ samples were analysed using both Quartz and EUSAAR II protocols for a comparison. Figures 4-13 to 4-16 show the comparison. No significant difference could be identified for these samples.



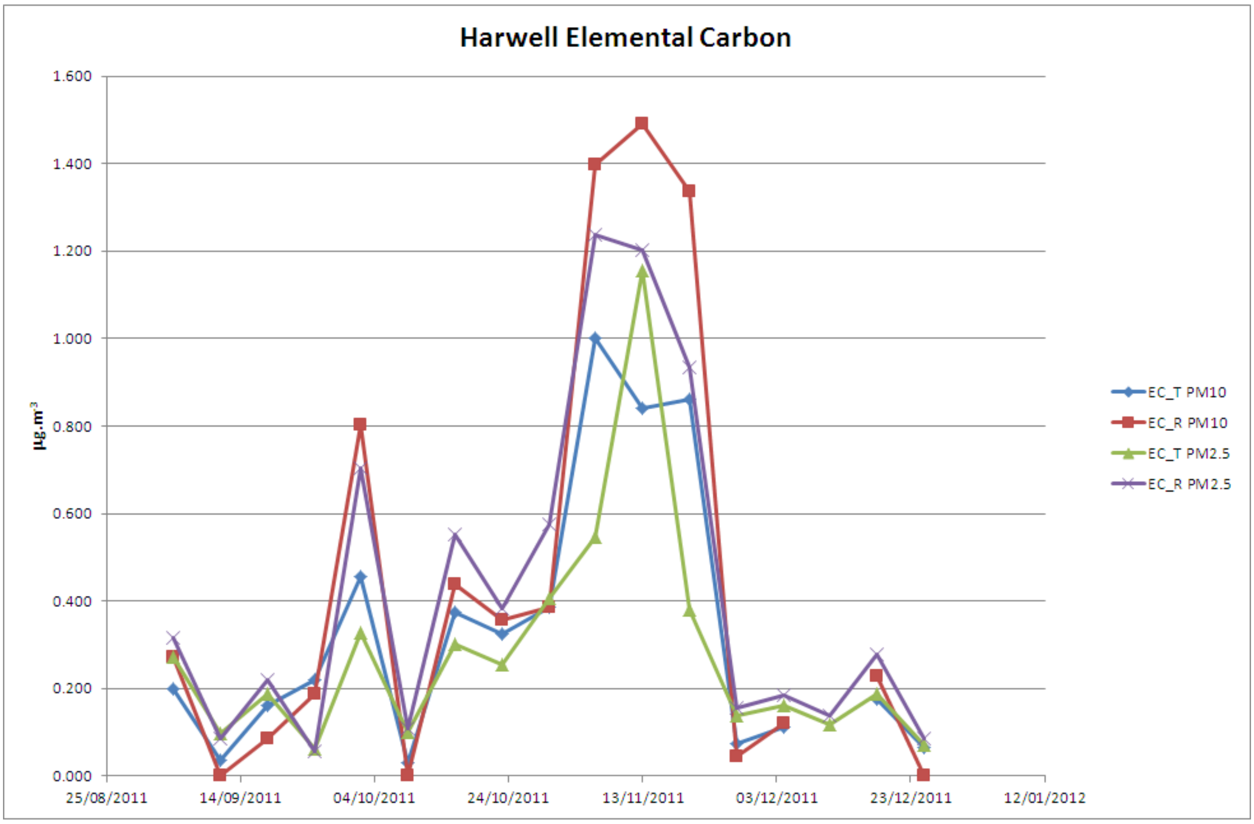


Figure 4-11 Comparison between $PM_{2.5}$ weekly OC/EC and PM_{10} averaged weekly OC/EC measurements at Harwell.

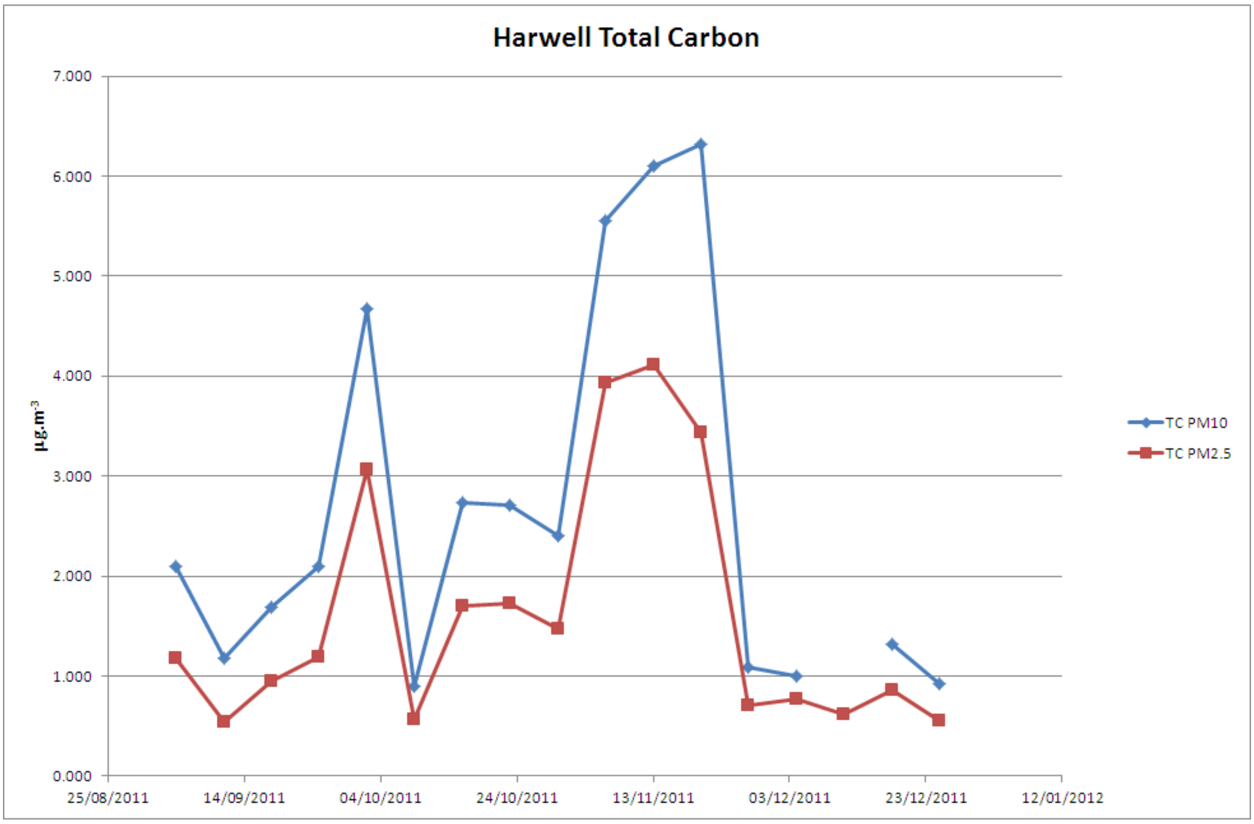
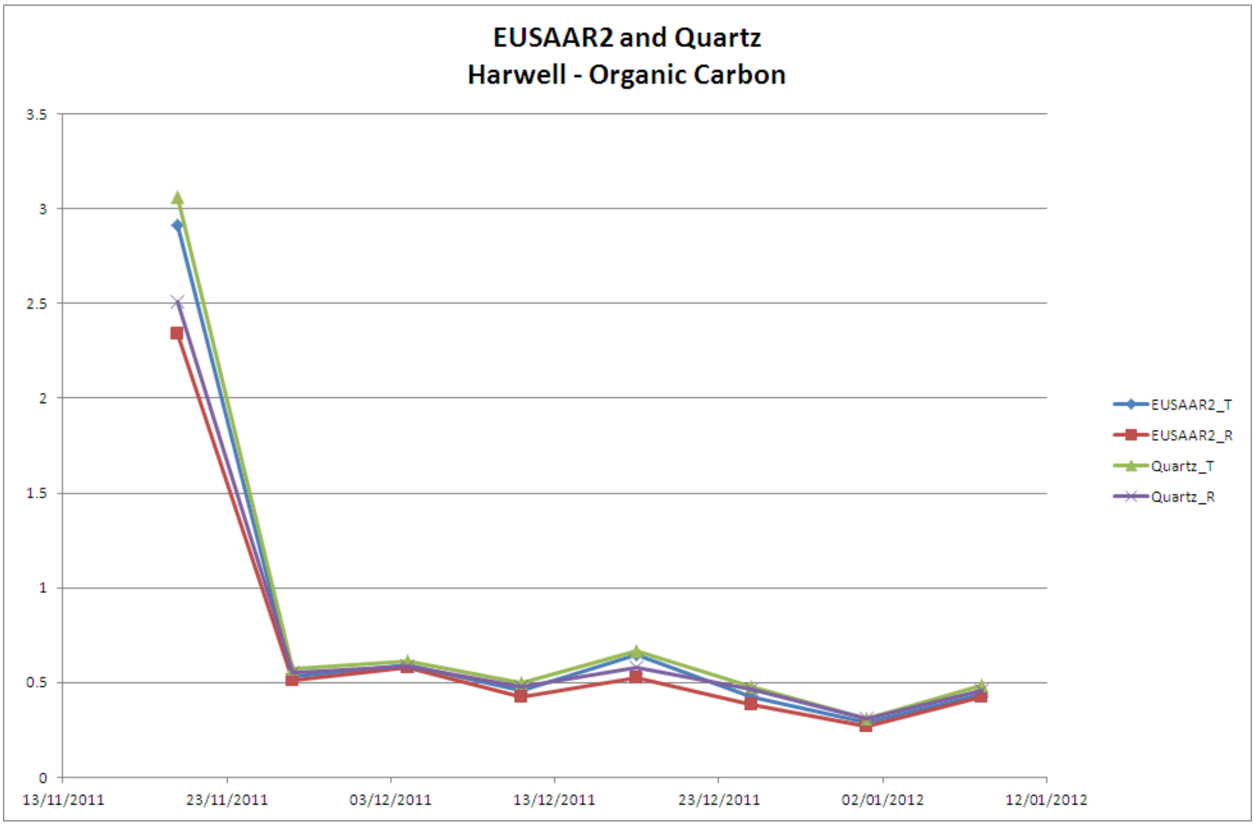


Figure 4-12 Comparison between $PM_{2.5}$ weekly TC and PM_{10} averaged weekly TC measurements at Harwell.



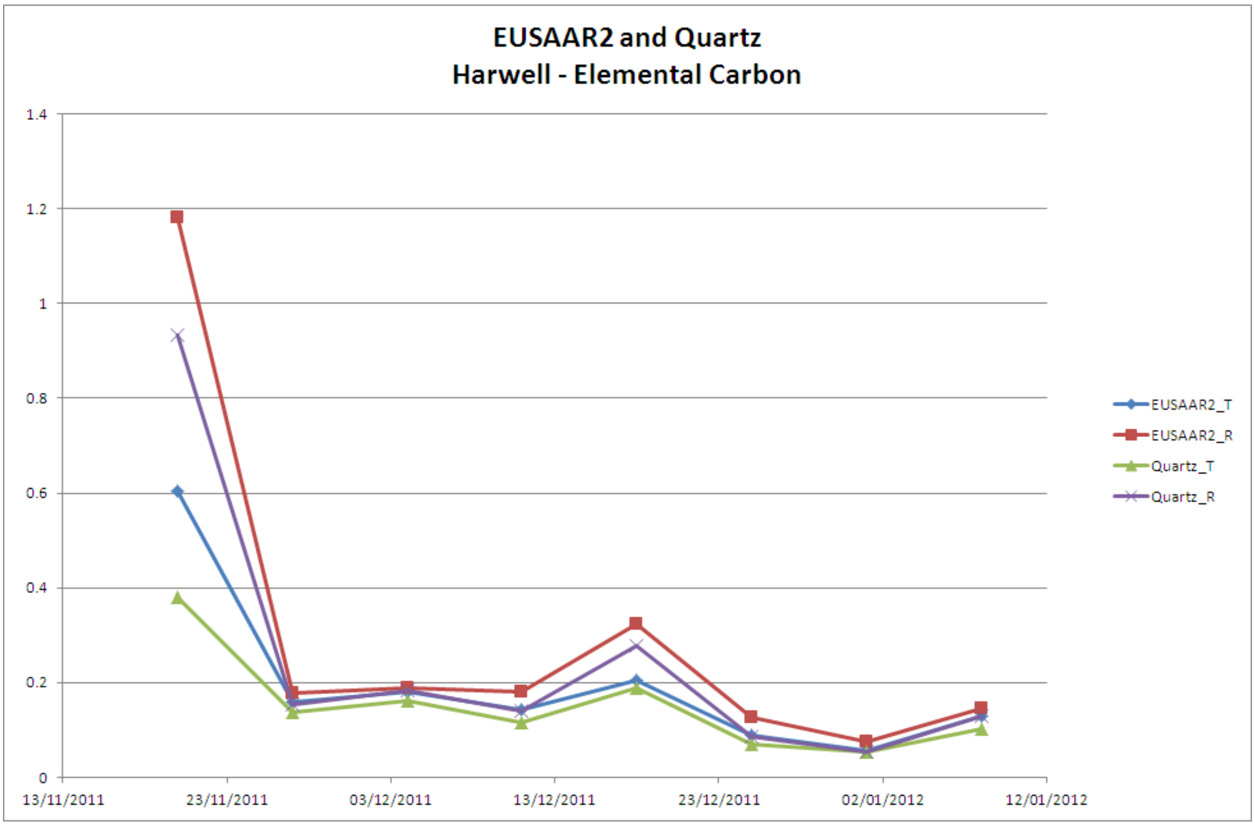


Figure 4-13 Comparison between Quartz and EUSAAR 2 protocols at Harwell for OC and EC

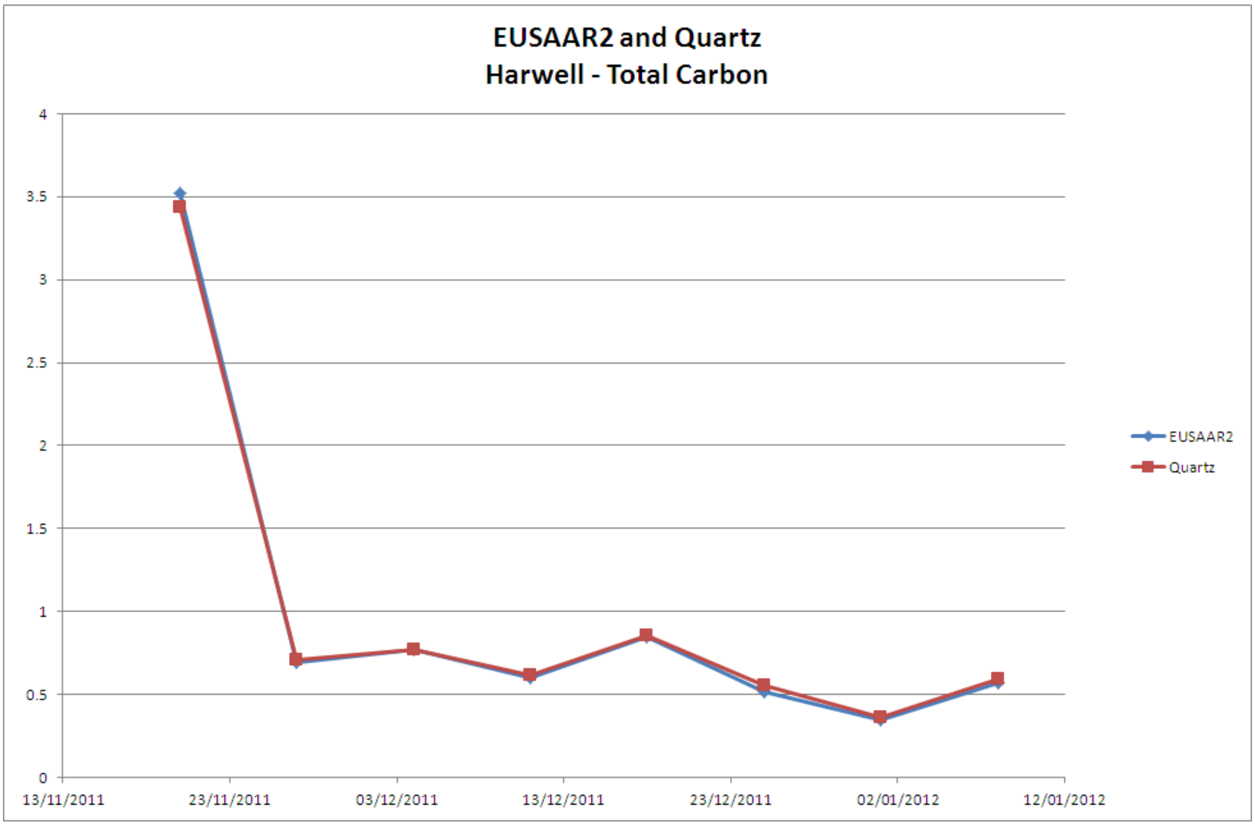


Figure 4-14 Comparison between Quartz and EUSAAR 2 protocols for TC at Harwell

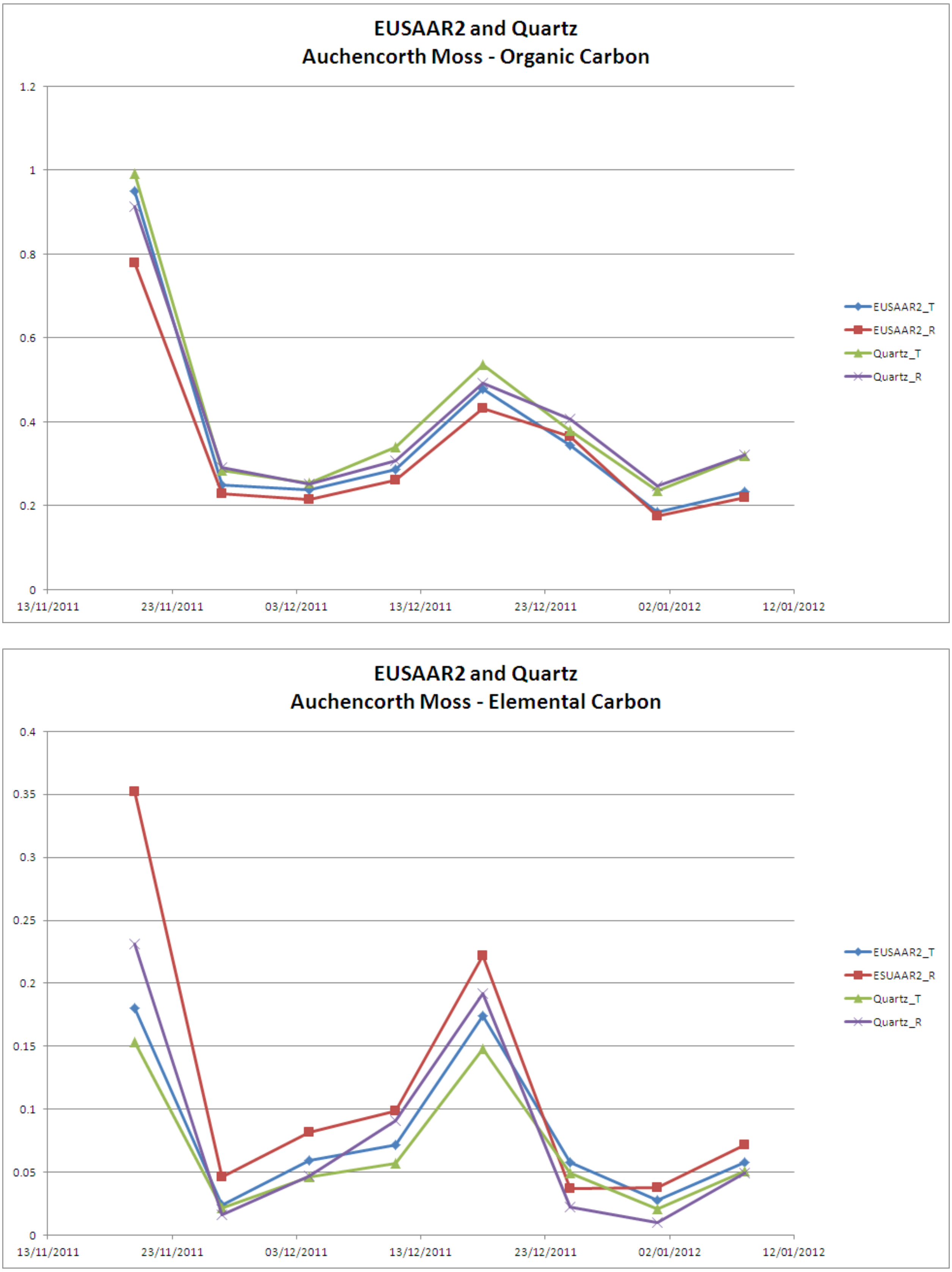


Figure 4-15 Comparison between Quartz and EUSAAR 2 for OC and EC at Auchencorth Moss

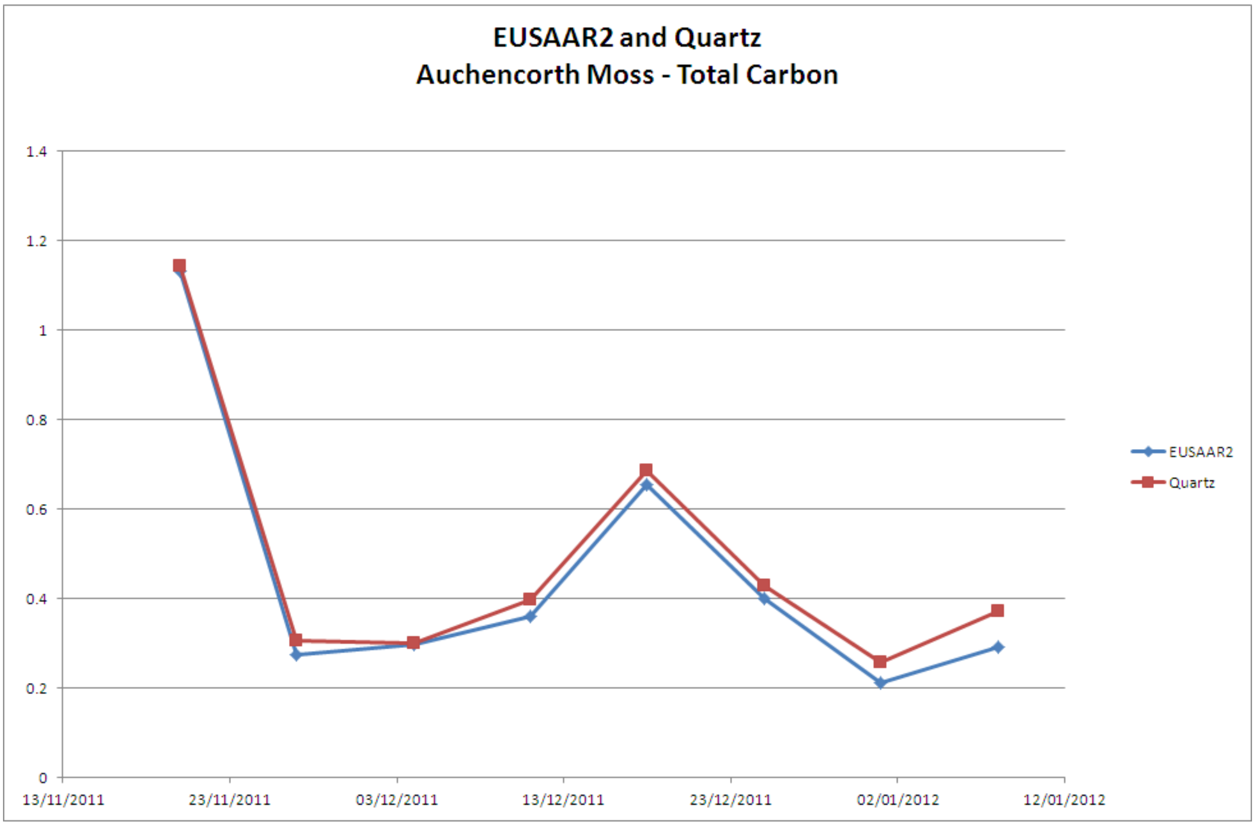


Figure 4-16 Comparison between Quartz and EUSAAR 2 protocols for TC at Auchencorth Moss

4.4 AUTOMATIC ANION AND CATION MEASUREMENTS (PM_{10})

4.4.1 Anion and cation hourly measurements

Two URG 9000B – AIM were installed at the two sites in London in February 2011. These instruments measure hourly concentration of chloride, nitrate, sulphate, sodium, ammonium, potassium, magnesium and calcium. Annual data capture was 68% for North Kensington and 54% at Marylebone Road.

Figures 4-17 to 4-19 show the time series for all the species.

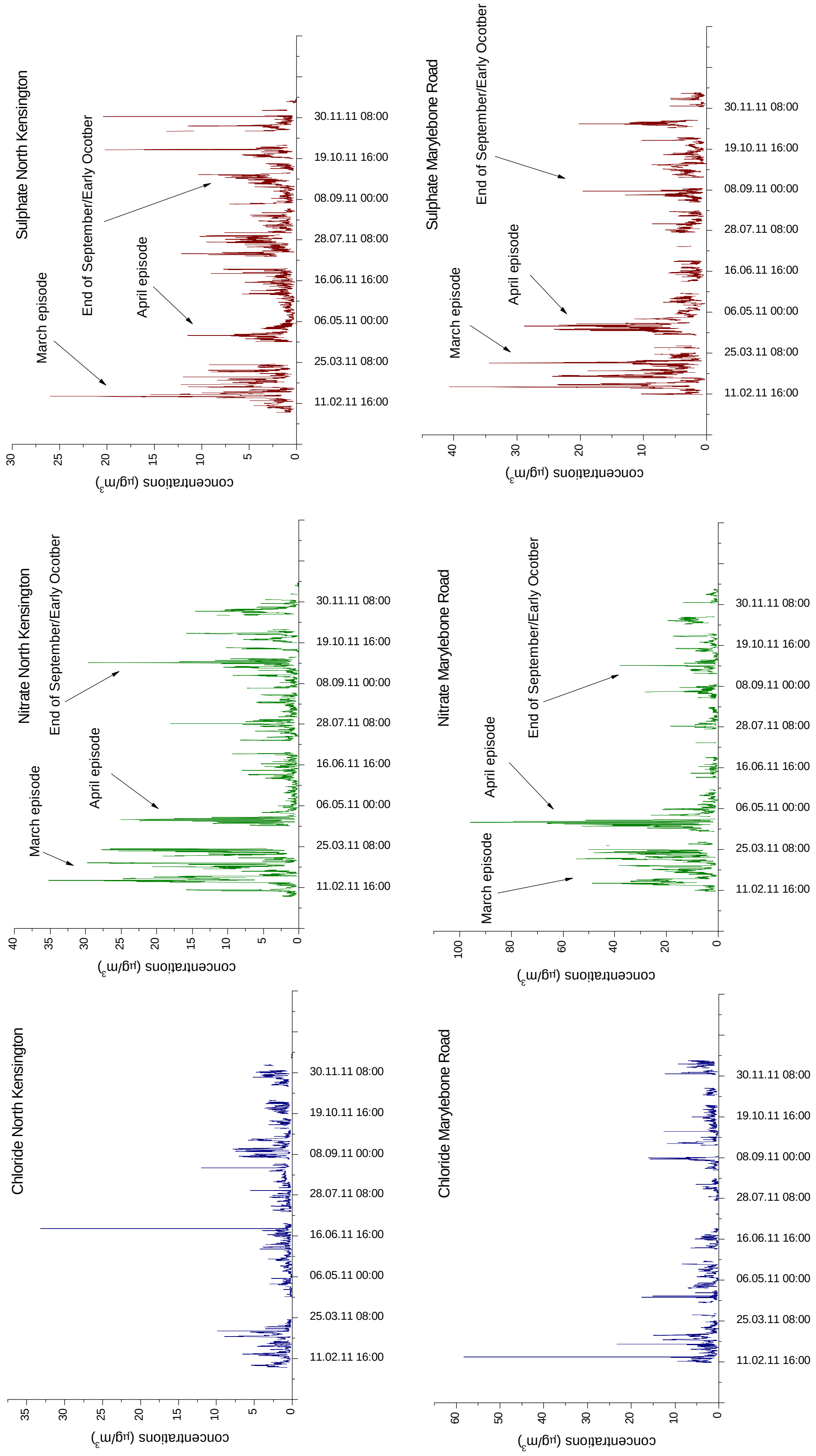


Figure 4-17 Anion concentration at the London sites in 2011

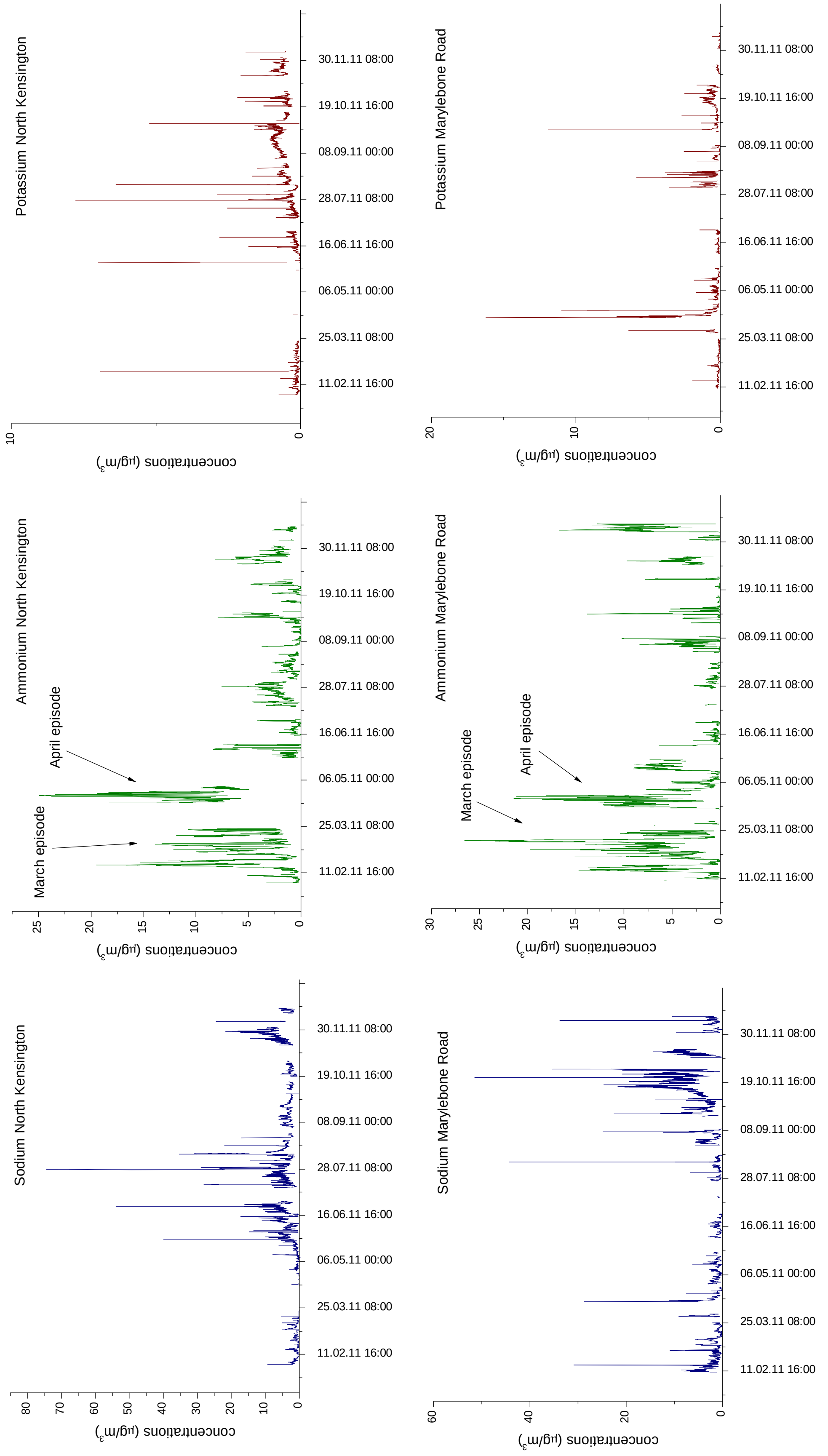


Figure 4-18 Sodium, ammonium and potassium concentrations at the London sites in 2011

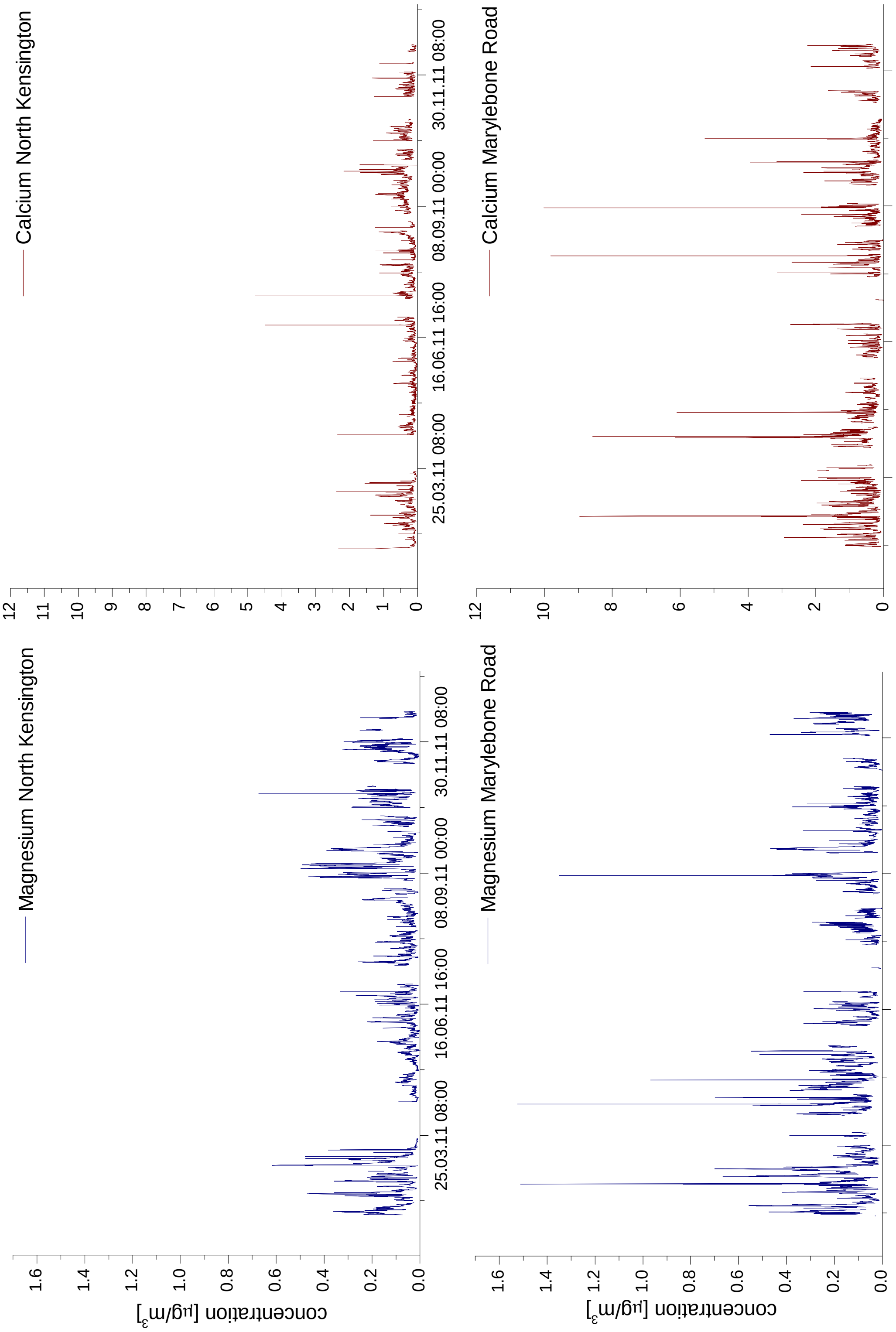


Figure 4-19 Magnesium and calcium concentrations at the two London sites in 2011

4.4.2 Comparison with anion measurements from filter samples

Some of the PM_{10} filter samples from North Kensington were analysed by ion chromatography for chloride, nitrate and sulphate content to be compared with URG daily averages. Time series and scatter plots are shown in Figure 4-20. While the general trends from the URG measurements follow the results from the filter based method well for all the anions, the scatter plots show that the URG analyser tends to under-read. It should be noted that negative and positive artefacts can occur on both measurements. Similar behaviour was found in other works using either the URG 9000 analyser[6] and other semi-continuous analysers like the MARGA[7].

However, the average concentrations over the period of time when both instruments (URG and Partisol) were running are very similar (see Table 4-2).

Table 4-2 Average concentrations expressed in µg / m^3

	Chloride	**Nitrate**	**Sulphate**
URG	1.104	3.231	2.020
Filter	1.077	3.575	2.187

---

[6] Comparison among filter-based, impactor-based and continuous techniques for measuring atmospheric fine sulfate and nitrate, Wei Nie, Tao Wang, Xiaomei gao, Ravi Kant Pathak, Xinfeng Wang, Rui Gao, Qingzhu Zhang, Lingxiao Yang, Wenxing Wang, *Atmospheric Environment 44 (2010) 4396-4403*

[7] Semi-continuous gas and inorganic aerosol measurements at A Finnish urban site: comparison with filters, nitrogen in aerosol and gas phases, and aerosol acidity, U. MAkkonen, A. Virkkula, J. Mäntykenttä, H. Hakola, P. Keronen, V. Vakkari, and P.P. Aalto, *Atmos. Chem. Phys. Discuss. 12, 4755-4796, 2012*

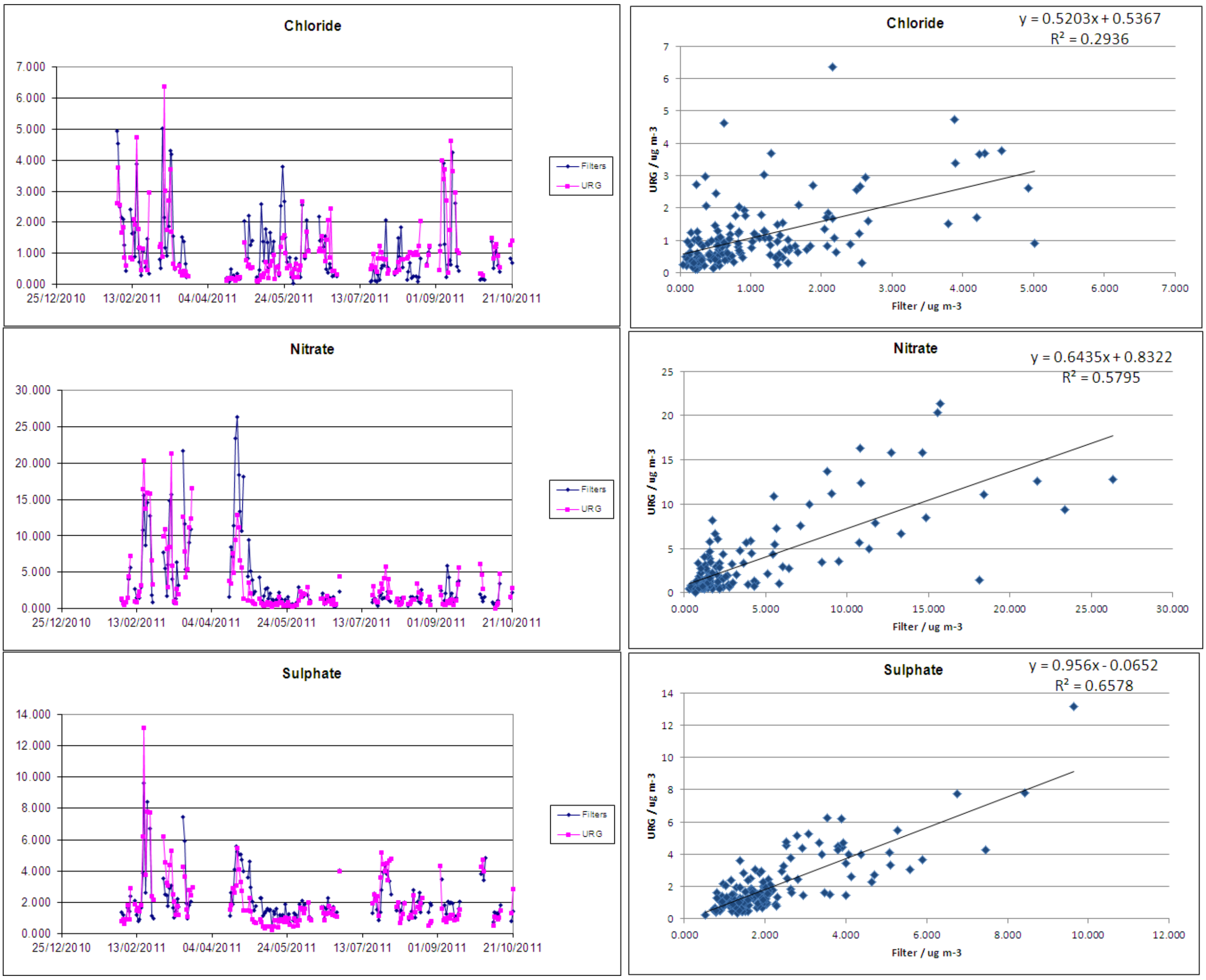


Figure 4-20 Comparison between daily filter based measurements of chloride, nitrate and sulphate and daily average concentration from the URG analyser at North Kensington.

4.5 MASS BALANCE

A basic attempt to do a mass balance of all the species measured in this network at the London sites has been done with respect to the daily averaged PM_{10} concentrations measured by the FDMS. The mass balance was calculated by summing the ratio of each species' concentration over the PM_{10} concentration. Particle-bound water was not taken into account.

Figure 4-21 shows the percentage of the measurements at both sites over the PM_{10} plus an un-accounted portion. The graphs show only the days were all the instruments were running. During the pollution episodes in March and April, the mass balance exceeded 100% of the PM_{10} concentrations.

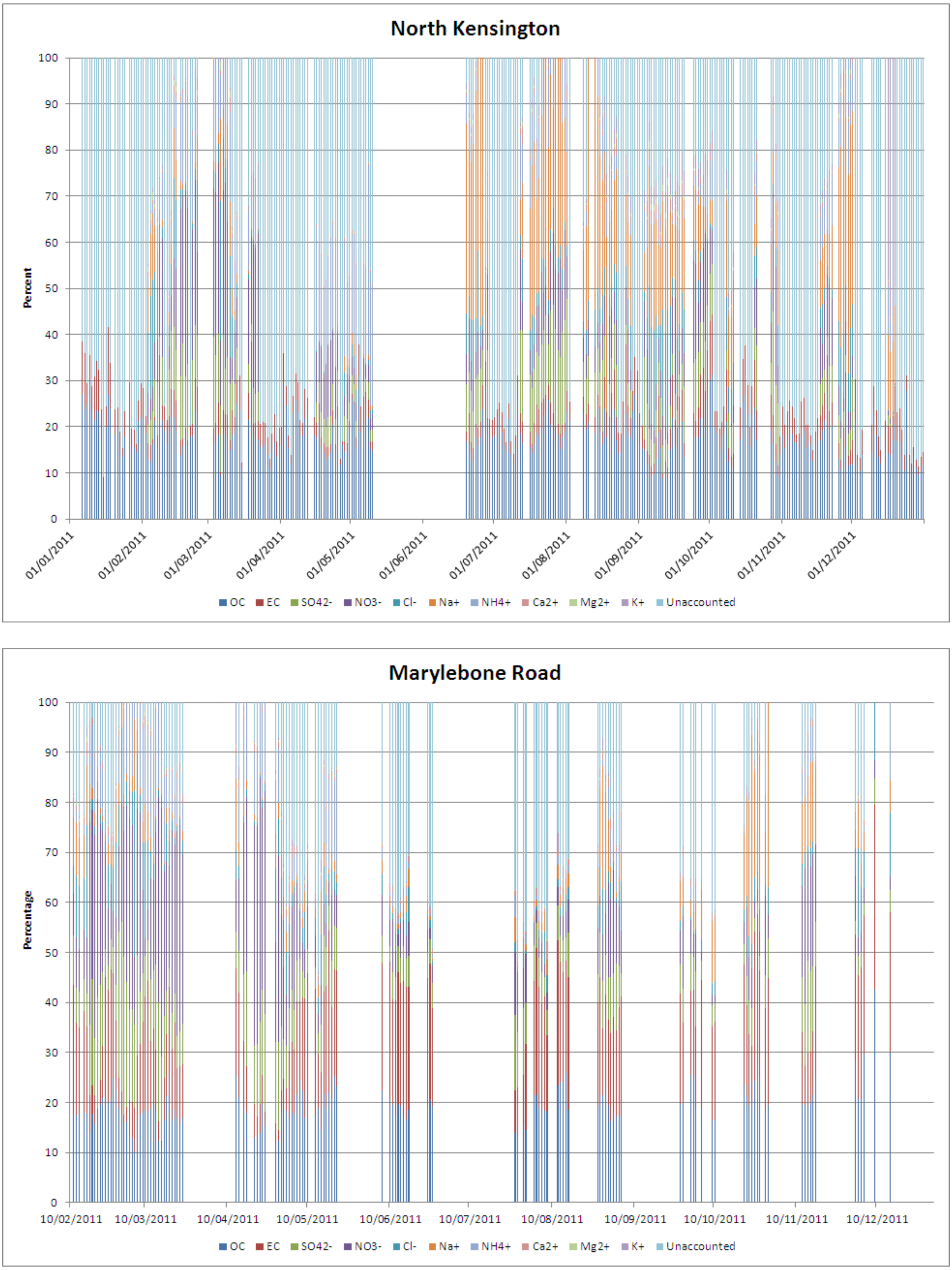


Figure 4-21 PM_{10} mass balance at North Kensington and Marylebone Road

4.6 PARTICLE NUMBER AND SIZE DISTRIBUTION

4.6.1 Particle number Concentrations (CPC)

Time series of hourly particle number concentrations (between about 7nm and several microns in diameter) measured at network sites during 2011 are shown in Figure 4-22.

The following should be noted:

- **Harwell.** The instrument was removed from site on the 18th of March for service and calibration at NPL, and re-installed on the 4th of April, and then suffered loss of data due to a computer virus. The CPC did not have major problems for the rest of the year.

- **Birmingham.** The data capture was 0% in February as the pump failed at the beginning of February and the instrument was taken to NPL for repair. It was then serviced and calibrated. The CPC did not have major problems for the rest of the year.

- **North Kensington.** The instrument was removed from site on the 12th of February for service and calibration at NPL and re-installed on the 23rd of February. In April the pump failed and was replaced at NPL. The CPC did not have any major problems for the rest of the year.

- **Marylebone Road.** The instrument was removed on the 3rd of February for service and calibration at NPL and reinstalled on 23rd of February. The CPC did not have major problems for the rest of the year.

Monthly data capture rates for the CPC instruments during 2011 are displayed in Table 4-2. Each instrument is removed from the site for a full service and calibration annually. This scheduled maintenance is expected to take two weeks, to include draining and drying, transit time, full service 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 in red.

Table 4-2 Monthly data capture for CPC instruments in 2011. Red figures indicate that the time period for preventative maintenance has not been counted as lost data in line with recommendations from CEN for calculating data capture.

Month	Birmingham	Harwell	North Kensington	Marylebone Road
January	83%	70%	70%	82%
February	0.0%	82%	91%	59%
March	50%	100%	79%	91%
April	73%	45%	41%	92%
May	100%	96%	75%	99%
June	81%	86%	67%	92%
July	99%	97%	99%	96%
August	100%	98%	95%	97%
September	93%	89%	89%	70%
October	89%	78%	93%	95%
November	93%	87%	76%	75%
December	100%	88%	81%	80%
Average	**81%**	**85%**	**80%**	**86%**

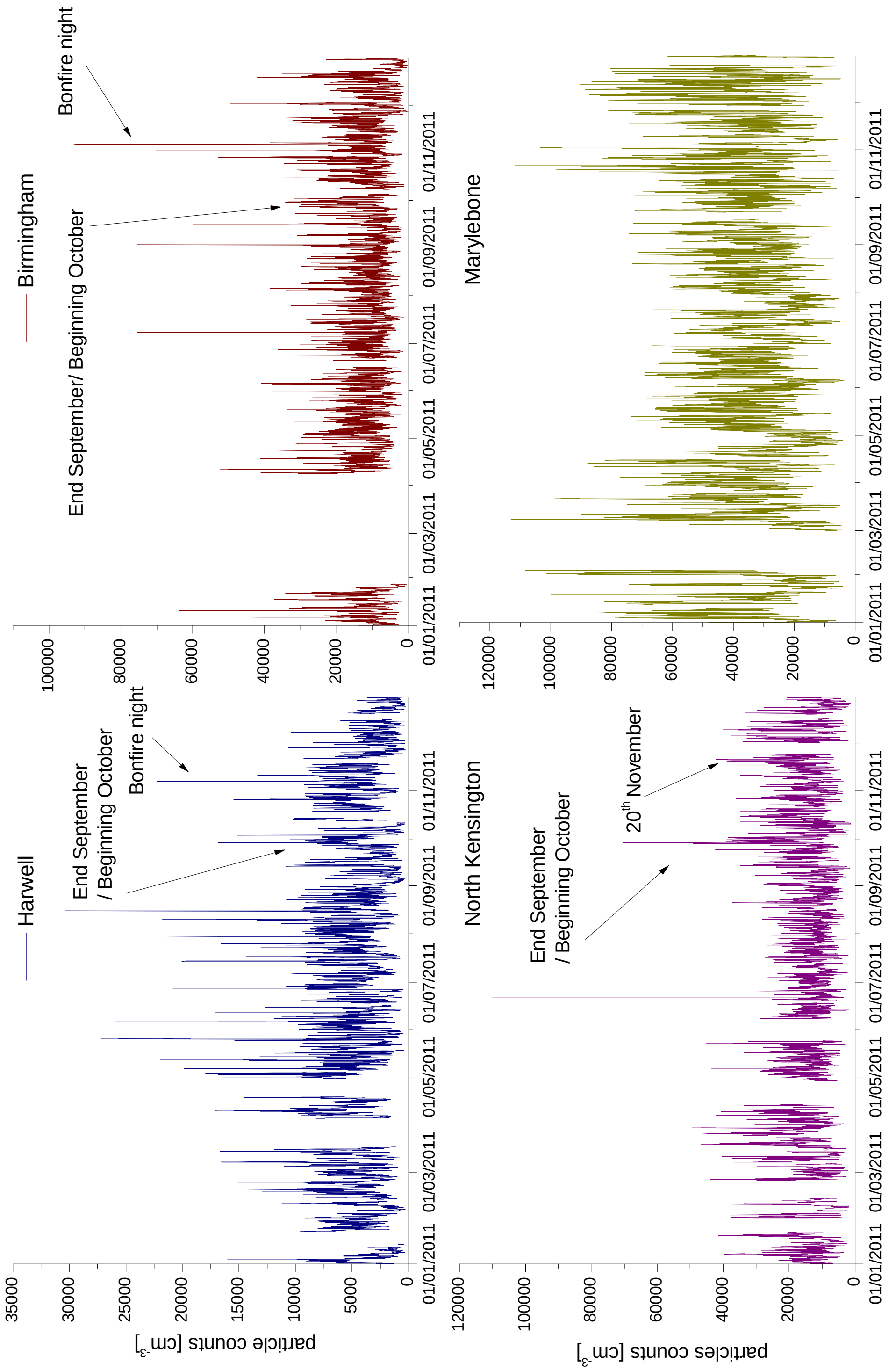


Figure 4-22 Particles counts at the Network sites in 2011

Figure 4-22 highlights some of the high pollution episodes. These episodes were mainly PM episodes, which affect the large size fraction of the particulate; therefore they are not expected to be seen in the particle counts which are driven by nanoparticles. At Marylebone Road none of the pollution episodes can clearly be identified as the number concentrations at a roadside site are mostly due to local traffic and local activities. However, there seems to appear a seasonal variation with lower concentrations during warm months.

There have been generally fewer operational problems with the 3022A CPCs since 2010, as shown by the higher data capture, especially for the CPC at the Marylebone Road site. This can be attributed, at least in part, to the introduction of the new inlet systems, including drying units and the PM_1 inlets, which prevent contamination from water and large particles. Also, the LSOs have been provided with a HEPA (High Efficiency Particle Attenuator) filter and a Gilibrator flow meter to perform a leak check and a flow measurement of the CPC and SMPS instruments during their usual fortnightly visit. Although these flow results are not used in the ratification of the data, they are a good means to assure the flow is stable and reasonable. Measuring the flow can detect blockage or butanol flooding. This has been found to be a quicker way to diagnostic a fault in the instruments and consequently to improve the quality of the data and data capture. Any anomaly is immediately reported to King's College London and, when necessary, the analysers are removed from site to be sent to NPL or TSI for repair.

It should be noted that the TSI 3022A is an old model that has been discontinued by TSI. Some of the 3022A Network CPCs have been working since 2000 and in normal circumstances the network would benefit from these being replaced by new models. Some new models have a much higher concentration range in counting (as opposed to photometric) mode, which would make compliance with the draft CEN Technical Specification easier (see Section 5.2).

In 2011 NPL ran a tendering exercise for new stand-alone CPCs, based on the draft CEN specification. However, it became clear from CEN meetings that the specification was still some way from being finalised, and moreover that the manufacturers were holding back from updating their models until the CEN specification became clearer. It was therefore decided to postpone the purchases and to run another tendering exercise when suitable models, based on a settled CEN specification, were available.

4.6.2 Particle number and size distributions (SMPS)

The SMPS instruments generate size spectra between 16 nm and 605 nm. Table 4-3 shows the monthly data captures.

The following should be noted:

- **Harwell.** The instrument was removed from site in January as the CPC pump had failed. It was removed again on 18th of March for service and calibration at NPL and re-installed on the 4th April. In October the instrument suffered from electrical interference which caused the SMPS software to stop repeatedly.

- **North Kensington.** The instrument was removed from site on the 12th of February for service and calibration at NPL and re-installed on the 23rd of February. It was removed at the end of August for flow problems on the CPC and repaired at NPL.

- **Marylebone Road.** Instrument was removed from site on the 3rd of February for service and calibration at NPL and re-installed on 23rd February. The instrument developed a leak in the system in November which was identified and fixed in January 2012.

Table 4-3 Monthly data captures for SMPS instruments during 2011. Red figures indicate that the time period for preventative maintenance has been counted as lost data in line with recommendations from CEN for calculating data capture.

Month	Harwell	North Kensington	Marylebone Road
January	37%	59%	87%
February	71%	100%	73%
March	100%	72%	88%
April	68%	89%	99%
May	97%	74%	98%
June	80%	64%	97%
July	98%	97%	96%
August	93%	31%	92%
September	69%	79%	78%
October	22%	97%	94%
November	74%	64%	3%
December	90%	63%	0%
Average	75%	74%	76%

The production of data from SMPS instruments is a complicated process, summarised schematically in Figure 4-23. 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. Extra checks were performed this year, as described in Section 4.6.4.

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. The data collection software has been upgraded to record these user definable settings. 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 4-24. The uncorrected spectrum is shown in blue. The effects of the multiple charge correction and diffusion loss corrections are shown in red and orange, respectively. The purple 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[8].

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[8] EURAMET Project 1027, Comparison of nanoparticle number concentration and size distribution

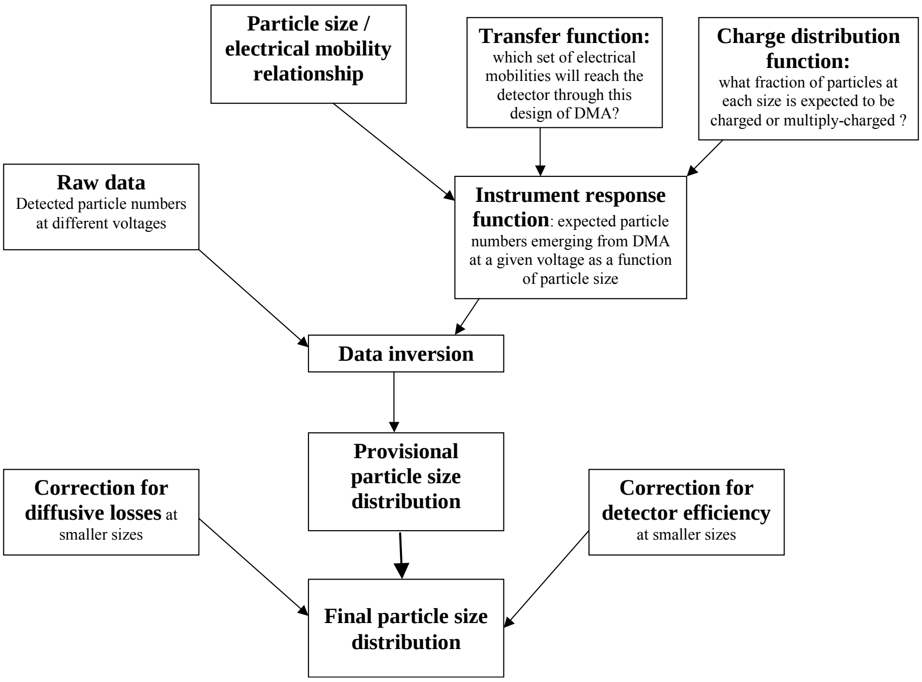

Figure 4-23 Schematic of the internal data processing of SMPS instrument in the Network

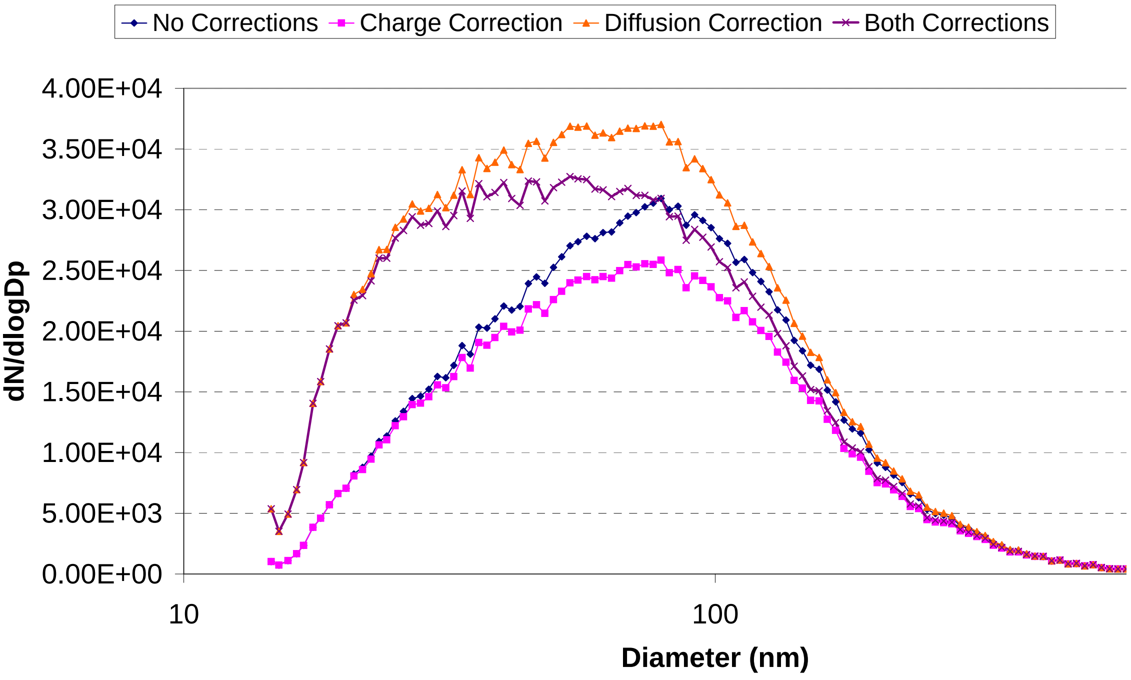

Figure 4-24 Effect of the multiple charge, the diffusion loss and the combined correction in the SMPS size spectrum.

The counts in each particle size bin measured during 2011 are presented as monthly averages in the left-hand panels of Figure 4-25 and as an annual average in the right-panel (only November and December were available for North Kensington in 2007).

It can be seen that the size distributions at Harwell during the warm months are characterised by higher nucleation modes ($d_p < 50$ nm). Unlike urban sites, where smaller particles are emitted by anthropogenic sources, in rural sites like Harwell high number concentrations of particles of this size are due to nucleation events. These episodes have been observed at Harwell previously and are likely to occur during warm days with high solar radiation when clean cool arctic or polar maritime air masses arrive in the UK[9,10].

In late 2009 the PM_1 inlets and the NPL drying units were installed at all sites, following the recommendations of the EUSAAR project. No significative difference can currently be seen in the shape of the size distributions between 2010/2011 and previous years. However, as for the stand-alone CPCs, a better performance of the instruments has been observed, with fewer blockages in the SMPS impactors and less contamination in the CPCs.

The annual-averaged size distribution at Marylebone Road in 2007 shows higher concentration for particles with diameter less than 50 nm. This aspect could be related with the drop in concentration observed after 2007 in the particle counts measured by the stand-alone CPC[11].

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[9] Factors Influencing New Particle Formation at the Rural Site, Harwell, United Kingdom, A.Charron, W. Birmili and R.M. Harrison, *J. Geophys. Res*., *112, (2007). D14210, doi:10.1029/2007JD008425*

[10] Fingerprinting particle origins according to their size distribution at a UK rural site, A. Charron, W. Birmili, R.M. Harrison, *J. Geophys. Res*., *113, (2007), D07202, DOI : 10.1029/2007jd008562*

[11] A large reduction in airborne particle number concentrations at the time of the introduction of “sulphur free” diesel and the London Low Emission Zone, A.M. Jones, R.M. Harrison, B, Barratt and G. Fuller, *Atmospheric Environment 50 (2012) 129-138*

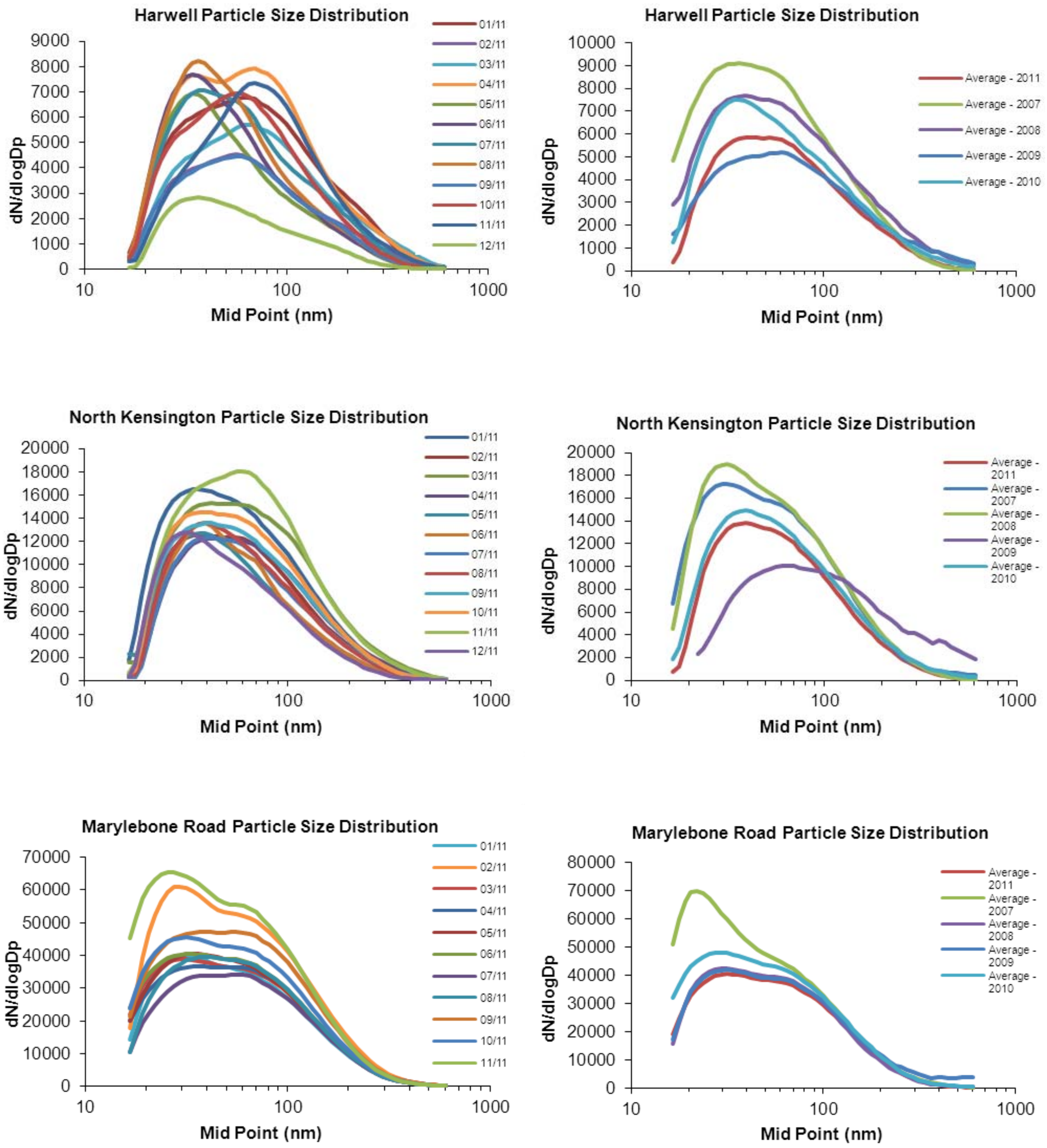


Figure 4-25 Monthly averaged particle size distributions at the Network sites during 2011 [left-hand panels] and comparison of the 2007, 2008, 2009, 2010 and 2011 annual-averaged size distributions [right-hand panles].

4.6.3 SMPS versus CPC data

Total integrated particles counts from the SMPS analysers have been compared with the CPC counts and scatter plots are presented in Figures 4-26, 4-27 and 4-28.

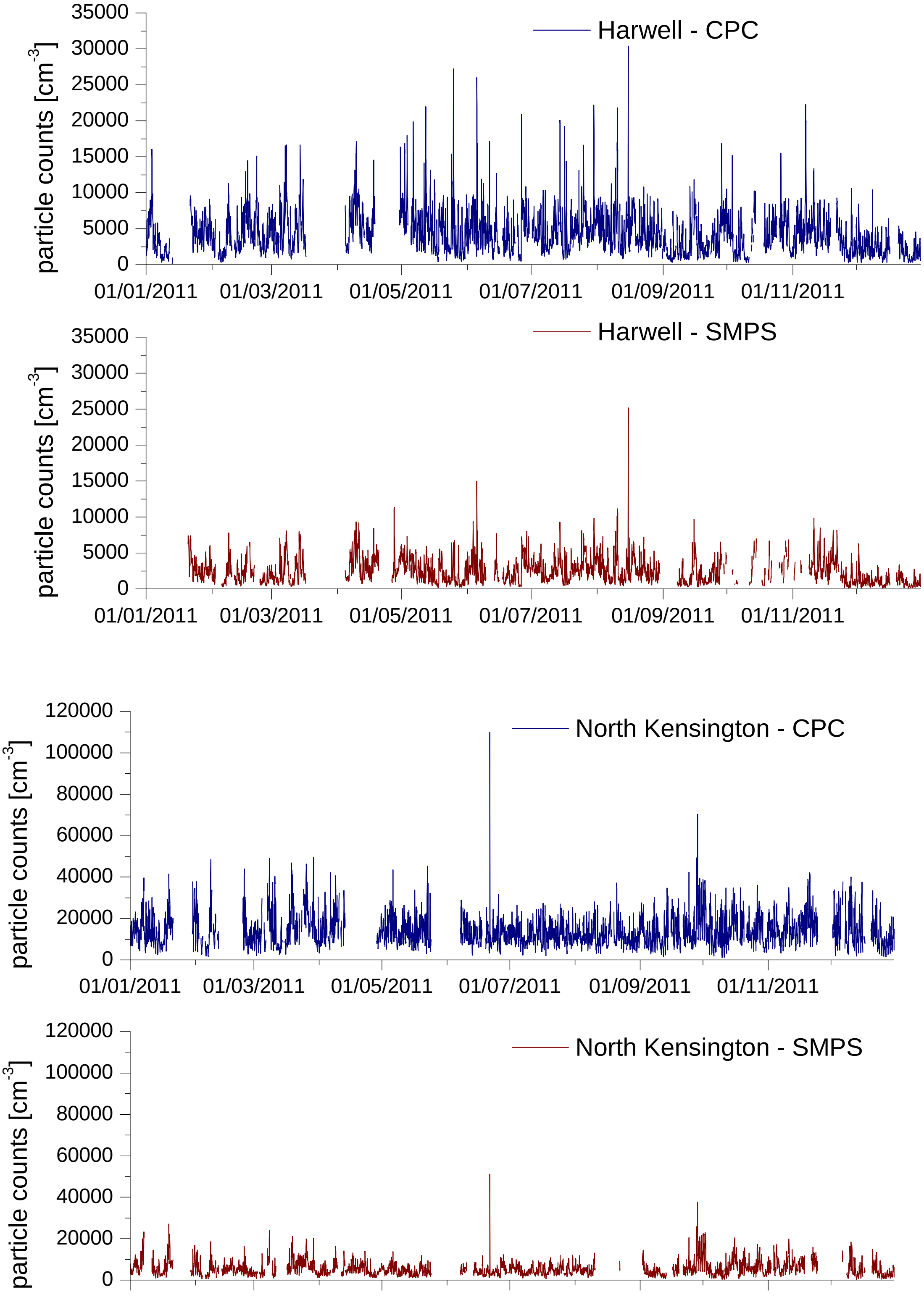


Figure 4-26 CPC and SMPS time series at Harwell and North Kensington sites in 2011

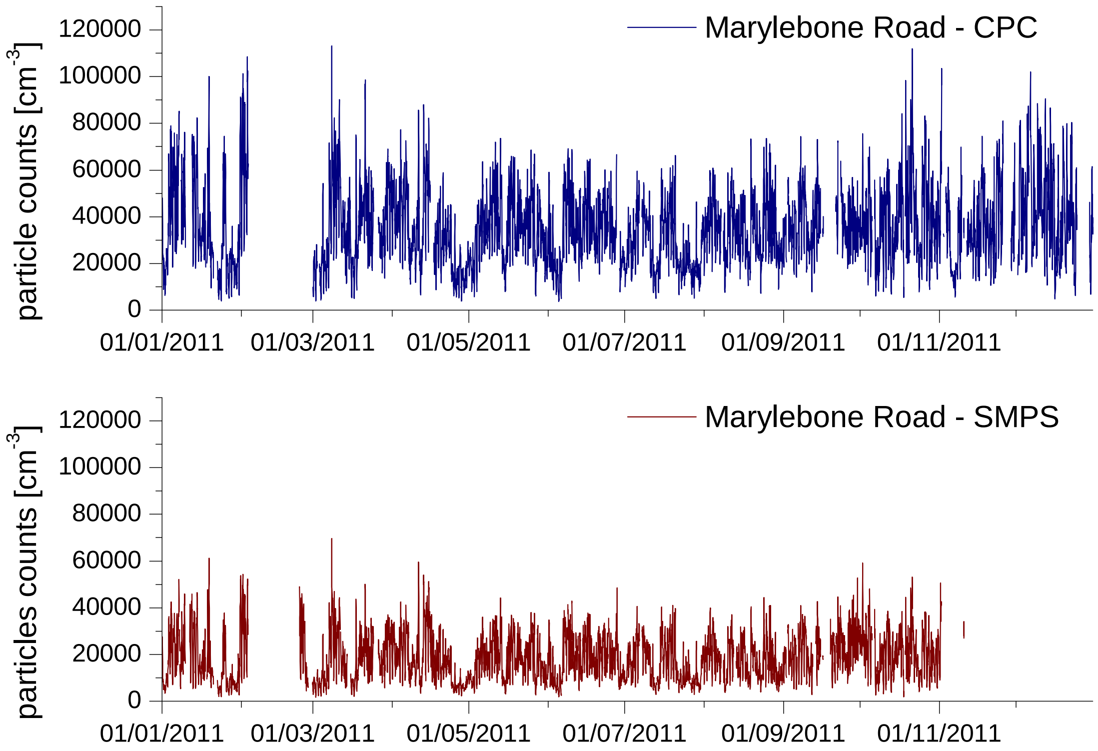


Figure 4-27 CPC and SMPS time series at Harwell in 2011

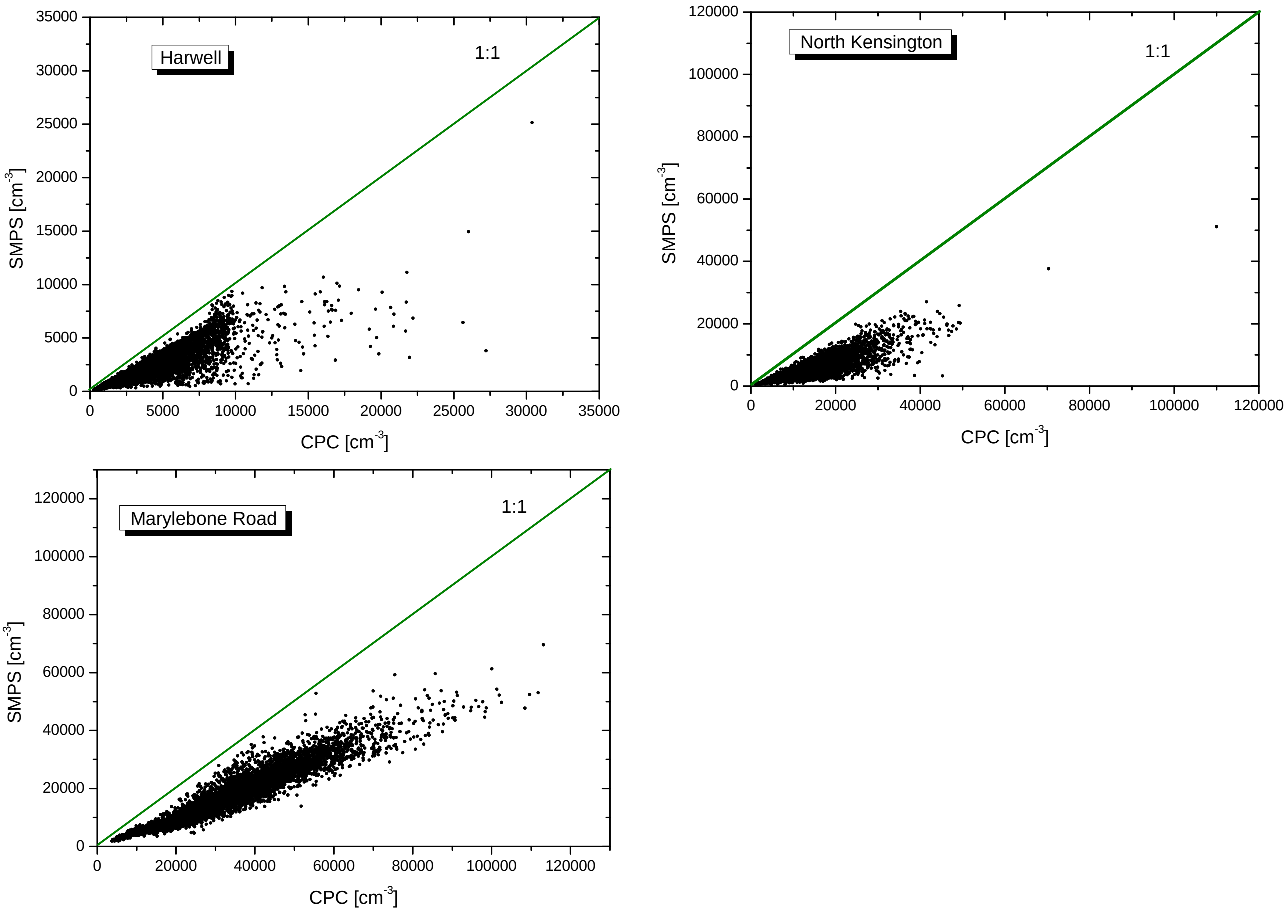


Figure 4-28 Scatter plots between SMPS and CPC concentrations in 2011 at the Network sites

The complicated data processing within SMPS instruments, described in Section 4.4.2, 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 will record higher concentrations than the SMPS. The comparability of number concentrations obtained from the two instruments will be clarified as the two measurements become standardised within CEN TC 264 WG 32.

4.6.4 SMPS checks and Intercomparison

Introduction

To assess the performance of the network SMPS instruments, a series of experiments were carried out in the Airborne Nanoparticles lab at NPL (28 February to 1 March 2012). The Marylebone (Mar), Harwell (Har) and North Kensington (NK) SMPSs were tested in parallel, under controlled lab conditions. Previous laboratory tests had been limited to size checks with certified latex spheres. This way, additional information could be extracted regarding the comparability of the network SMPSs, as well as of the NPL infrastructure for performing such intercomparison studies.

Experimental

The sites' SMPS units (consisting of TSI classifier 3080 and CPC 3775) were transported to NPL without their respective nuclear source (neutraliser). An in-house neutraliser (TSI 3077A) was therefore shared with all SMPS units. Three different setups were used for the experiments:

Setup-1: Every network SMPS was tested in series with the same source of particles. PSL (polystyrene latex) beads aerosols were used, by means of suspension, nebulisation and subsequent drying. The three NIST traceable PSLs used had nominal diameters of 59 ± 2 nm, 92 ± 3 nm and 203 ± 5 nm.

Setup-2: All three network SMPS units were tested in parallel through the NPL sampling chamber. The source was soot particles, formed by a CAST generator. The nominal aerosol sizes tested were 26, 55 and 156 nm, with an additional bimodal distribution also measured. The common neutraliser was positioned after the source and before the chamber, in order for the three SMPSs to sample the same charge distribution.

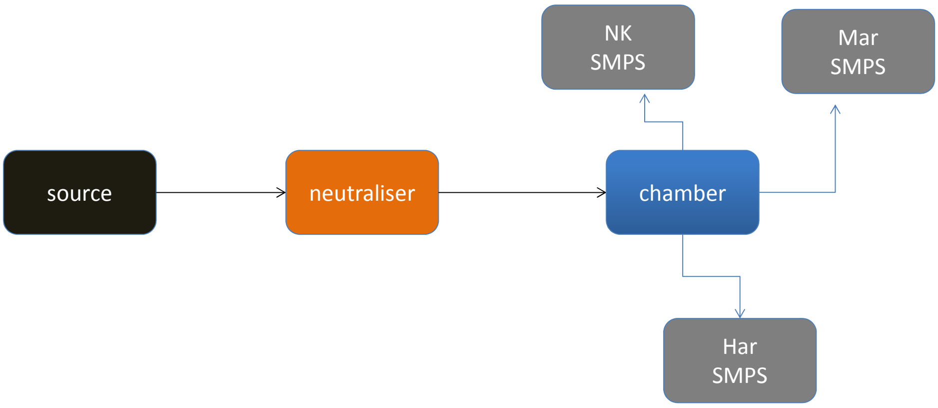


Figure 4-29 Schematic showing the parallel sampling of the three SMPS when connected to the chamber and fed with a single particle source (CAST-soot), conditioned with a single neutraliser.

Setup-3: All three network SMPS units were tested in parallel through a simple flow splitter. The source was soot particles, formed by a CAST generator. The aerosol sizes tested were 55 nm and bimodal distribution. Again, a common neutraliser was used, positioned after the source and before the flow splitter. This arrangement allowed any effect of the chamber on the size distribution of the particles to be evaluated.

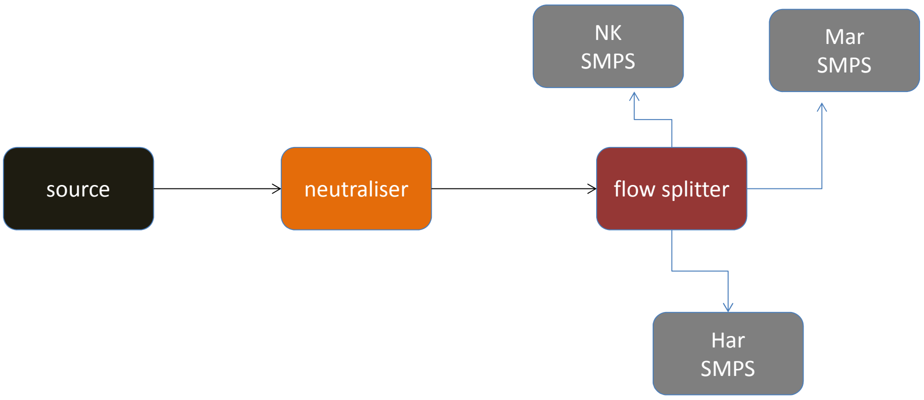


Figure 4-30 Schematic showing the parallel sampling of the three SMPS when connected to a flow splitter and fed with a single particle source (CAST-soot), conditioned with a single neutraliser.

Results and Discussion

Setup-1

In Table 4-4 the SMPS results for the three site instruments are summarised and compared with the nominal diameters of the latex spheres. It is clear that there is very little variation between the three sites, and for the 92 and 203 nm PSL the geometric means measured are well within the nominal uncertainties of the certified sizes. There is a size overestimation for the 59 nm particles of around 10%, but it should be noted that the SMPS measurement is based on the estimation of the electrical mobility diameter, compared to the PSL nominal diameter, which is defined by electron microscopy. This discrepancy has been noted in previous years, and will be one of the topics being discussed within CEN when they consider SMPS standardisation (see Section 5.2).

Table 4-4 Comparison of SMPS measured distributions with PSL nominal values.

			PSL	
Site		**59** ± 2 nm	**92** ± 3 nm	**203** ± 5 nm
Mar	Geometric mean	**66.12**	**92.87**	**200.99**
	Geometric st. dev.	1.09	1.08	1.06
Har	Geometric mean	**65.15**	**91.53**	**200.23**
	Geometric st. dev.	1.10	1.08	1.06
NK	Geometric mean	**66.28**	**93.19**	**202.33**
	Geometric st. dev.	1.09	1.09	1.06

Setup-2

In Figure 4-31 an example of the bimodal distribution recorded by the three instruments, when sampling in parallel from the chamber, is illustrated. All results are plotted on the same scale. The agreement is very good for most of the size bins selected, with some variation in the region below 25 nm.

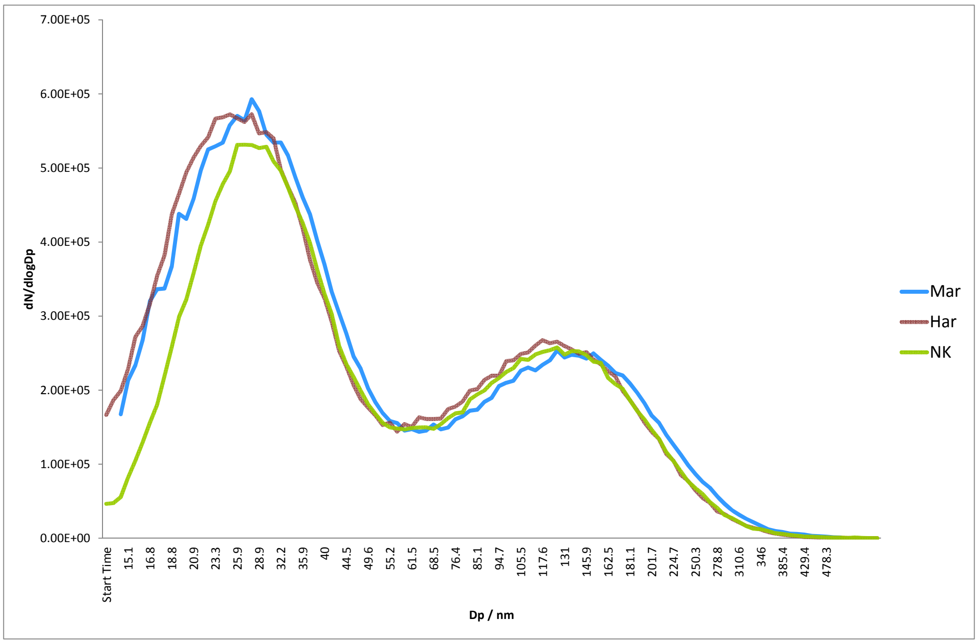


Figure 4-31 CAST generated bimodal distribution as measured by the three site SMPS.

Sequential scanning of three discreet soot sizes (26, 55 and 156 nm) confirmed the behaviour observed in the bimodal distribution (Figure 4-32). The distribution modes are in agreement with the nominal diameter of the aerosol, and the three site instruments give almost identical results, at least for sizes above 50 nm. There is again indication of relative under-counting for the North Kensington SMPS, for sizes below 25 nm. The deviation is likely to be due to diffusion losses and the TSI protocol used to correct for them. For example, variations in the sheath flow of the SMPSs may be causing a miscalculation of the diffusion losses. Further experiments are underway to investigate this, using the in-house NPL SMPS.

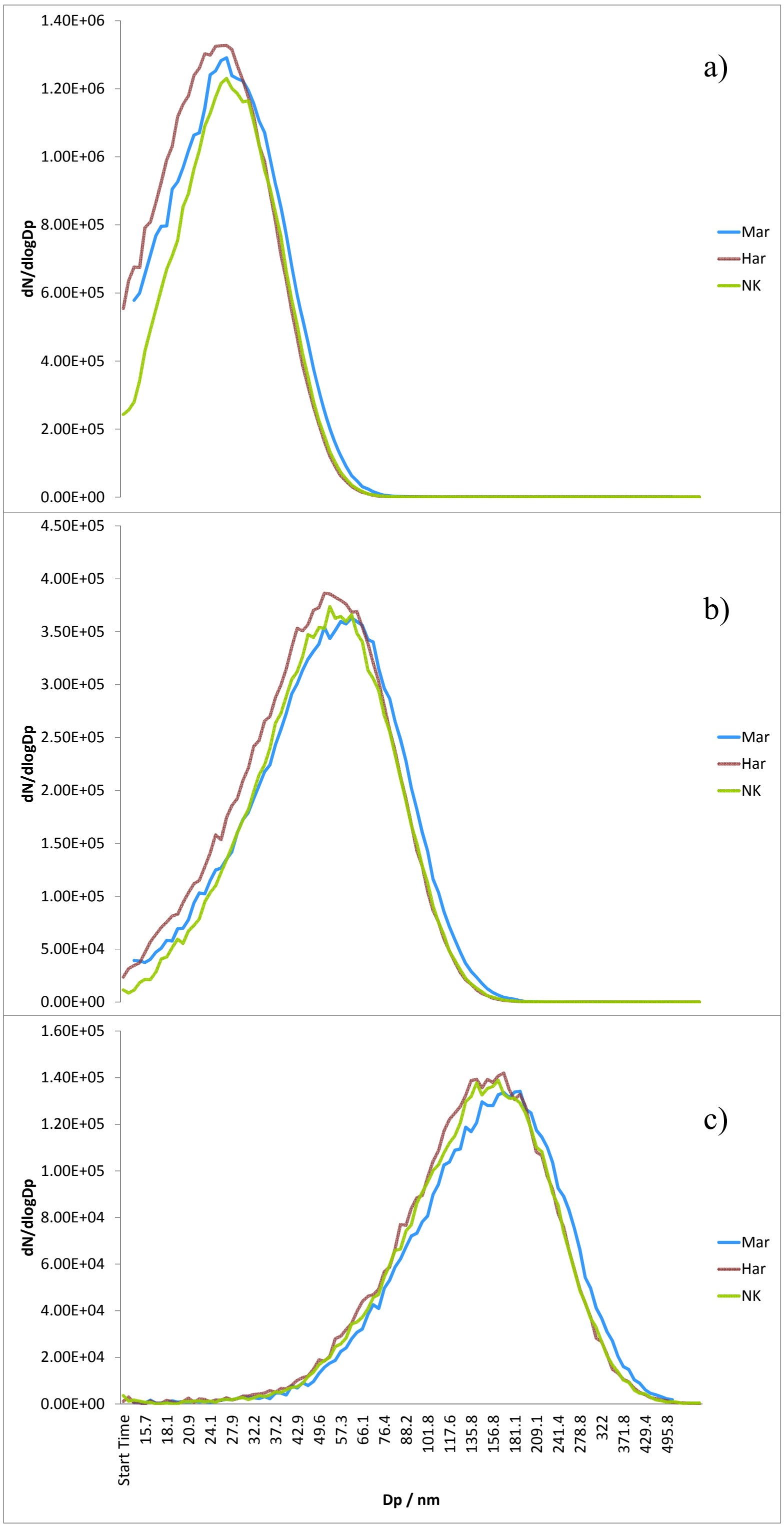


Figure 4-32 SMPS scans of the three site instruments when fed with CAST generated particles at nominal diameters of a) 26 nm, b) 55 nm and c) 156 nm.

Setup-3

When, instead of the chamber, the three SMPSs were connected in parallel using a simple flow splitter, the distributions measured were identical in shape, but differing in total particle concentration. This is an expected behaviour, as significant dilution of the feeding stream takes place when sampling from the chamber (observed as a factor of 32 in concentration). Figure 4-33 shows a superimposed example of the 55 nm soot aerosol distribution recorded by the Harwell SMPS, for the case of splitter and chamber configurations. It is clear, therefore, that the NPL chamber can be used for multi-instrument sampling without significant size-dependent losses of particles.

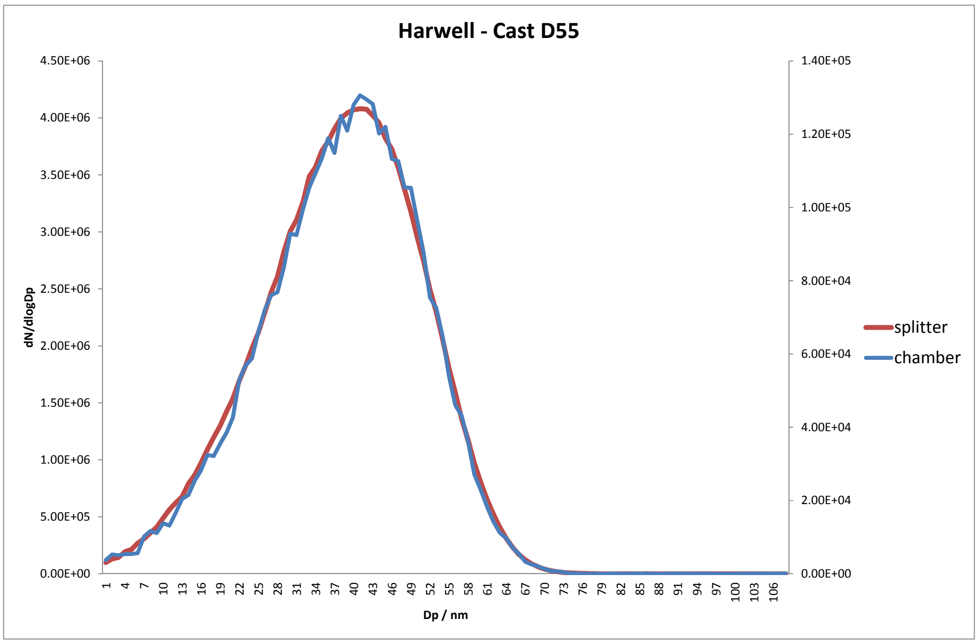


Figure 4-33 Comparison of the CAST soot 55nm distribution recorded by the Harwell SMPS, when configured with the flow splitter (left y-axis) and the chamber (right y-axis).

Implications for SMPS uncertainties

Accepted procedures for assigning uncertainties to SMPS data are expected to come in due course through CEN TC 264 WG 32 (Section 5.2). In practice, an uncertainty needs to be assigned to the dN/dlogDp value in each size bin, and also to the diameter given to each size bin. These results highlight two important points: firstly, that the limited ability to correct for diffusion losses means a larger uncertainty on the dN/dlogDp values at sizes below around 25 nm. Above this size, inter-instrument variability is around ± 5%. Secondly, the size calibration needs to be carefully defined, as different methods for determining the diameters will give different answers, especially at lower sizes.

4.7 METEOROLOGICAL DATA

Although not a formal part of this measurement programme, meteorological data have been collated from the measurements made at Rochester as part of other Defra monitoring networks. Monthly data capture rates for the meteorological masts during 2011 are displayed in Table 4-5.

Table 4-5 Monthly data capture for meteorological instruments at Rochester in 2011

	Data capture
January	97%
February	100%
March	100%
April	100%
May	100%
June	100%
July	100%
August	100%
September	100%
October	100%
November	100%
December	100%
Average	100%

Wind roses are shown in Annex 1.

4.8 TRENDS AND PROFILES

4.8.1 Monthly trends

Using data from this contract, this section seeks to show trends in the average monthly values for all species at all sites during the past several years (see Figures 4-34 and 4-35).

Organic Carbon/Elemental Carbon. Monthly trends are plotted for both methods (transmission and reflectance corrections) at all sites. There seems to be a downward trend for organic carbon at Harwell and Marylebone Road, between 2008 and 2010, but later results have nullified this trend. The measurements at North Kensington do not show any significant change across the years.

Particles counts. There is clear drop in concentration at Marylebone Road between 2007 and 2008, which continues in 2009, 2010 and 2011. The particles counts at North Kensington show a smaller decrease and a loss of seasonal variation in 2011. Figure 4-36 shows the annual average for particles counts at the two sites in London since 2005. The reason is likely to be the change in sulphur content of fuel. This is discussed in a Topic Report published in 2011 and will be discussed further in Section 6.

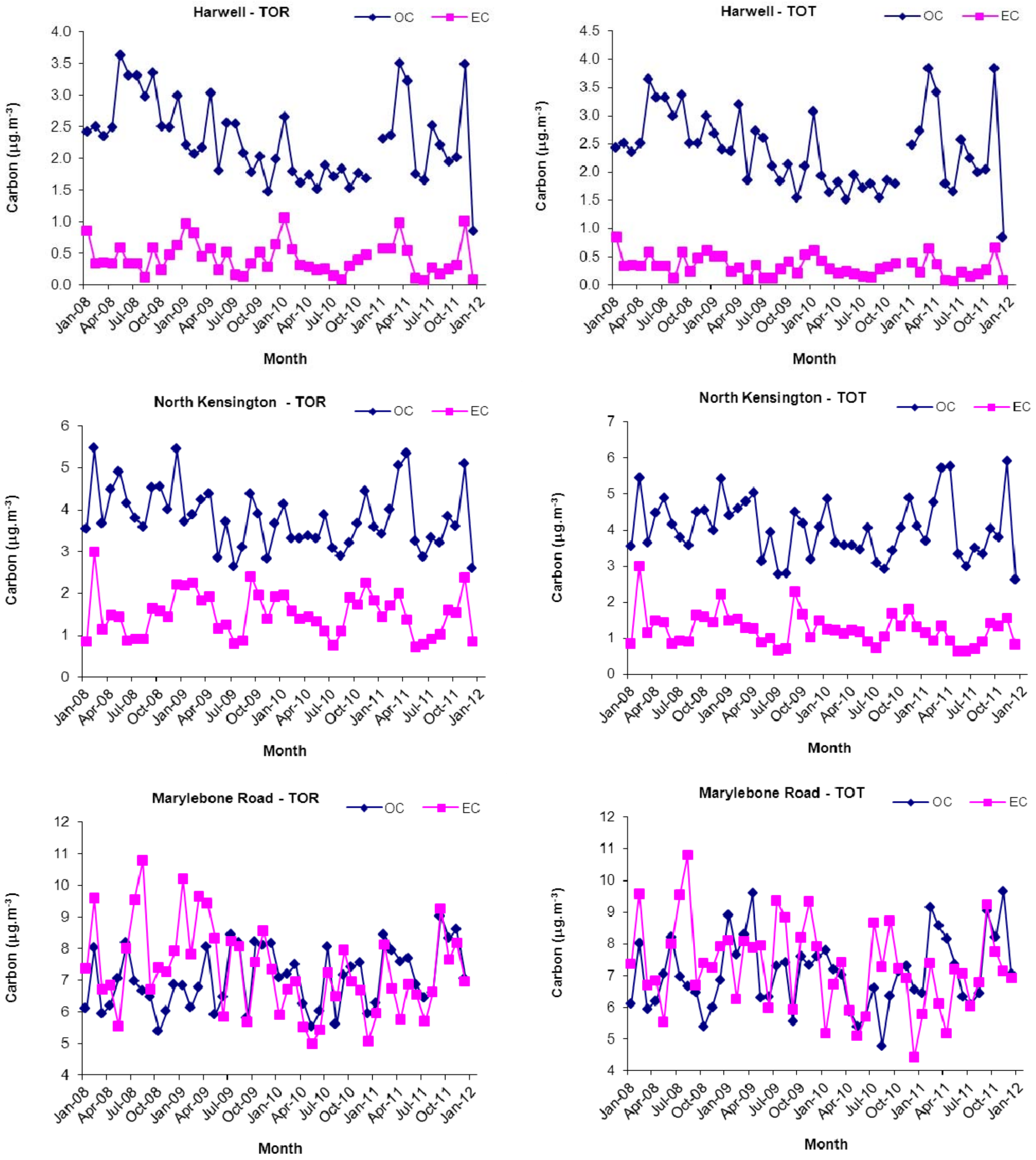


Figure 4-34 Monthly trends for PM_{10} concentrations at the Network sites

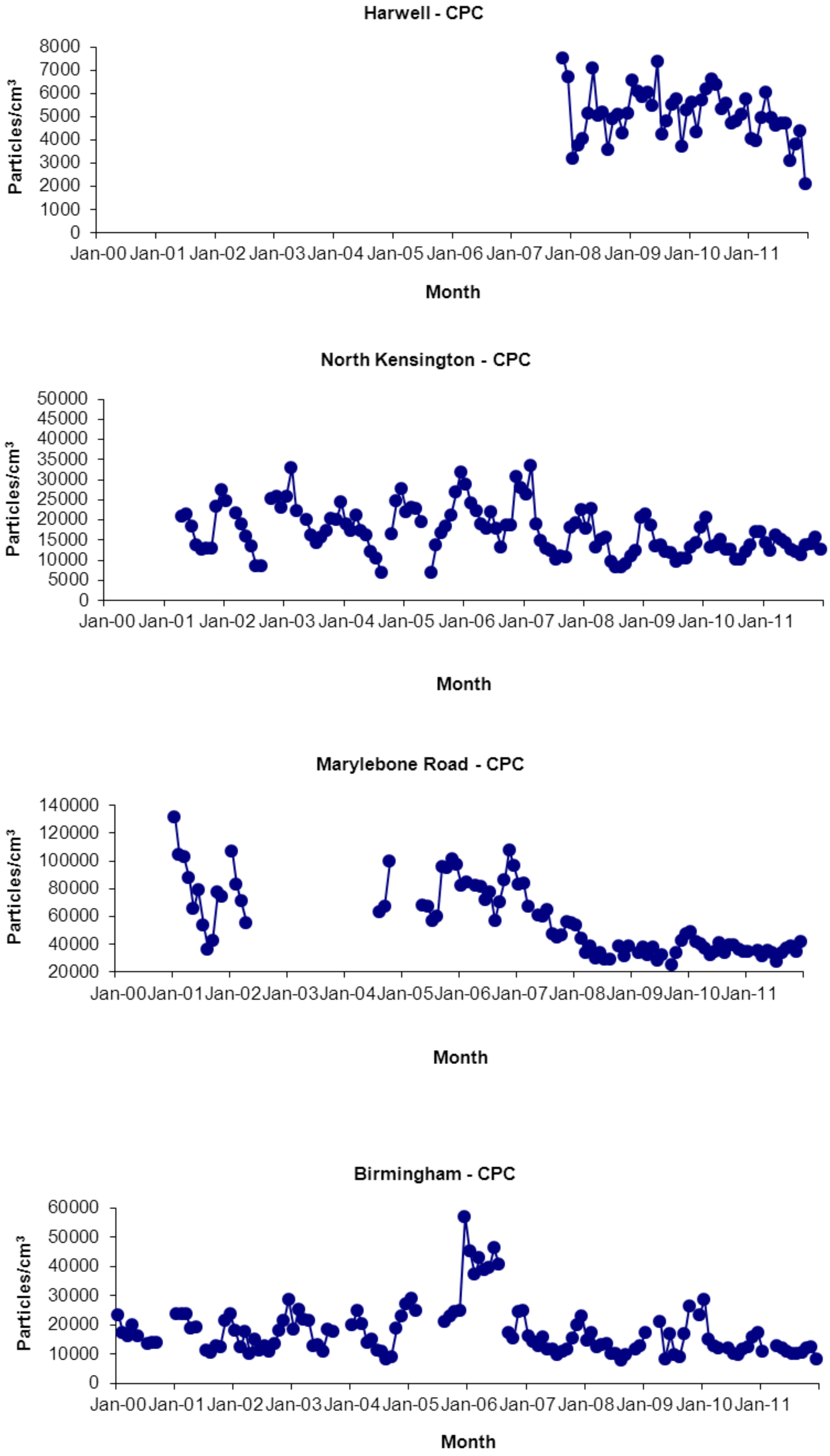


Figure 4-35 Monthly trends for CPC counts at the Network sites

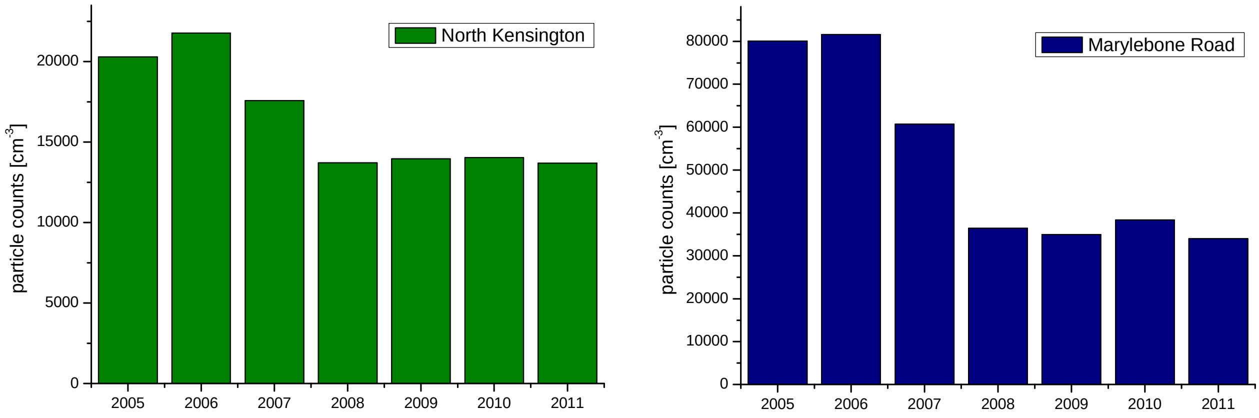


Figure 4-36 Annual averages of particle counts since 2005 at the London sites

4.8.2 Diurnal and weekly profiles

The following graphs show diurnal and weekly trends along with monthly averages in 2011 for all the measurements in the network.

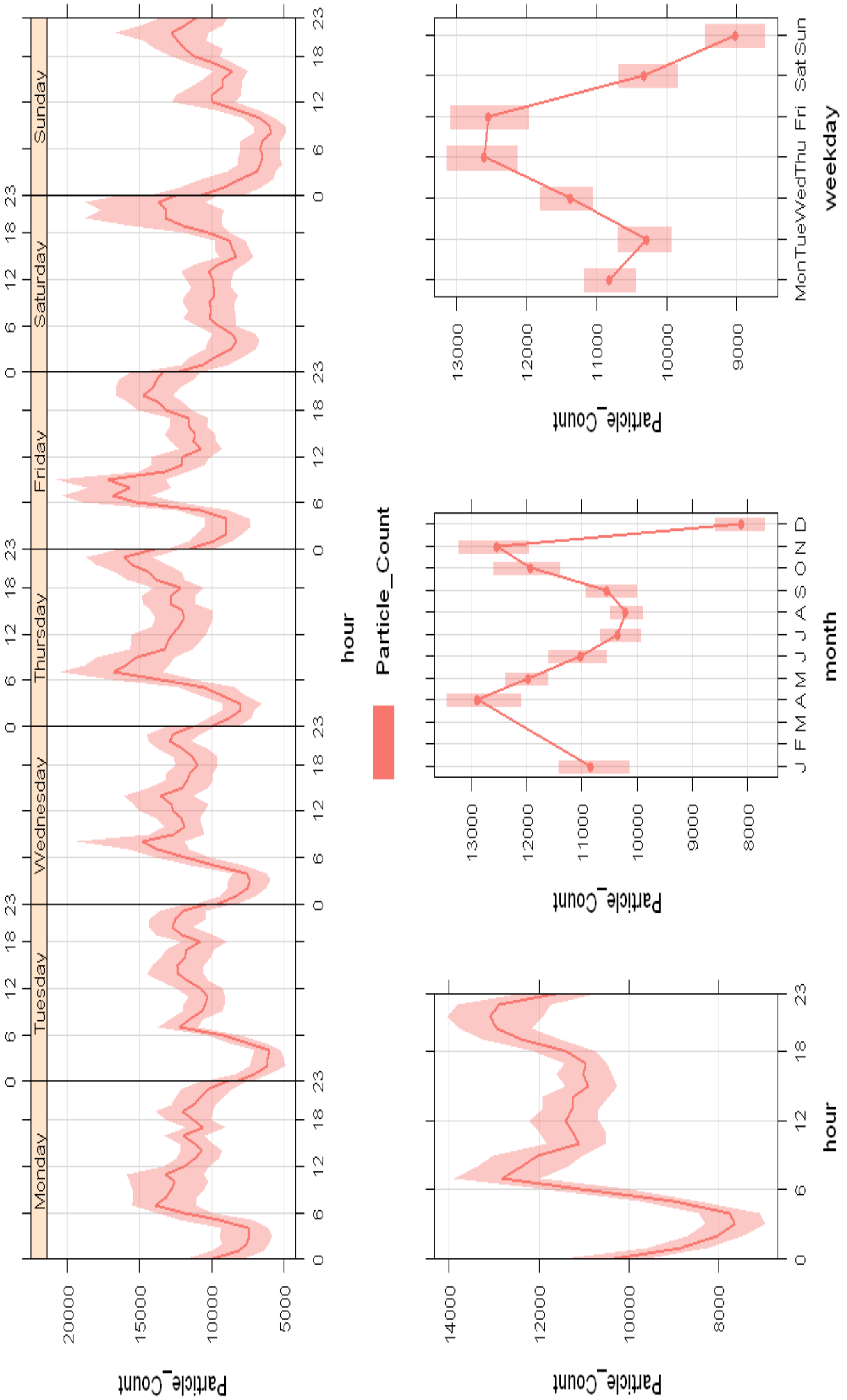
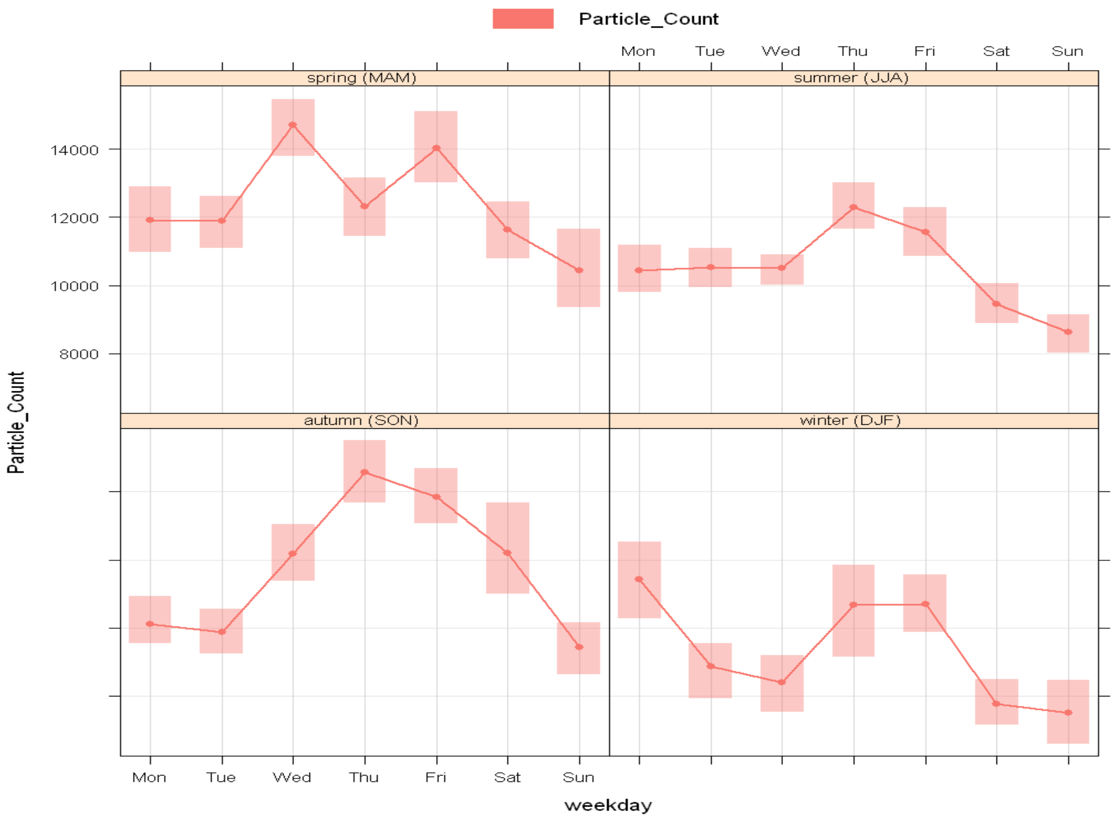


Figure 4-37 Diurnal and weekly trends for the Birmingham CPC measurements



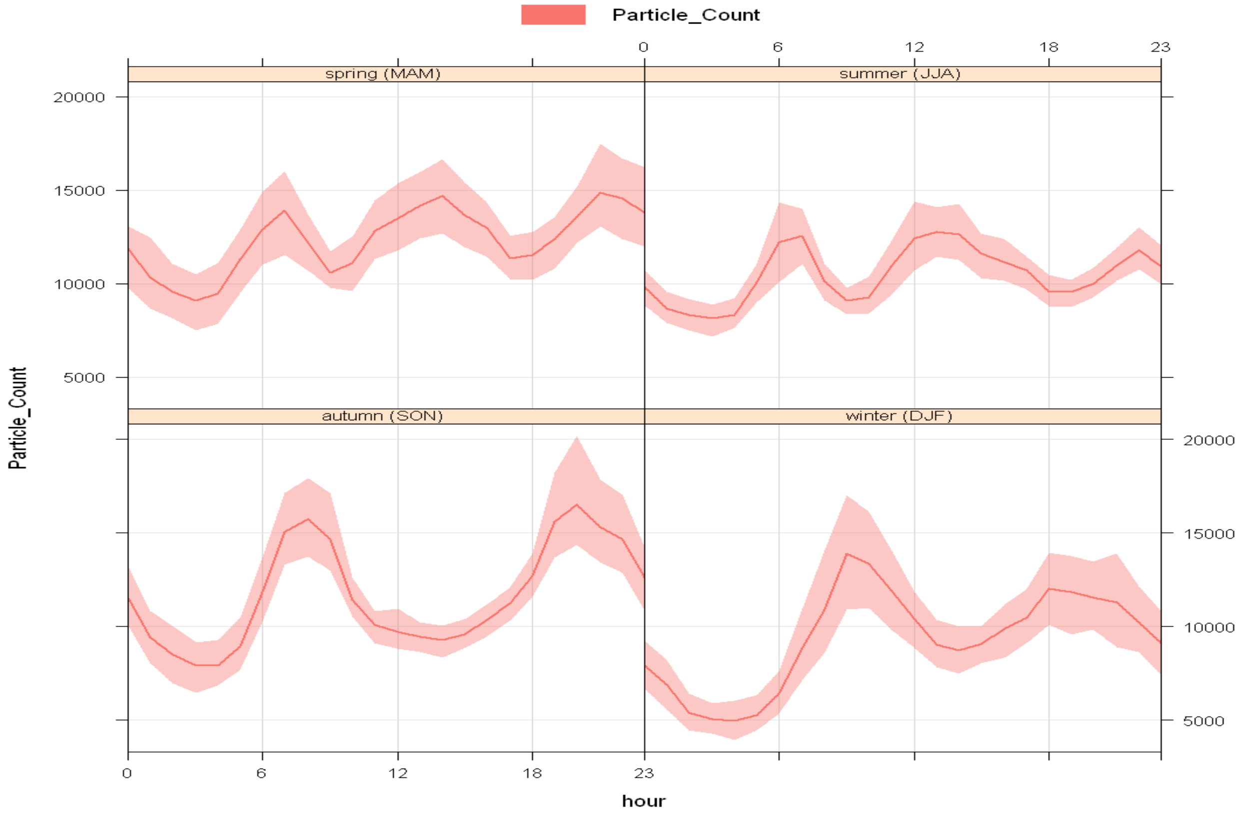


Figure 4-38 Seasonal weekly and diurnal trends for the Birmingham CPC measurements

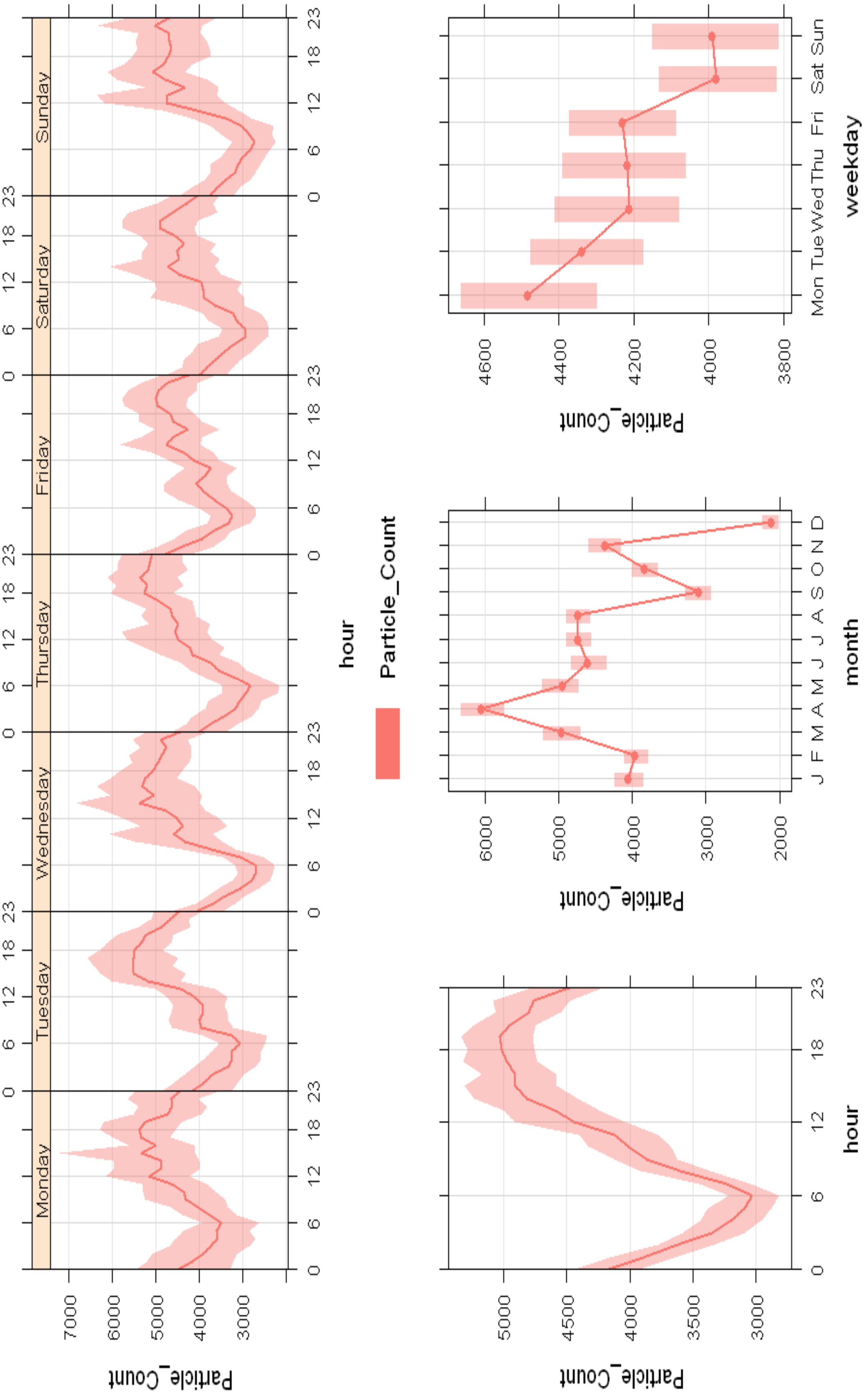
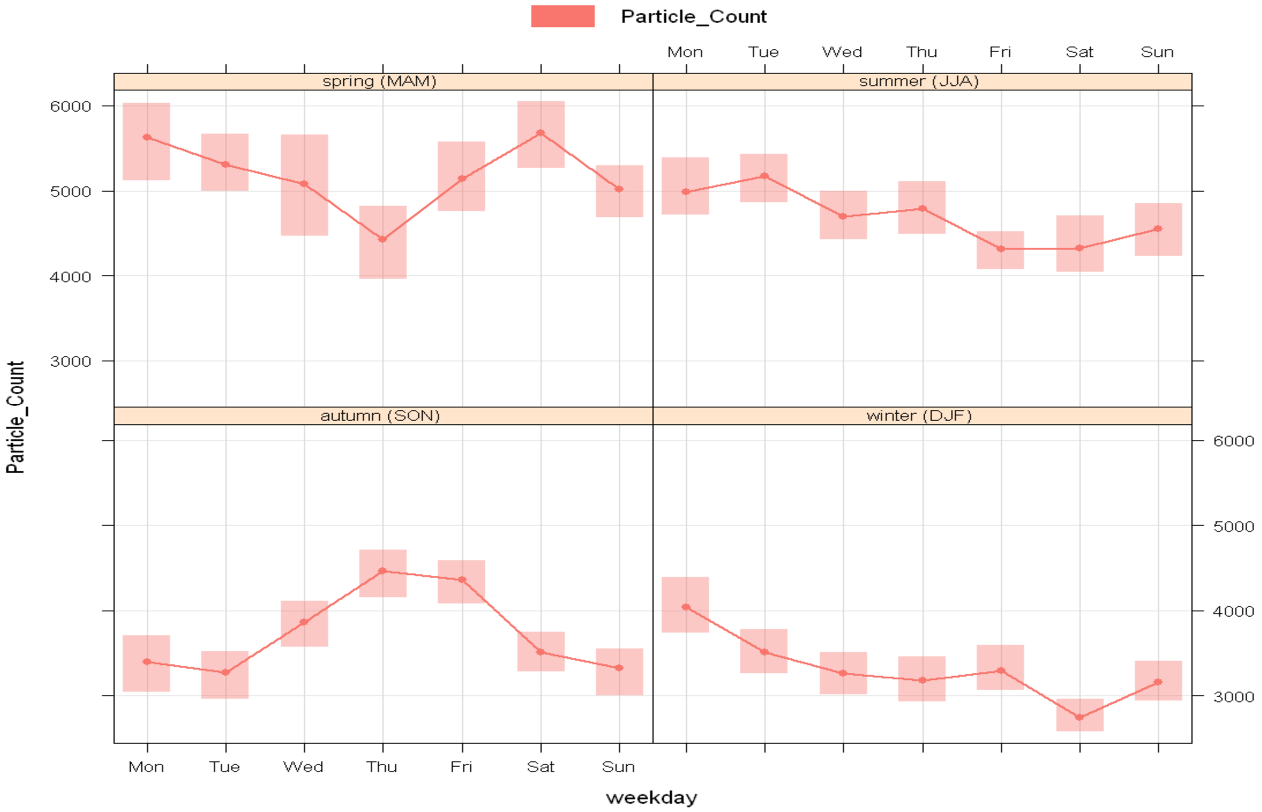


Figure 4-39 Diurnal and weekly trends for Harwell CPC measurements



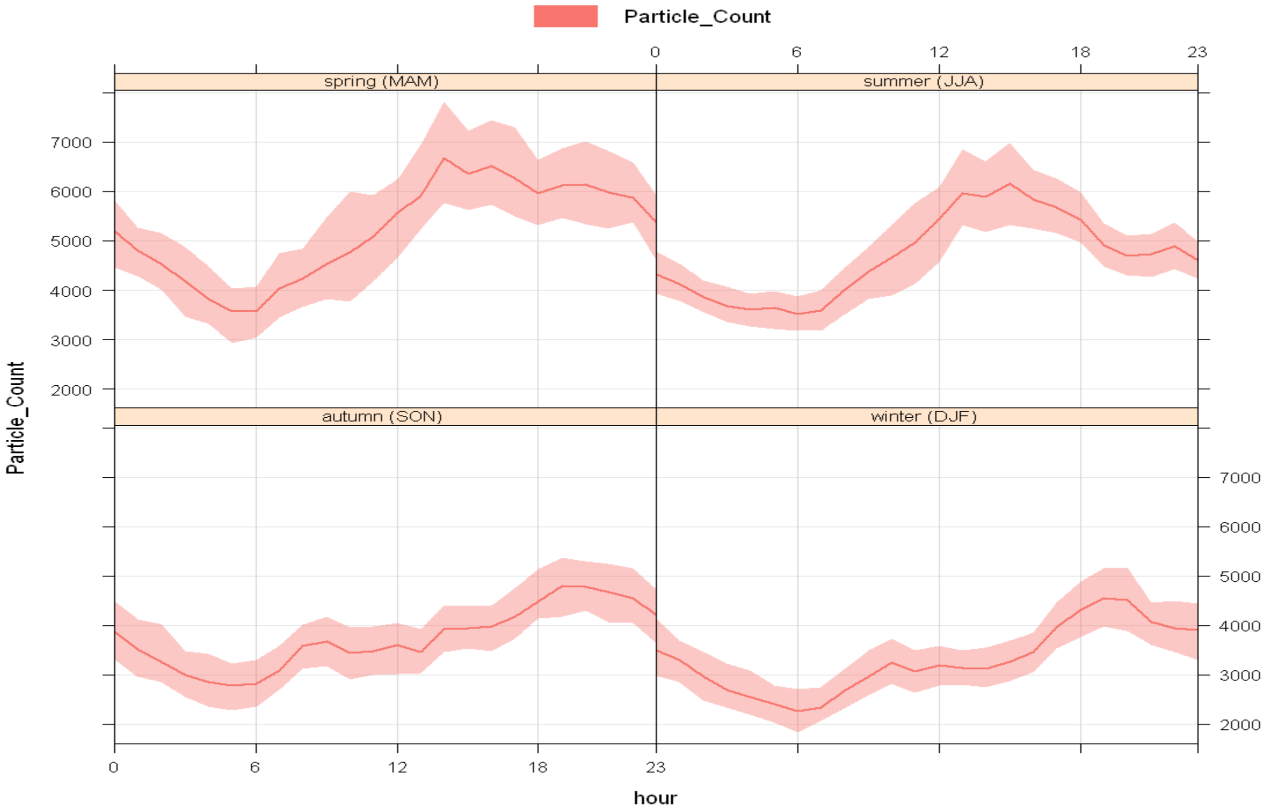


Figure 4-40 Seasonal weekly and diurnal trends for Harwell CPC measurements

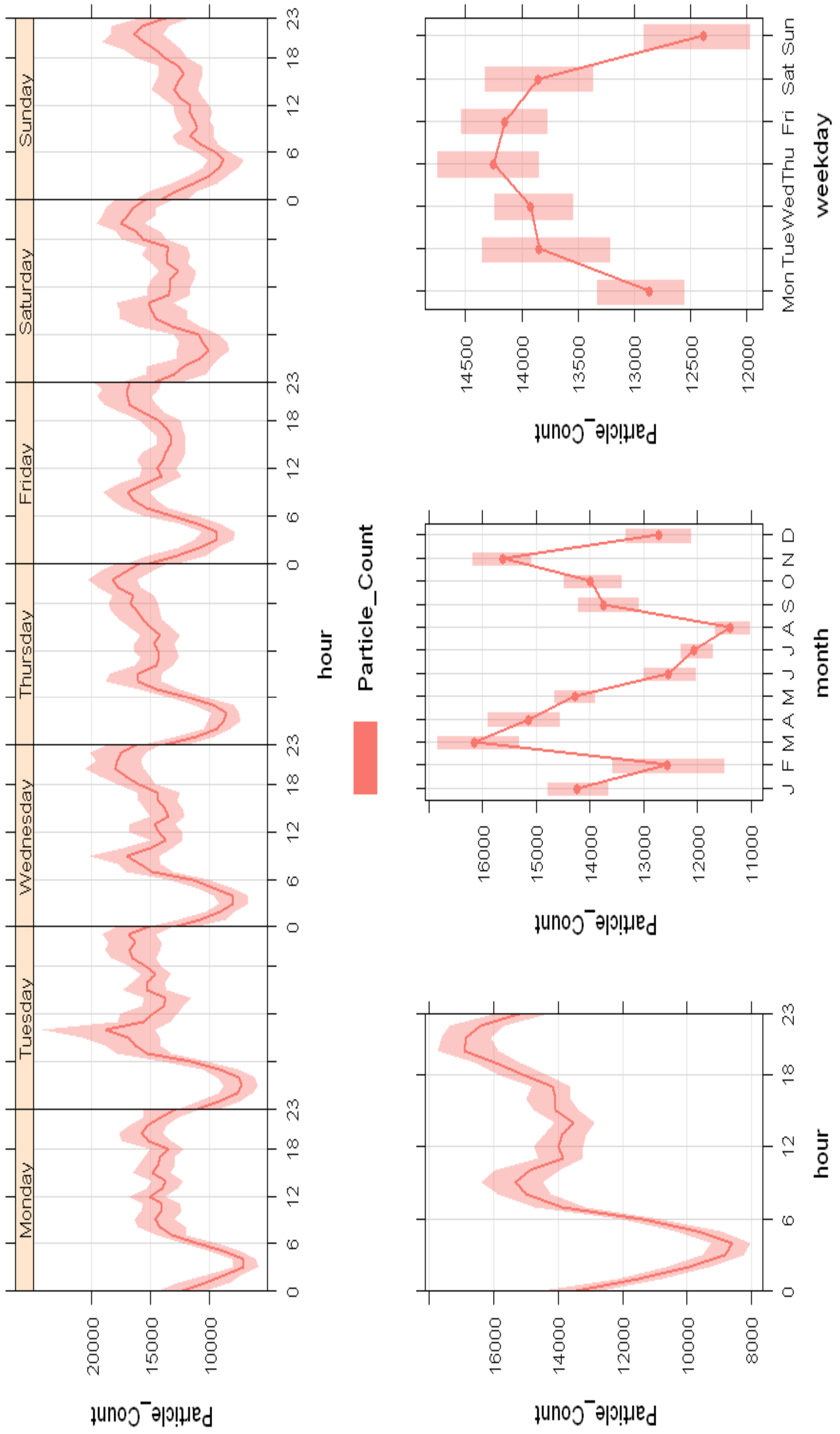


Figure 4-41 Diurnal and weekly trends for North Kensington CPC measurements

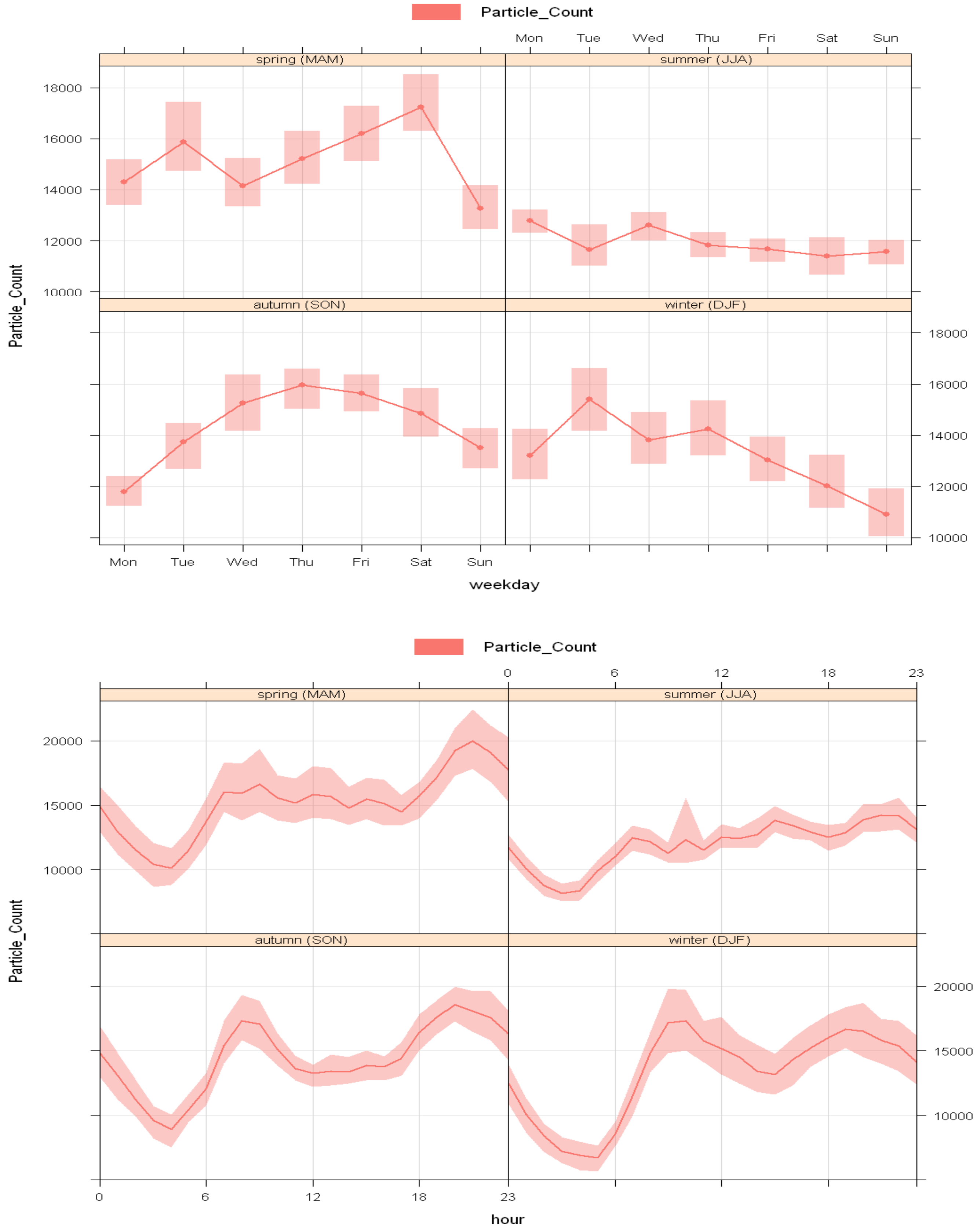


Figure 4-42 Seasonal weekly trends for North Kensington CPC measurements

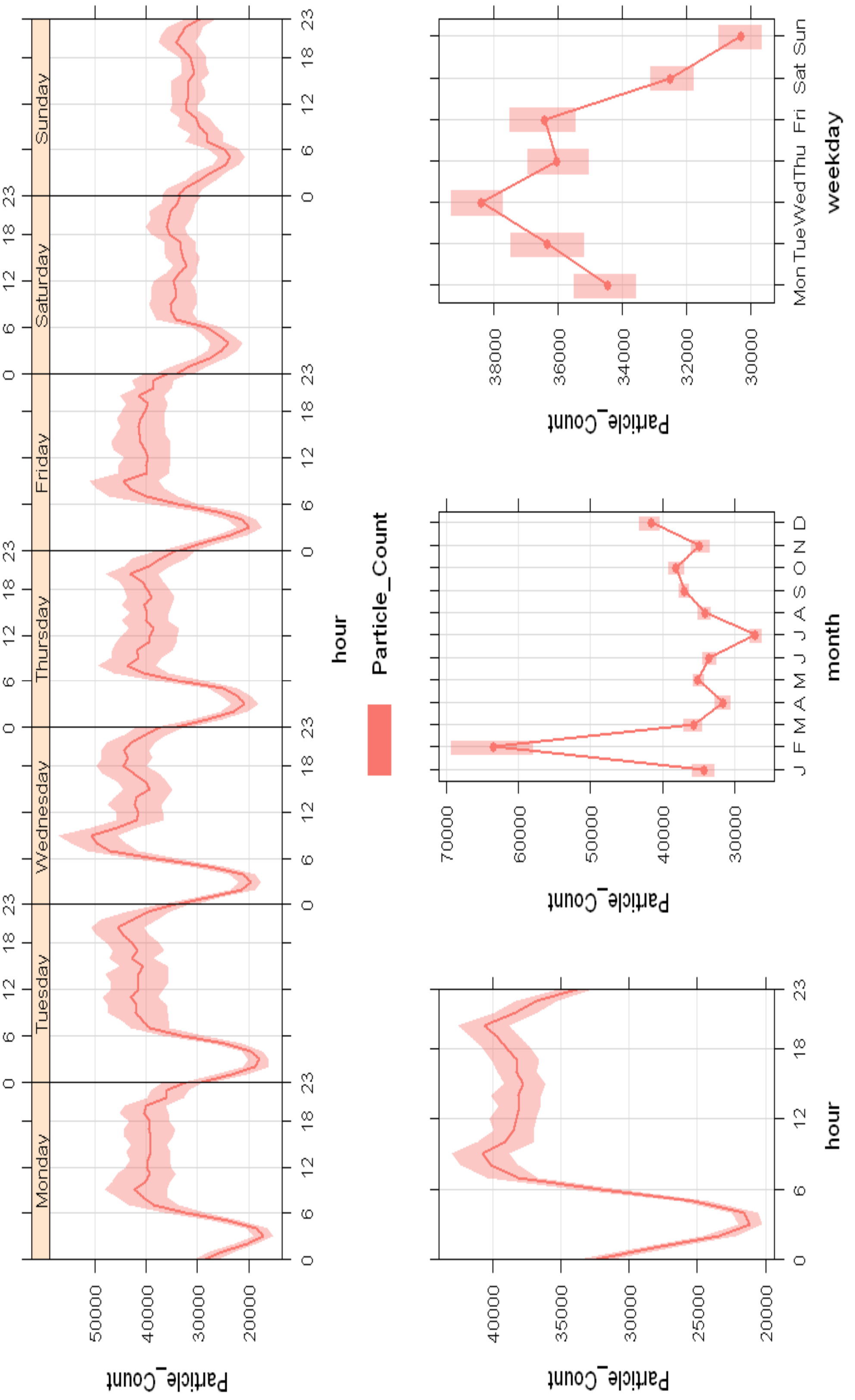
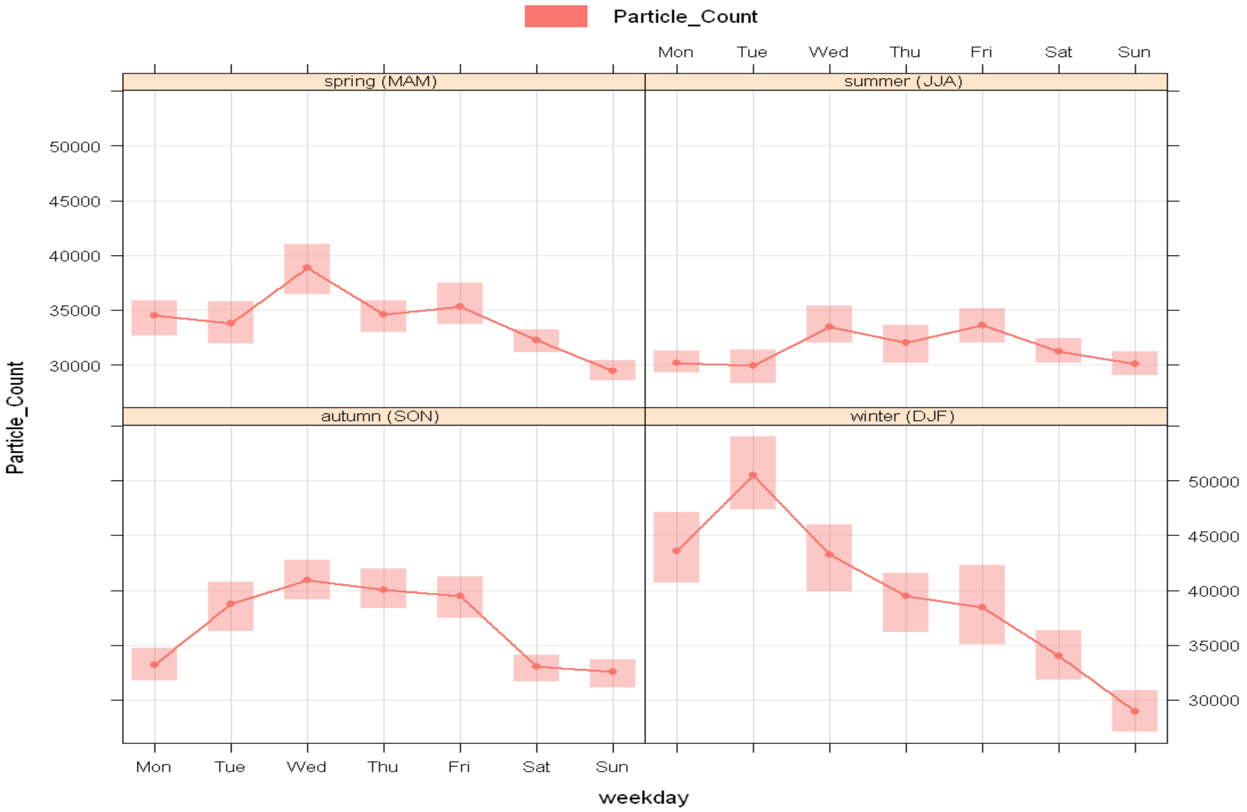


Figure 4-43 Diurnal and weekly trends for Marylebone Road CPC measurements



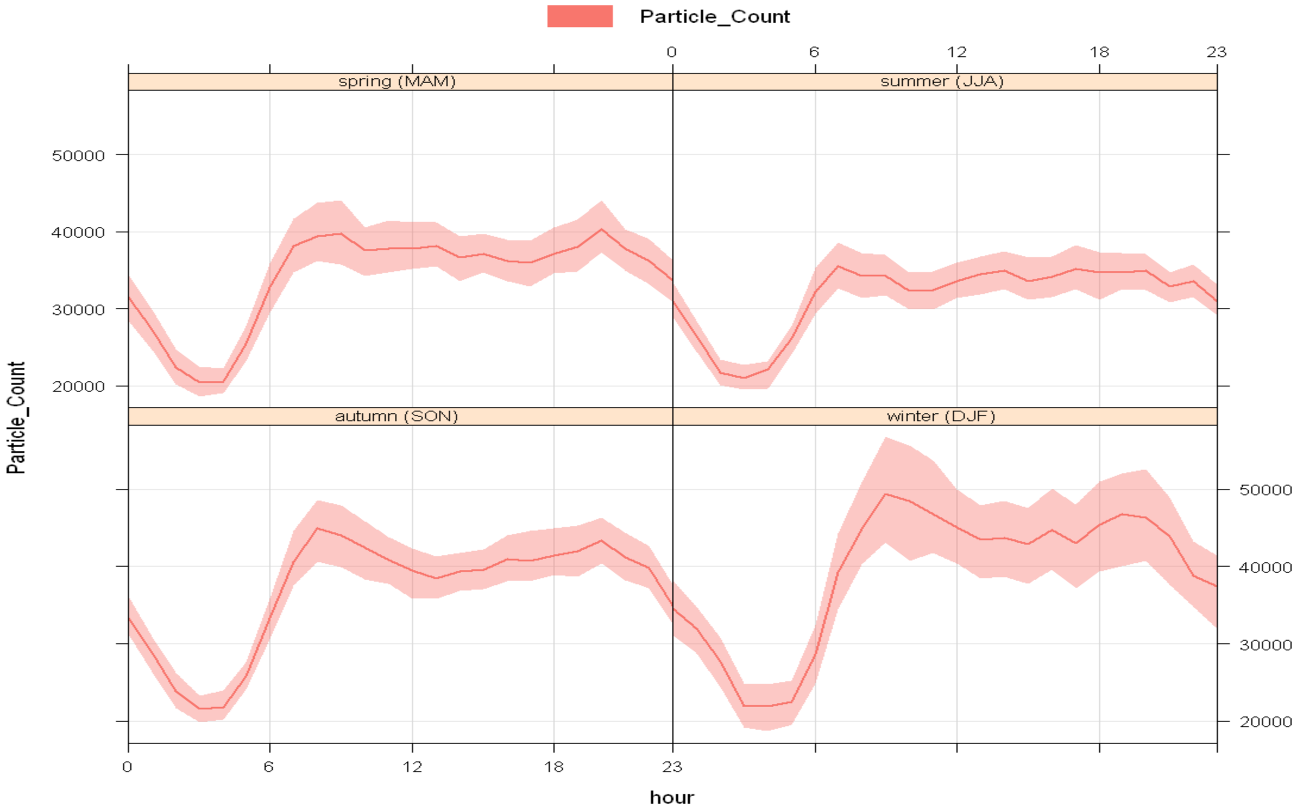


Figure 4-44 Seasonal weekly and diurnal trends for Marylebone Road CPC measurements

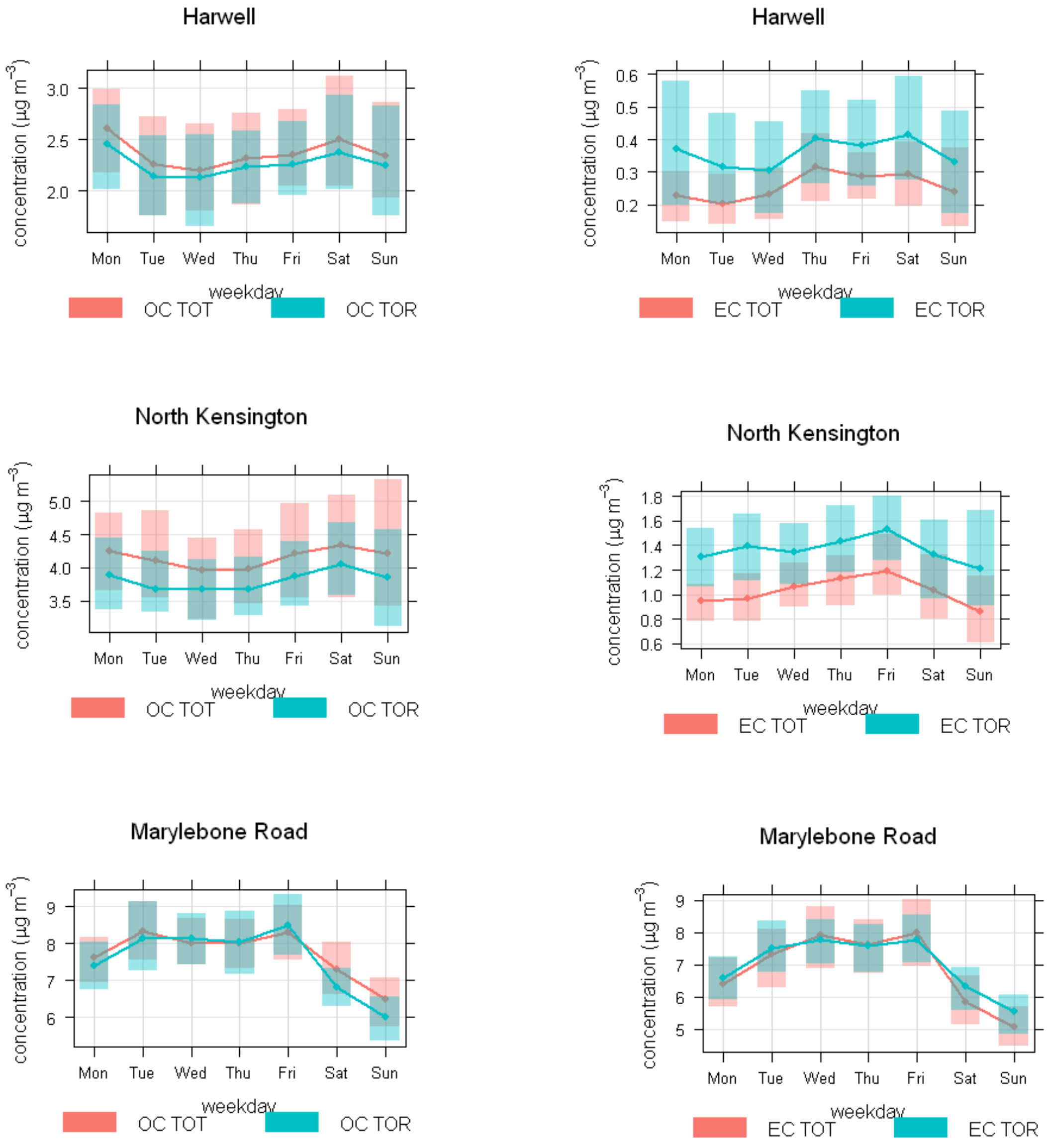


Figure 4-45 Weekly profiles for OC and EC at the Network sites in 2011

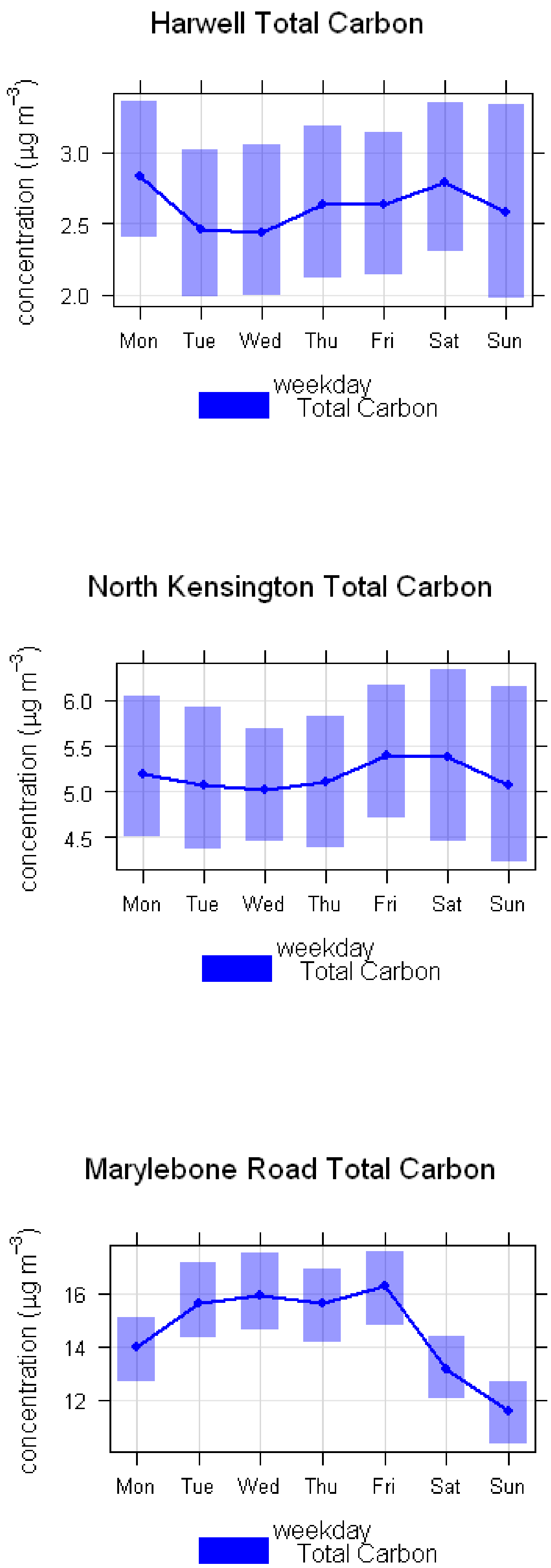


Figure 4-46 Weekly profiles for TC at the Network sites in 2011

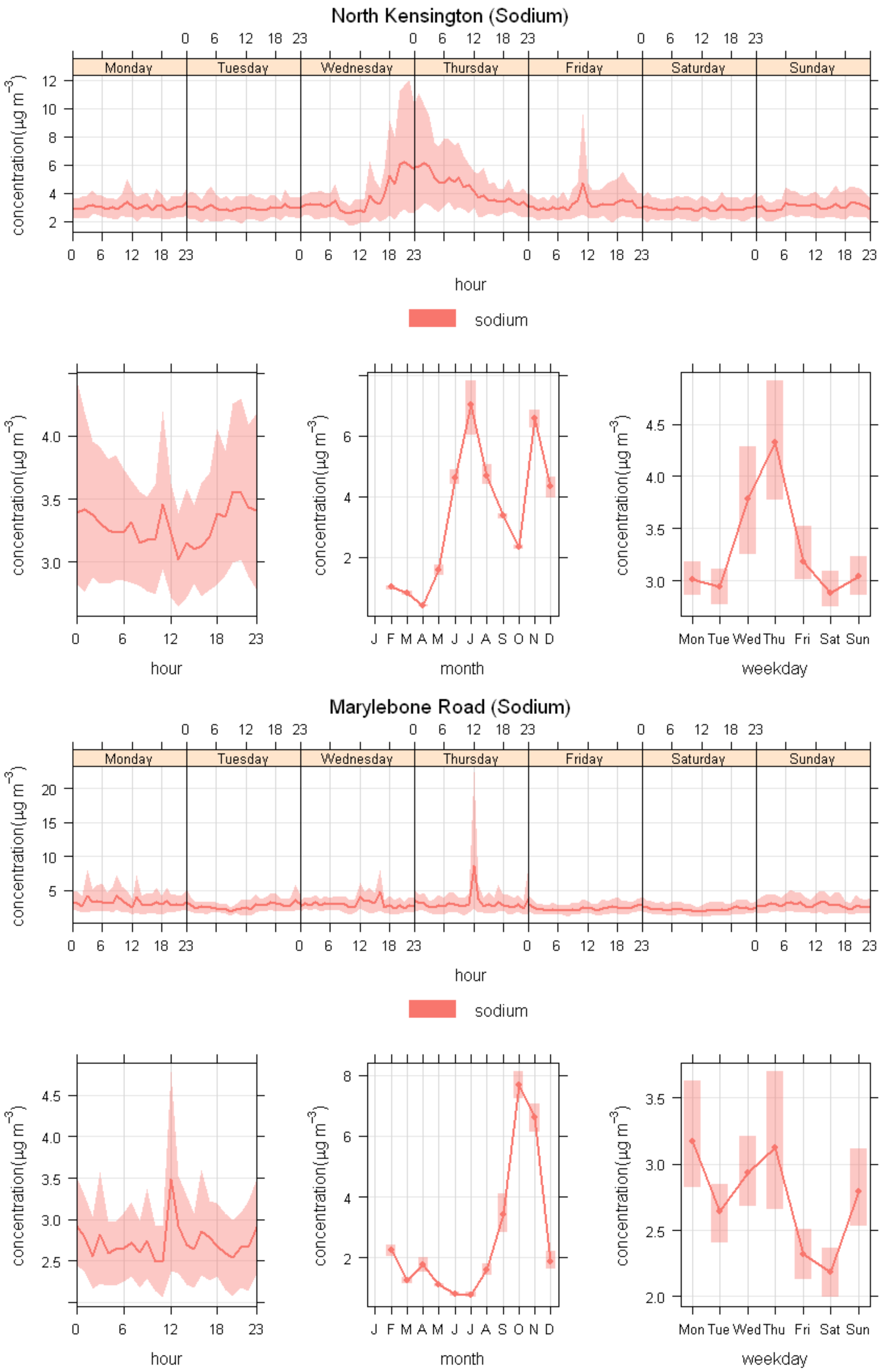


Figure 4-47 Sodium profiles at the London sites in 2011

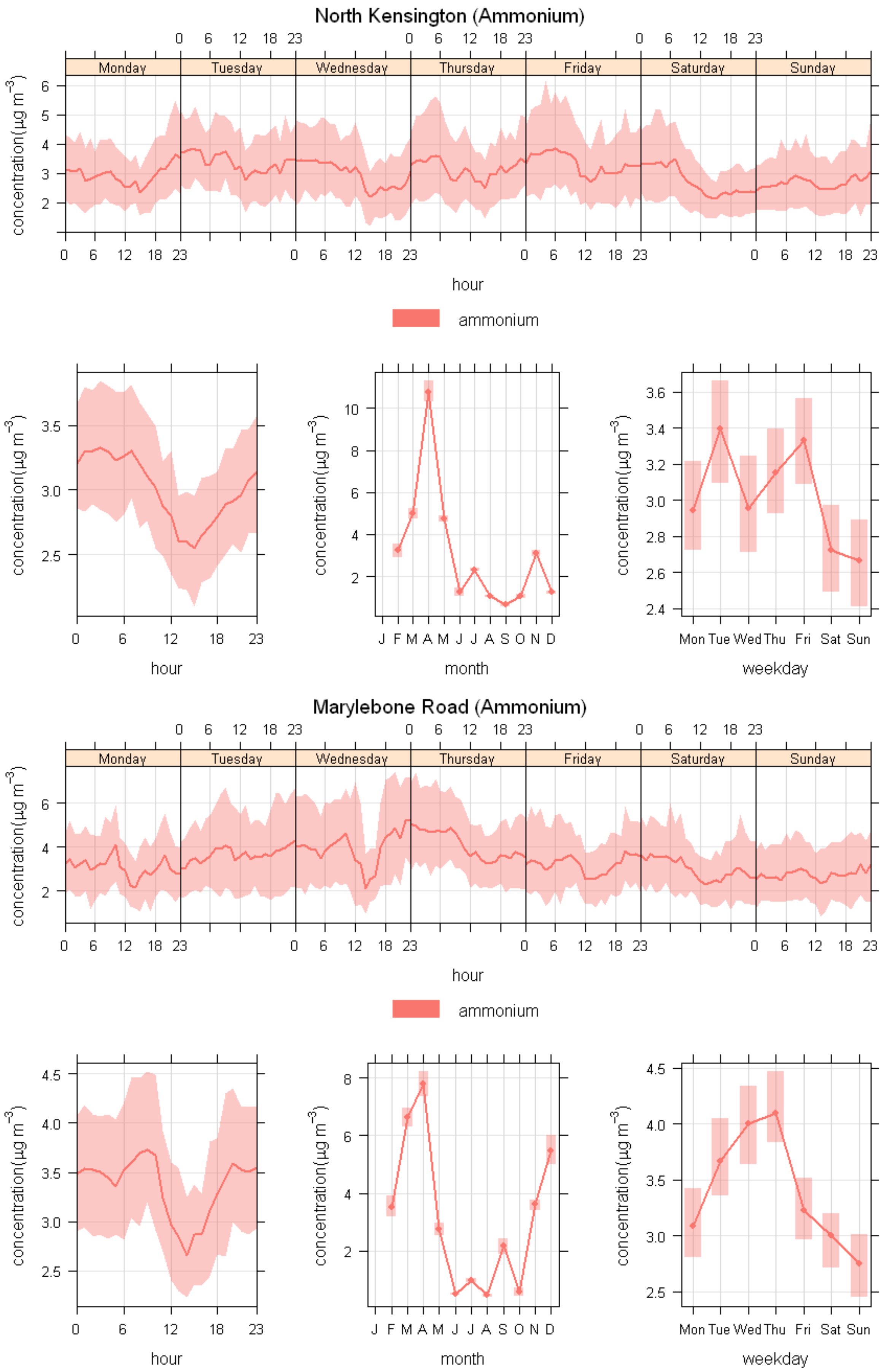


Figure 4-48 Ammonium profiles at the London sites in 2011

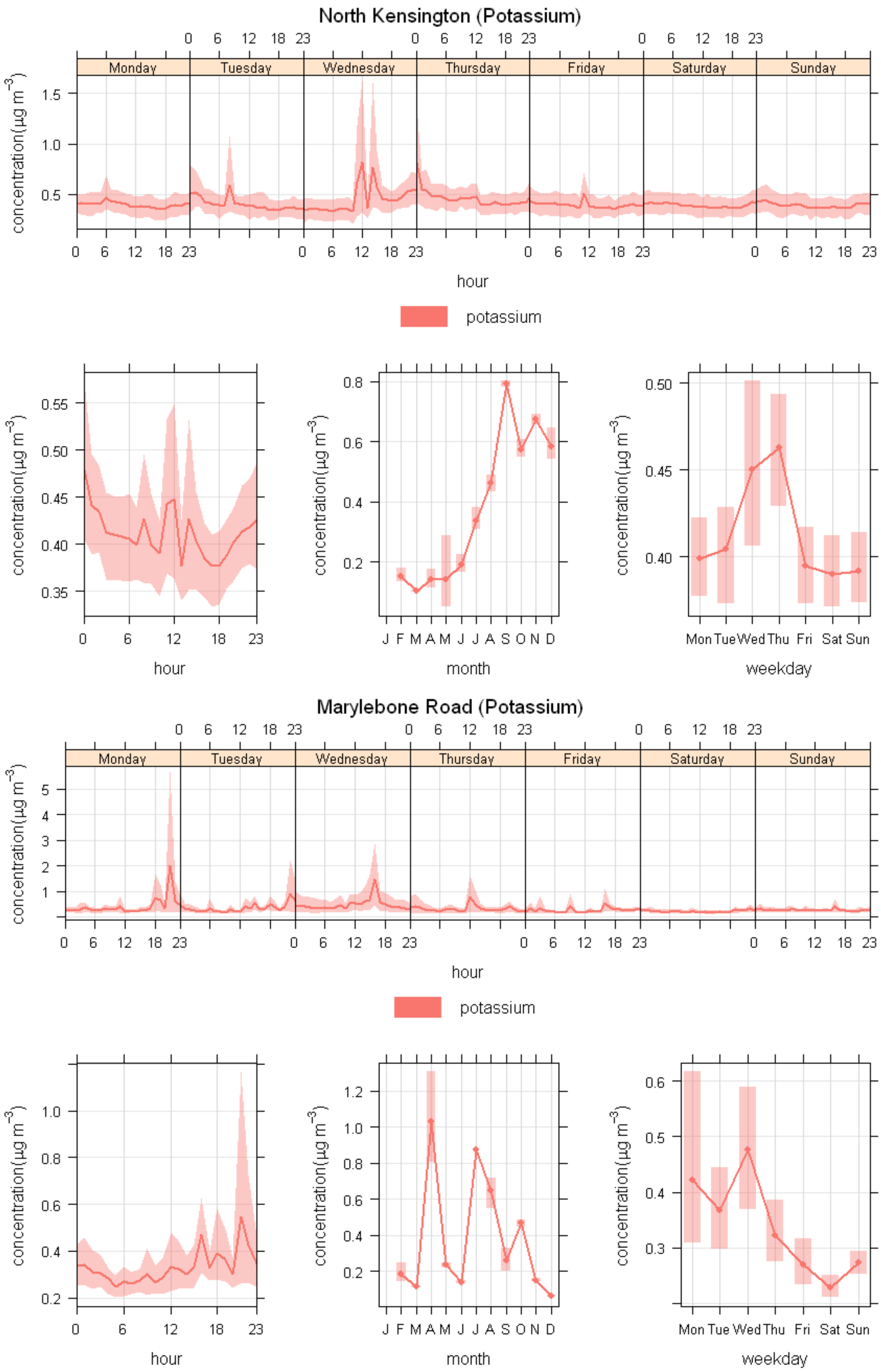


Figure 4-49 Potassium profiles at the London sites in 2011

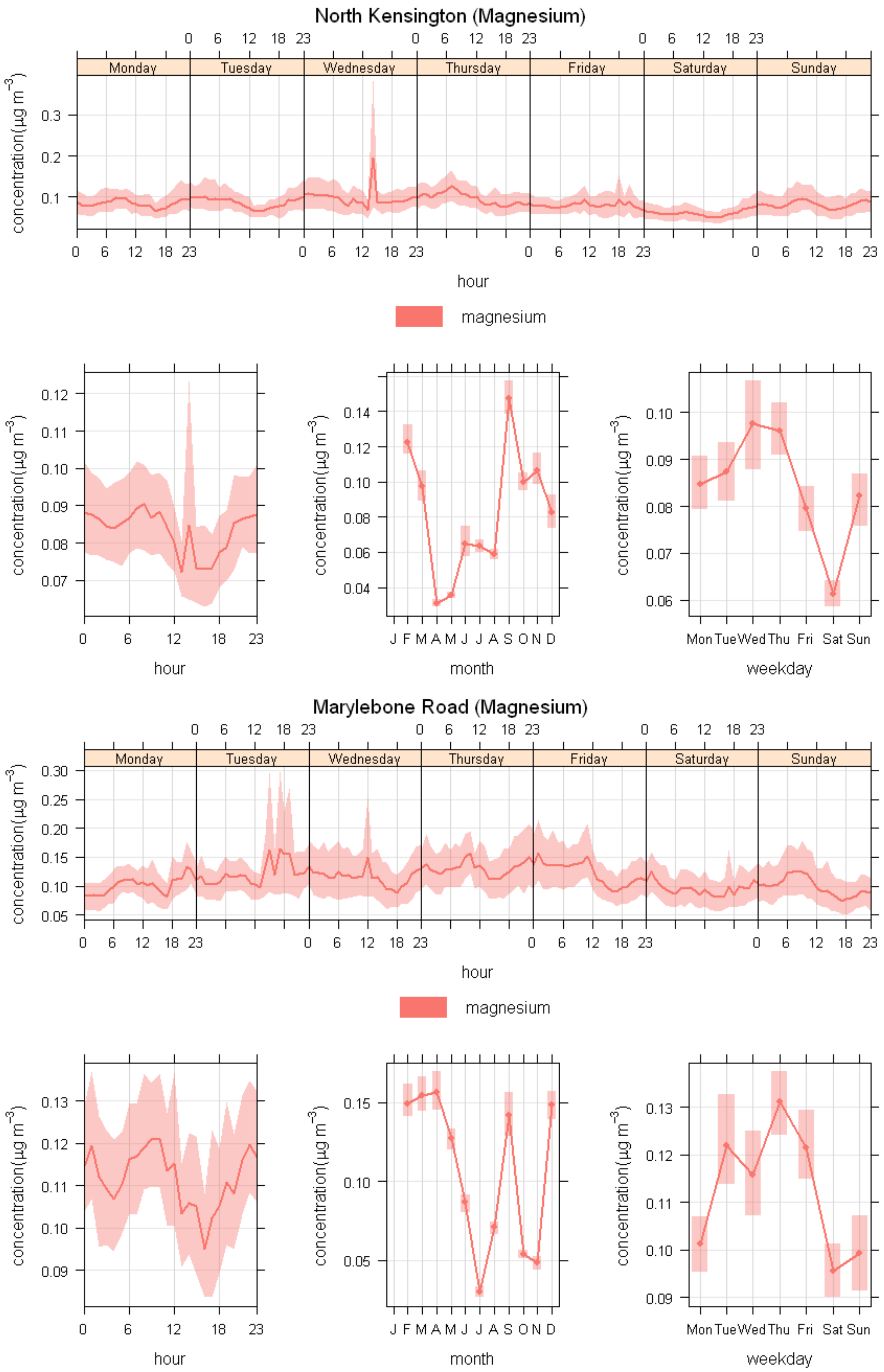


Figure 4-50 Magnesium profiles at the London sites in 2011

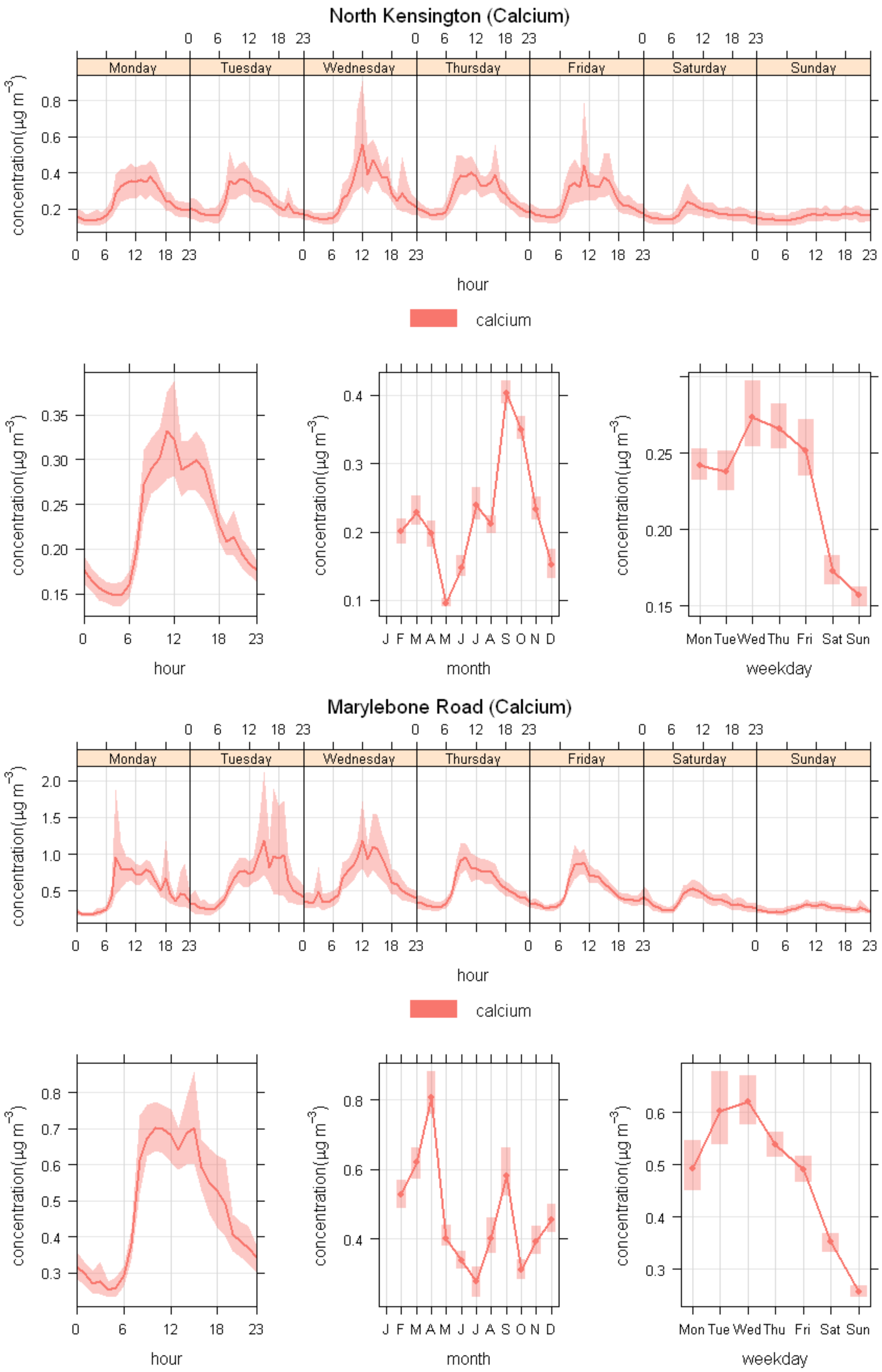


Figure 4-51 Calcium profiles at the London sites in 2011

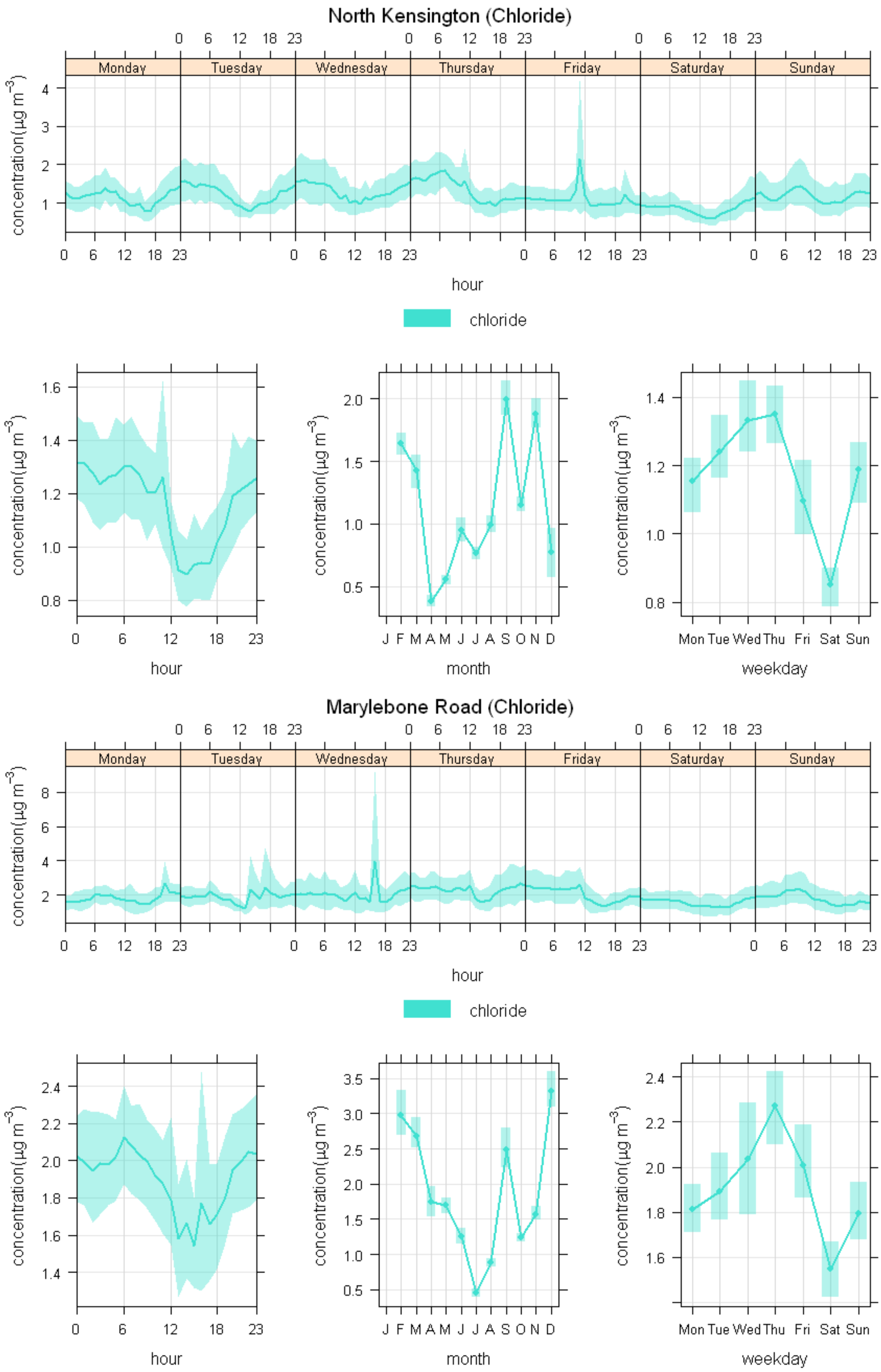


Figure 4-52 Chloride profiles at the London sites in 2011

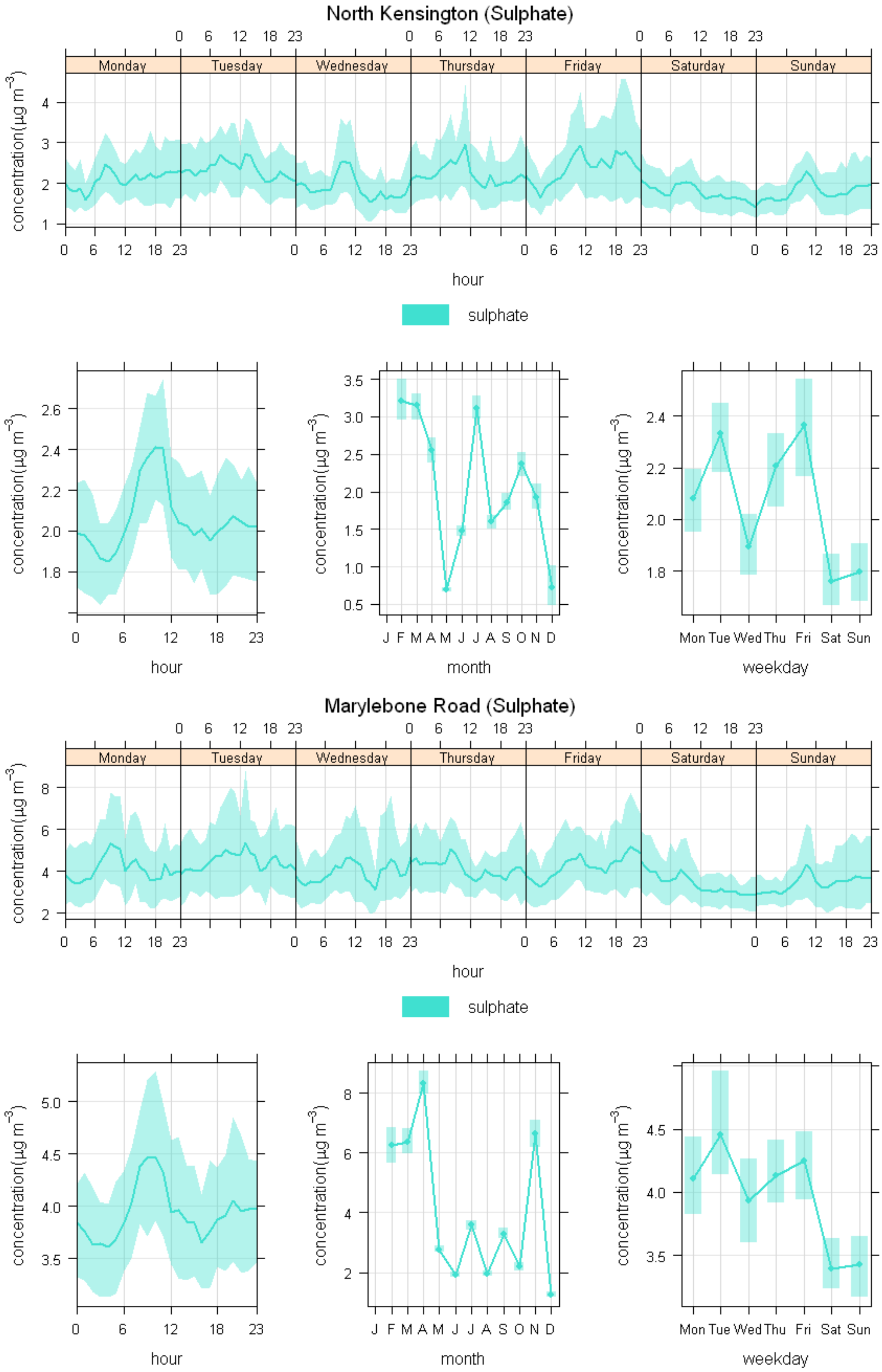


Figure 4-53 Sulphate profiles at the London sites in 2011

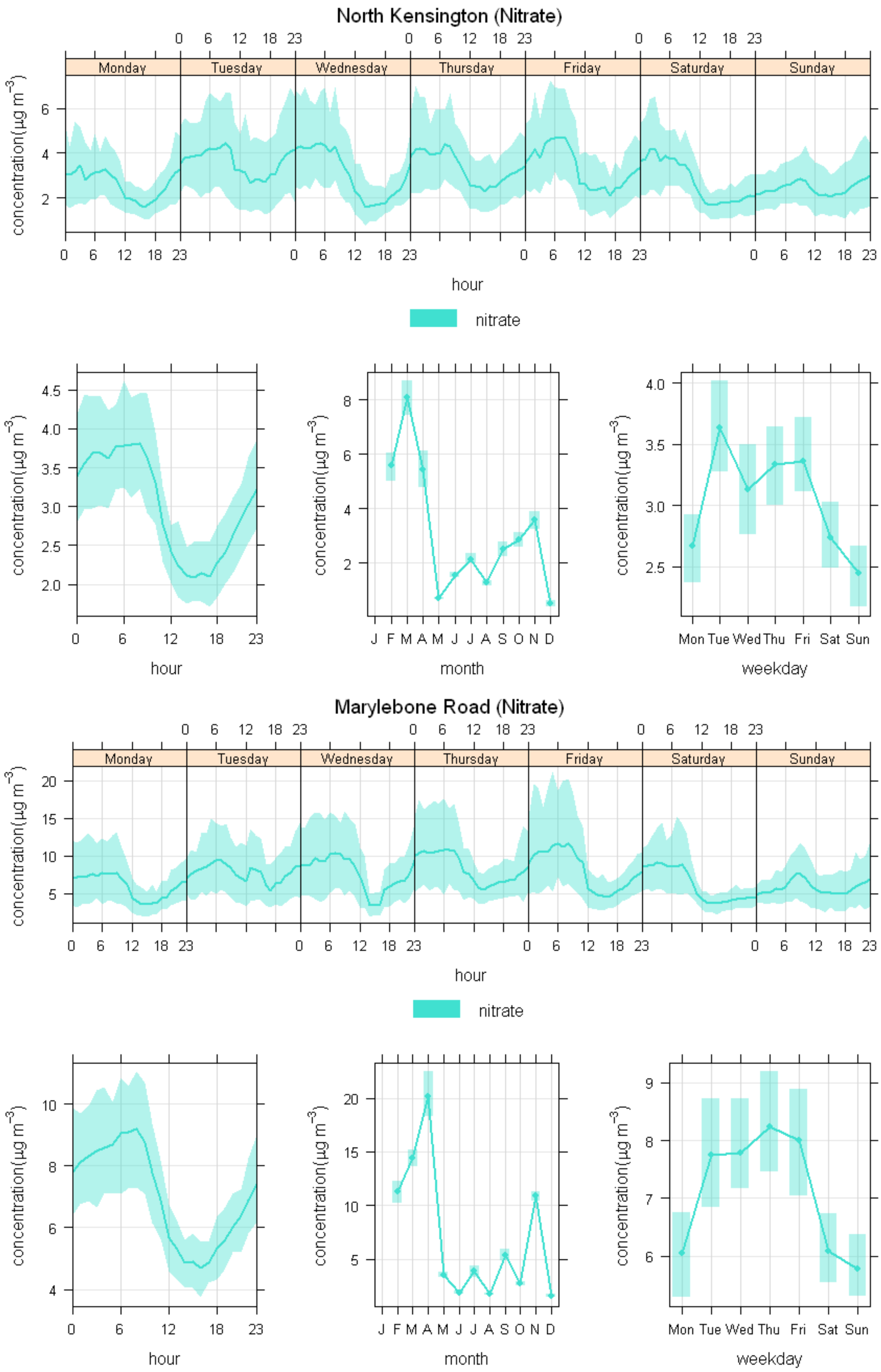


Figure 4-54 Nitrate profiles at the London sites in 2011

5 UNPDATE ON THE WIDER POLICY AND RESEARCH CONTEXT

The measurements made within this Network are one research programme amongst many in the UK and EU. 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 London specific measures

The characterisation 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 Defra's modelling. An understanding of the chemical composition is vital to understand the sources of PM and the impact of local, regional, national and international emissions abatement. It is especially important to assess the impact of the short-term measures applied as a requirement of the time extension notification.

London is also the subject of the largest Low Emission Zone in Europe, which began in February 2008 with emissions restrictions for heavy lorries. Further emissions restrictions for lighter lorries were bought in during July 2008 and larger vans, minibuses and other specialist diesel vehicles needed to meet the Euro 3 standard for particulate matter by January 2012.

Mayor's Air Quality Strategy focuses effort on three key corridors in central London, which are the locations of most of the pollution hot spots, one of these corridors includes the Marylebone Road. Many of the novel approaches to PM abatement, such as the application of dust suppressants currently underway, will require detailed validation using the chemical composition measurements made using this network at this site. The promotion of cleaner vehicles on these routes and across London will also require assessment using particle number concentrations.

5.1.2 Research Council Activities in London

ClearfLo is a large NERC-funded project involving 11 UK partners. The ambition is to provide integrated measurements of the meteorology, composition and particulate loading of London's urban atmosphere, made at street level and at elevated sites, complemented by modelling to improve predictive capability for air quality. Long-term measurements have begun, which will be complemented by more detailed Intensive Observation Periods (IOPs). The aims of the IOPs are (i) to measure the vertical structure of the urban boundary layer, (ii) to determine the oxidation potential of the urban atmosphere, (iii) to measure the properties and composition of particulates in the urban atmosphere. Both the long-term monitoring and the IOPs are centred on the London PM network site. In particular, the IOPs will be undertaken in the school adjacent to the North Kensington site. Both sites have also been augmented with additional monitoring equipment including number concentrations of the larger PM size fractions. However, much of the analysis will be based on the existing measurements made for the PM network and AURN.

Traffic is a four-year project for the MRC-HPA Centre for Environment and Health funded though the Living with Environmental Change (LWEC) partnership. It seeks to understand the patterns of exposure of the population to traffic pollution and their relationships to health through an improved understanding of the relative toxicity of air pollution from traffic sources using in vitro studies of oxidative potential, the development of an integrated dynamic model of exposure to traffic pollution and the quantification of the relationships between traffic pollution and a suite of health outcomes.

NCAS (National Centre for Atmospheric Science) research funded through the University of Birmingham has continued to be active in London; measurement campaigns were undertaken in June 2010 and in February/March 2011. Samples of particulate matter were collected at both London Marylebone Road and London North Kensington as bulk coarse and fine fractions but also size fractionated by cascade impactors.

5.1.3 Defra and other National Monitoring Activities

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

Any investigation of PM should ultimately be linked to the officially reported PM_{10} and $PM_{2.5}$ measurements from the AURN, which are based primarily on TEOM-FDMS instruments, with some gravimetric data using Partisol (1 m^3/hr) and reference (2.3 m^3/hr) samplers. The link is explicit for the anion and EC/OC parts of this Network. There is frequent communication on this topic between this Network and the key organisations in the AURN, for example through Equivalence trials, CEN committee membership, and AQUILA.

Black Carbon Measurements

There are currently 20 sites in the Black Carbon Network that measure optically using aethalometers at two wavelengths. The infrared wavelength metric is designed to approximate to Elemental Carbon. There are strong links to this Network through NPL's involvement in both, and Black Carbon data have been incorporated in this Report.

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.

5.2 UPDATE ON EUROPEAN ACTIVITIES

5.2.1 EU Air Quality Directive 2008/50/EC

The EU Air Quality Review Process, aimed at the revision of the Directive on Ambient Air Quality and Cleaner Air for Europe, is underway. Consultation is being sought through several channels, such as through the association of air quality reference laboratories AQUILA, through a group representing EU-funded research projects, and through stakeholder meetings. There is input from the operators of this network through AQUILA, and though EU projects such as AirMonTech.

5.2.2 CEN standards

2011 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, together with the gravimetric $PM_{2.5}$ standard EN 14907:2005, which will be combined in a revised EN 12341. The draft document is out for formal enquiry. Validation work is necessary, especially in the areas of filter selection and the handling of field blank values, and this is expected to start later in 2012. The proposed changes in the standard, for example limiting the relative humidity during filter conditioning to 45-50% rather than the present 45-55%, are expected to reduce variations rather than produce step changes to the data.

The working group has also drafted a CEN Technical Specification for automatic PM measurement, which incorporates type approval of PM instruments, equivalence testing against the reference methods, ongoing QA/QC, and ongoing determination of equivalence. This document has also gone for formal enquiry.

CEN TC 264 WG 32 covers particle number concentration and size distribution measurements (ie CPC and SMPS-type). It is producing 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. The current proposal is to standardise the cut-off at 7 nm, this being a compromise between the desire to include nucleation mode particles, but with the constraint that the monitoring of smaller sizes will be dominated by the sampling system rather than the instrument, making standardisation impractical. The particle material to be used to determine this cut-off size (which is material-dependent) is still being discussed. Another relevant proposal is to exclude photometric mode CPC measurements from the reference method. In the case of this Network, this can be addressed by changing to instruments with a larger counting mode range, incorporating a dilution system, or relying on calibration of the photometric mode, as at present. Calibration of CPCs is being delegated to the ISO TC 24 group, as described below.

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. This document will be addressed after the first one and has not been started yet.

CEN TC 264 WG 34 covers anions and cations, while CEN TC 264 WG 35 covers Elemental Carbon and Organic Carbon, both for laboratory analysis of samples collected on filters. In both cases Technical Reports have been written to provide guidance on methods for Member States, (CEN/TR 16269:2011 and CEN/TR 16243:2011 respectively) with CEN standards only being produced when validation work has been carried out. In both cases the guidance is in line with current practice on this Network.

One significant issue to be explored during validation work is whether there are practical limits to the concentrations for EC (and OC) – in $\mu g.cm^{-2}$ on the filter - that the methods can be used for. While values of EC+OC (known as TC, total carbon) are expected to be reliable, the split into EC and OC, based on changes in the optical properties of the sample, may become less reliable for very dark samples. Most research (such as within EUSAAR, below) has looked at rural background samples rather than roadside samples like those from Marylebone Road.

5.2.3 EUSAAR

The EUSAAR project (European Super-sites for Atmospheric Aerosol Research) included 20 sites across Europe including Harwell. Amongst other topics it made recommendations for standardizing measurements with CPCs and SMPSs, and of EC/OC. For example, it recommended that SMPS instruments should standardise the aerosol size distribution by sampling under dry conditions (<40% RH). Changes to sampling systems in the Network to conform with these have been implemented.

To a large extent the EUSAAR proposals are now being dealt with within CEN WGs 32 (which includes Alfred Wiedensohler) and 35 (which includes Jean-Philippe Putaud).

The EUSAAR project ended on 31 March 2011, and many elements of it continue in the EU FP7 project ACTRIS.

5.2.4 ISO standards

The most relevant standards are being developed by ISO TC24 SC4 WG12.

ISO 15900 *Determination of Particle Size Distribution – Differential Electrical Mobility Analysis for Aerosol Particles* was published in 2009. It is a very useful description of the principles of SMPS operation (for all purposes), but does not include requirements for calibrating the number concentration part of the measurement – i.e. CPCs, and other field operation requirements, which will be addressed by the CEN WG 32.

ISO Preliminary Work Item 27891, *Aerosol particle number concentration – calibration of condensation particle counters* is at an advanced draft stage. It will be aimed at users (especially those with internal calibration programmes), instrument manufacturers who certify their equipment, and specialist calibration laboratories (including National Metrology Institutes (NMIs)). It should provide a general procedure suitable for users in the areas of vehicle emissions and workplace as well as ambient air. Traceability is ultimately expected to be to the NMI structure. This will be a very useful underpinning standard for the CEN WG 32 work.

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

6 TOPIC REPORTS AND PUBLICATIONS

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

6.1 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.

May 2008-April 2009

CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2), Annual Report 2008.

The Merging of Atmospheric Particle Size Distribution Data Measured using Electrical Mobility and Time-of-Flight Analysers, David C. S. Beddows and Roy M. Harrison

Review and Interpretation of Black Carbon Data Measured by Magee Aethalometers, Alan M. Jones And Roy M. Harrison

The Temporal Trends in Particulate Sulphate and Nitrate Concentrations at UK Sites, Alan M. Jones And Roy M. Harrison

Quantifying the London Specific Component of PM10 Oxidative Activity,
Ian S Mudway, Gary Fuller, David Green, Chrissi Dunster and Frank J Kelly

May 2009 - December 2010

CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2), Annual Report 2009.

Review and interpretation of particulate carbon data from Marylebone Road and North Kensington in the period 2006 – 2009 Alan M. Jones and Roy M. Harrison

Long and short-term temporal trends in airborne particle number concentration in the UK Alan M. Jones and Roy M. Harrison

December 2010 – May 2011

CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 2), Annual Report 2010.

Investigation into the large reduction in ambient particle number concentrations in late 2007 Alan M. Jones and Roy M. Harrison

The effect of varying the emissions of NO_x*,* SO_2 *and* NH_3 *on the concentrations of inorganic aerosols predicted by the Photochemical Trajectory Model* Alan M. Jones and Roy M. Harrison

6.2 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* ($PM_{2.5\text{-}10}$) *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).

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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 $\mu g\ m^{-3}$) at a heavily trafficked London site? A. Charron, R.M. Harrison and P.G. Quincey, Atmospheric Environment, **41**, 1960-1975 (2007).

Factors Influencing New Particle Formation at the Rural Site, Harwell, United Kingdom, A.Charron, W. Birmili and R.M. Harrison, J. Geophys. Res., **112**, (2007). D14210, doi:10.1029/2007JD008425.

Fingerprinting Particle Origins According to their Size Distribution at a UK Rural Site, A. Charron, W. Birmili and R.M. Harrison, J. Geophys. Res., **113**, D07202 (2008). doi:10.1029/2007/JD008562

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, Atmos. Environ., **42**, 4467-4479 (2008).

Comparison of Average Particle Number Emission Factors for Heavy and Light Duty Vehicles Derived From Rolling Chassis Dynamometer and Field Studies, D.C.S. Beddows and R.M. Harrison, Atmos. Environ., **42**, 7954-7966 (2008).

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, G Hayman Atmospheric Environment **43** (2009) 689-696.

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A large reduction in airborne particle number concentrations at the time of the introduction of "sulphur free" diesel and the London Low Emission Zone, A.M. Jones, R.M. Harrison, B. Barratt and G. Fuller, Atmospheric Environment **50**, 129 – 138 (2012)

6.3 MAIN FINDINGS OF TOPIC REPORTS IN 2011

6.3.1 Further analysis of the large reduction in particle number concentrations in late 2007

The cumulative sum of the difference technique identified a rapid reduction in particle number concentrations (Figure 6-1) at two sites in London and one in Birmingham over a period of a few months in late 2007 with particle number concentrations reduced by between 30% and 59%. This change occurred at the same time as the introduction of "sulphur free" diesel fuel and in the run up to the enforcement of the London LEZ for heavy goods vehicles. In the light of the reduction in Birmingham, and the limited change in vehicle technologies at the time, the change is probably primarily due to the change in fuel sulphur. Hourly values of particle number and NOx concentration at Marylebone Road were sorted by wind direction and the means are plotted against each other in Figure 6-2 for two periods before and after the major change in particle number concentrations. The identification of this major reduction in particle number concentrations, in the absence of any similar reduction in the concentrations of the regulated air quality mass metrics, provides an opportunity to evaluate the long discussed effects (Seaton et al., 1995; Knol et al., 2009) of ultrafine particle concentrations on human health while excluding the possible confounding effects of other air quality metrics.

Paper: Jones A M, Harrison R M, Barratt B and Fuller G (2012). A large reduction in airborne particle number concentrations at the time of the introduction of "sulphur free" diesel and the London Low Emission Zone. Atmospheric Environment **50** 129-138

Topic Report: Investigation into the large reduction in ambient particle number concentrations in late 2007

References: **Knol, A.B.**, de Harthog, J.J., Boogaard, H., Slottje, P., van der Sluijs, J.P., Lebret, E., Cassee, F.R., Wardekker, J.A., Ayres, J.P., Borm, P.J., Brunekreef, B., Donaldson, K., Forastiere, F., Holgate, S.T., Kreyling, W.G., Nemery, B., Pekkanen, J., Stone, V., Wichmann, H.-E., Hoek, G., 2009. Expert elicitation on ultrafine particles: likelihood of health effects and causal pathways. Particle and Fibre Toxicology **6**, 19.

Seaton, A., MacNee, W., Donaldson, K., Godden, D., (1995). Particulate air pollution and acute health effects. The Lancet **345**, 176-178.

6.3.2 Further analysis of chloride concentrations

The previous analysis of chloride data was extended to include data from the APCNN site at Belfast Centre and the relationship between chloride concentration and wind speed examined. The use of chloride concentration data from various campaigns at a number of Midlands sites allowed chloride concentrations in both the $PM_{2.5}$ and $PM_{2.5-10}$ size fractions to be compared with the concentrations of sodium and potassium (Figure 6-3) and with wind speed (Figure 6-4). The relatively higher concentrations of chloride at low wind speed in the $PM_{2.5}$ fraction are indicative of a non-maritime source for part of the lower size fraction of chloride.

Topic Report: Chloride concentrations at various UK sites

6.3.3 Use of the Photochemical Trajectory Model to examine effects of changes in emissions of SO_2, NO_x and NH_3.

The Photochemical Trajectory Model (PTM) was used to examine the effect on concentrations of ammonium, nitrate, sulphate and chloride (and coincidentally nitric acid and hydrochloric acid vapours) and the sum of the four particulate components (which for the purpose of the report was described as secondary inorganic aerosol) of reductions in the emissions of sulphur dioxide (SO_2), oxides of nitrogen (NOx) and ammonia (NH_3) from sources in the UK, from sources in the rest of the EU, and from both areas combined. SO_2 was varied between 100% and 50%, NOx was varied between 100% and 40%, while NH_3 was varied between 120% and 70% of 2007 emissions. Figure 6-5 shows an example of the effect of abatement policies applied uniformly across the UK and the remainder of Europe. In the three-dimensional plots, one pollutant has been held constant (ammonia emissions have been held constant at 100% of their 2007 value) and plots then show the concentrations of the species indicated resulting from levels of sulphur dioxide emission between 50% and 100% and NO_x emission between 40% and 100% of those in 2007. it may be seen that nitrate concentrations as expected fall with the abatement of NO_x emissions, but that that fall is reduced by the abatement of sulphur dioxide. This confirms that the model is reflecting the atmospheric chemistry well. The reason for this effect is that the abatement of sulphur dioxide reduces the formation of sulphate (as seen in the graph for sulphate), which in turn reduces the irreversible uptake of ammonia into ammonium sulphate. This in turn implies that more ammonia remains in unneutralised form in the atmosphere which then contributes to additional formation of nitrate by reaction with nitric acid. Abatement of sulphur dioxide and NO_x appears to contribute monotonically to a reduction in ammonium in the aerosol, but also leads to modestly increasing concentrations of chloride in the particles. This is a consequence of diminished scavenging of ammonia by sulphuric acid which is then free to react with hydrogen chloride, leading to a reduction in this species, and an increase in chloride.

These results demonstrate that the enhanced PTM is an effective way of investigating complex emission reduction scenarios. The results give a clear view of pollutant interactions and show reductions in some cases, and in others increases in concentrations that are qualitatively the same as Derwent et al. (2009) and quantitatively relatively similar.

Topic Report: The effect of varying the emissions of NO_x, SO_2 and NH_3 on the concentrations of inorganic aerosols predicted by the Photochemical Trajectory Model

Reference: **Derwent, R.**, Witham, C., Redington, A., Jenkin, M., Stedman, J., Yardley, R. and Hayman, G., 2009. Particulate matter at a rural location in southern England during 2006: Model sensitivities to precursor emissions, Atmos. Environ., 43, 689-696.

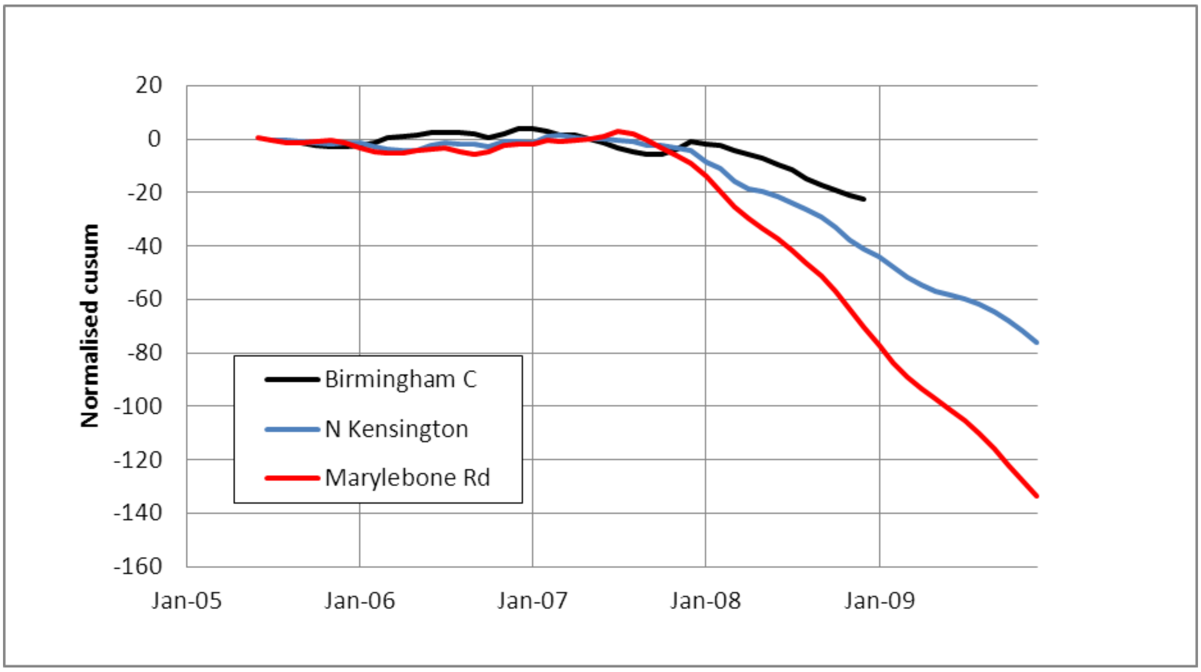


Figure 6-1 Normalised monthly cumulative sums of particle number concentration difference

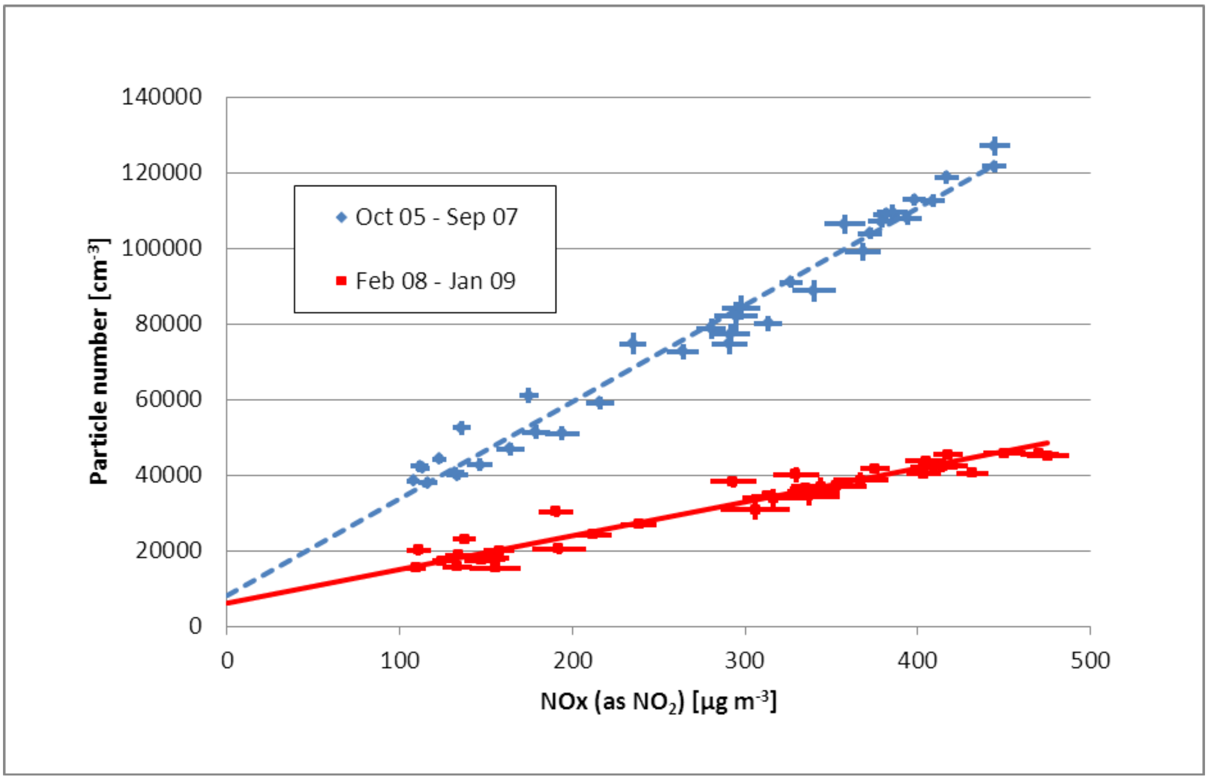
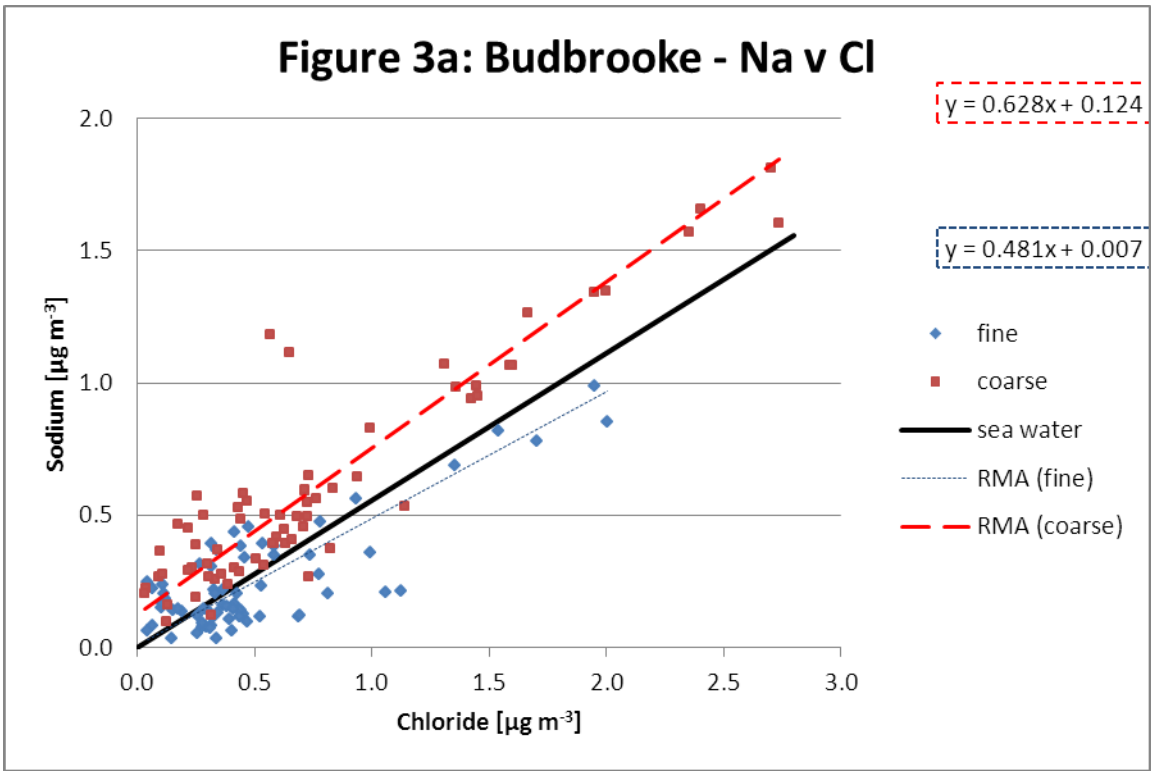


Figure 6-2 Particle number v NOx at Marylebone Road (Data sorted by 10^0 wind direction)



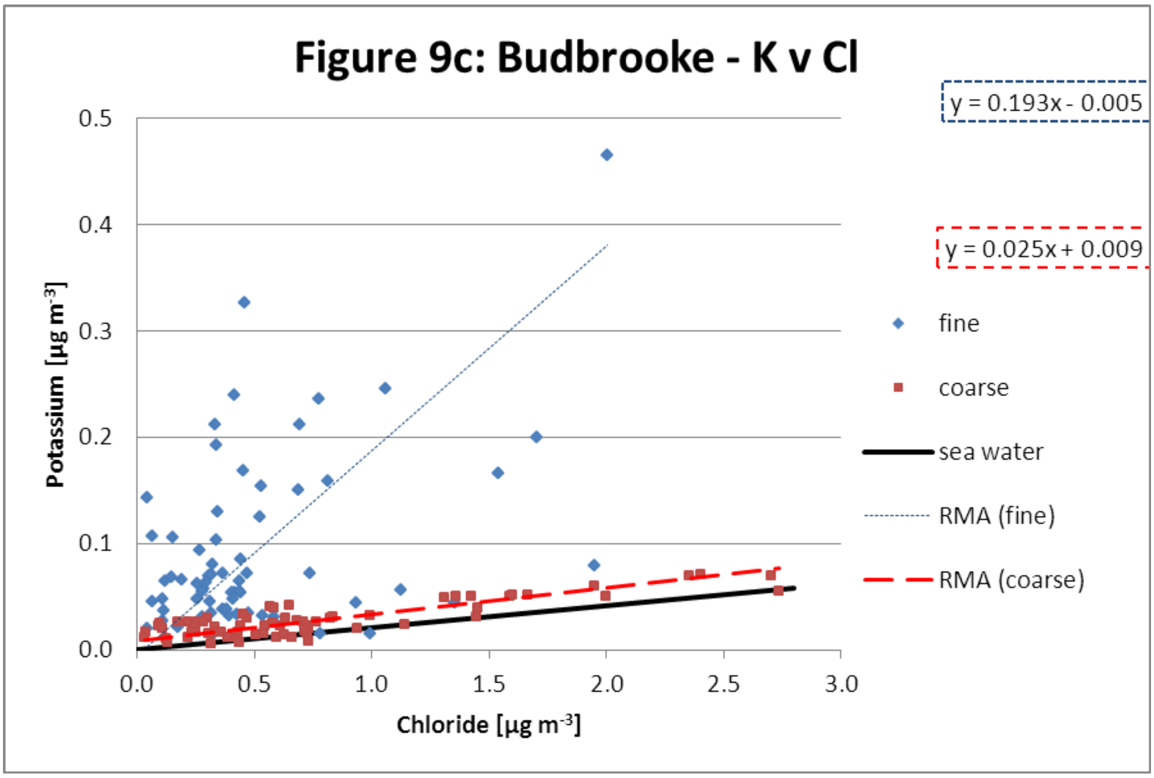


Figure 6-3: Sodium and potassium v chloride concentrations at Budbrooke, a Midlands rural Site ($PM_{2.5}$ and $PM_{2.5\text{-}10}$ size fractions).

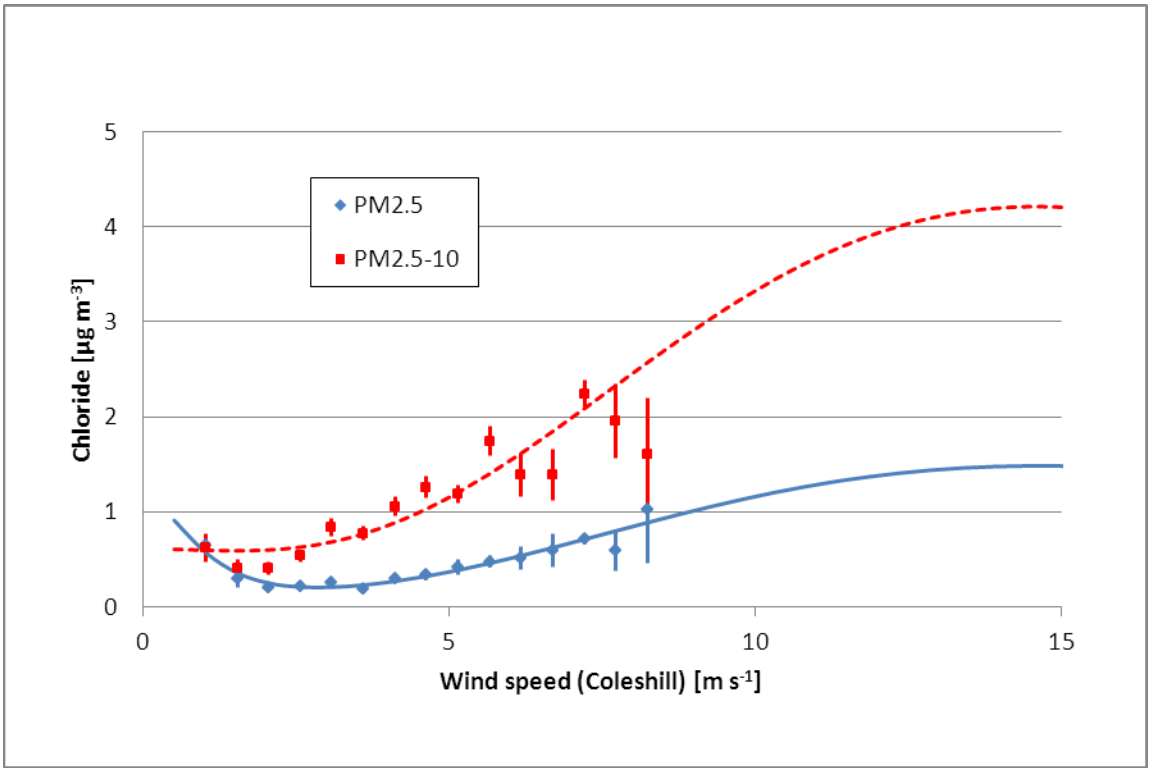


Figure 6-4: Midland sites - fine and coarse chloride

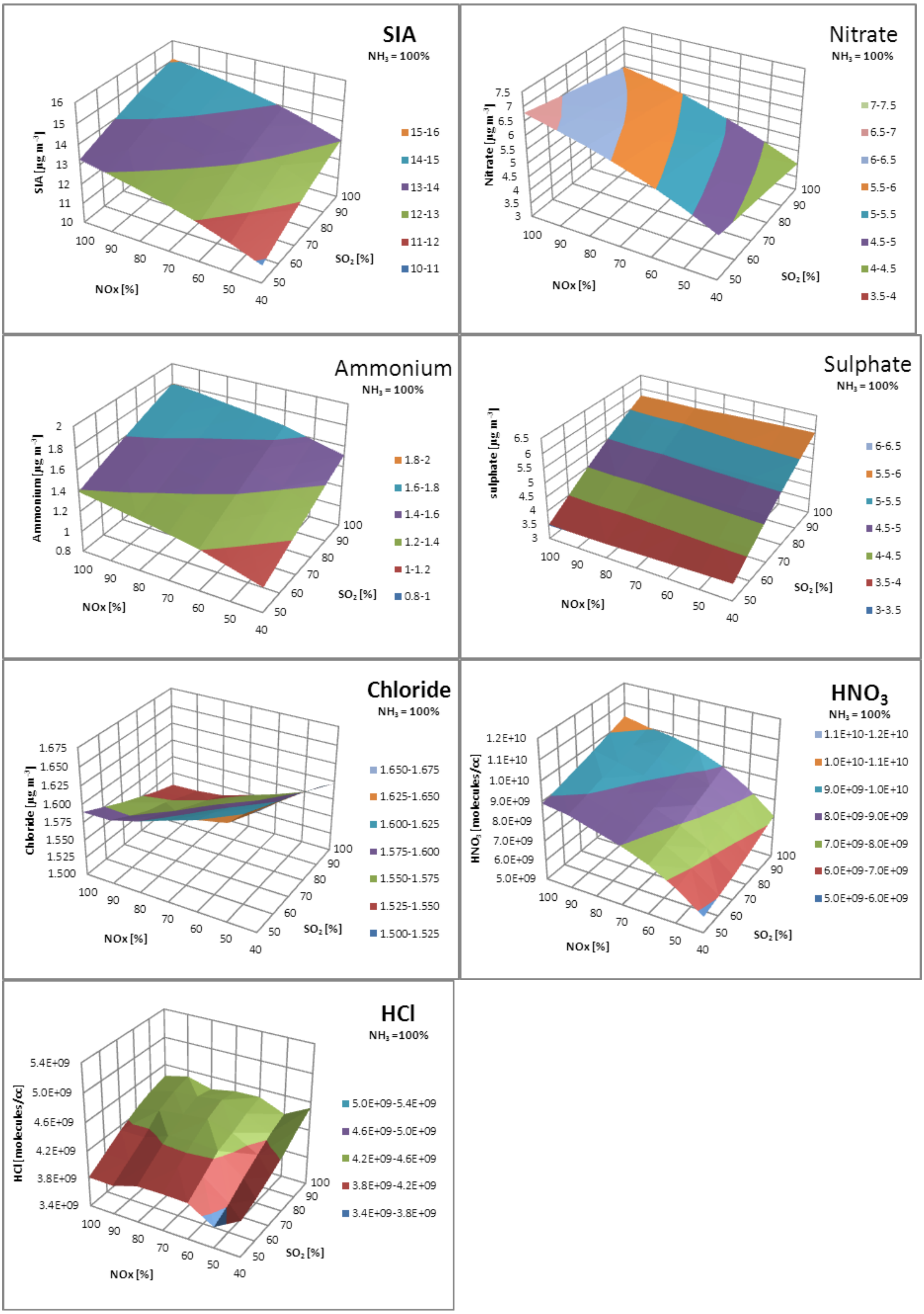


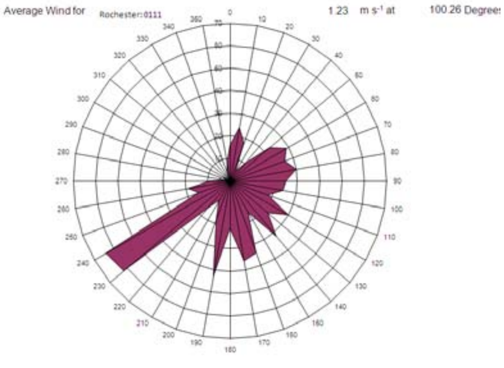
Figure 6-5: Effect of emission reductions in UK and Europe, NH_3 = 100%

7 ACKNOWLEDGEMENTS

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

Annex 1. Wind roses at Rochester

January 2011



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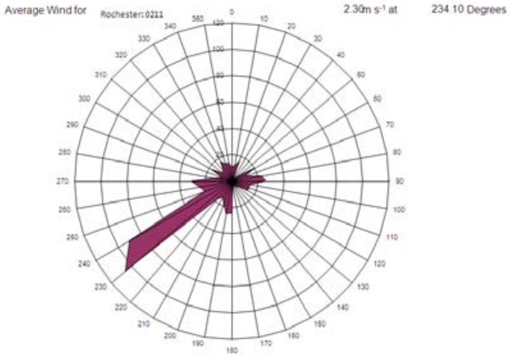

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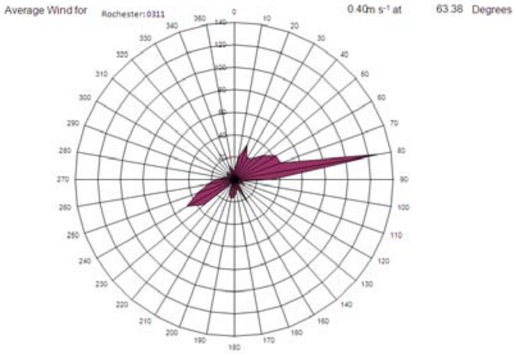

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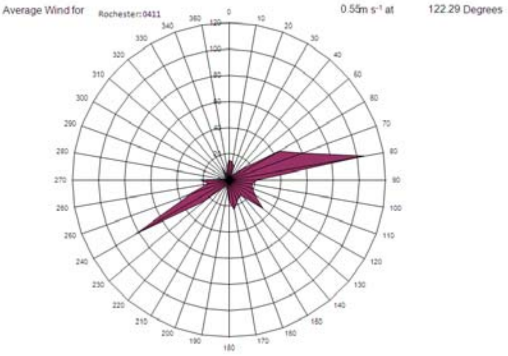

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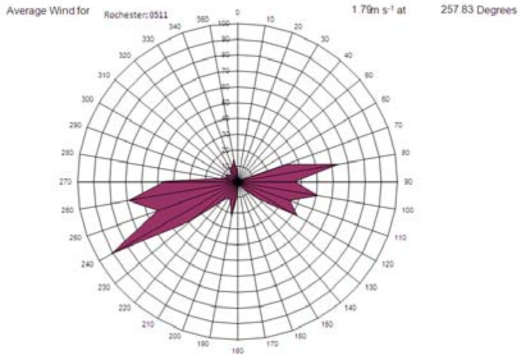

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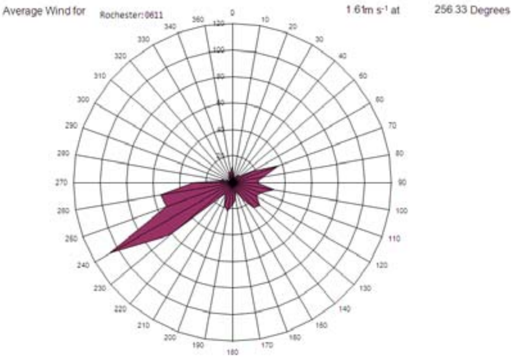

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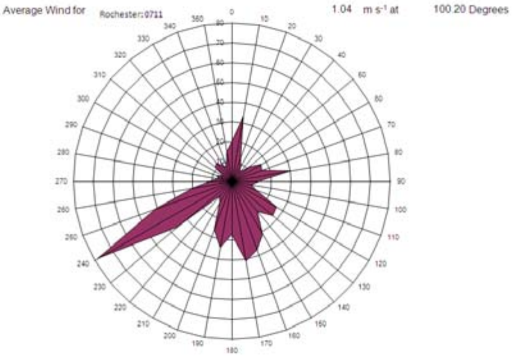

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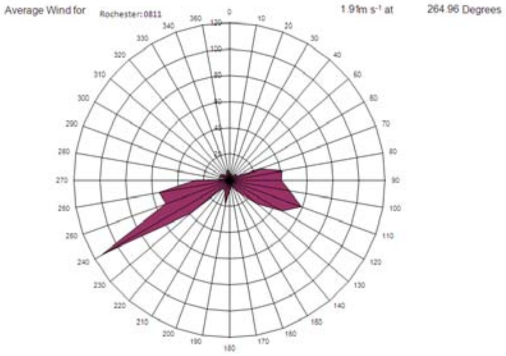

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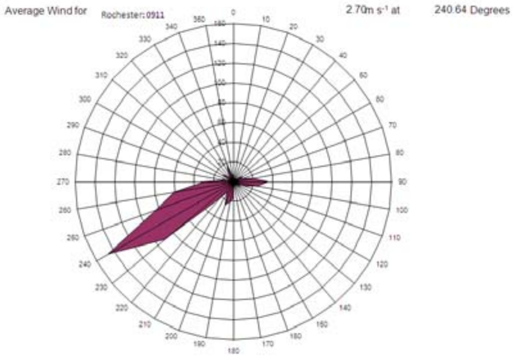

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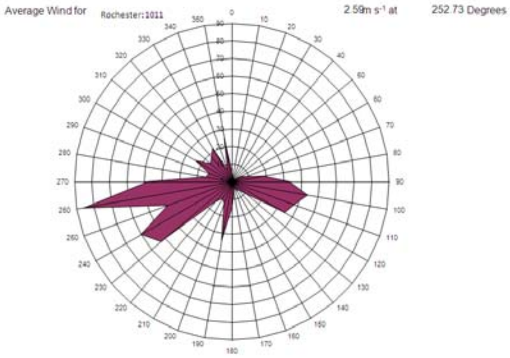

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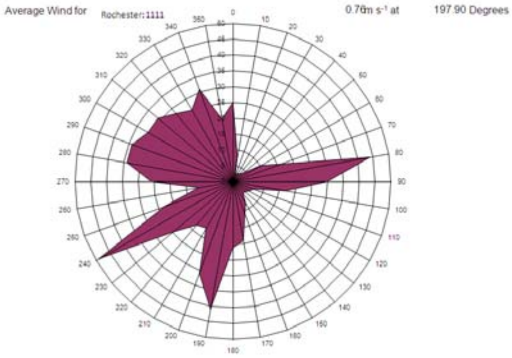

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