Airborne Particulate Concentrations and Numbers in the United Kingdom (phase 3)
Annual report 2012

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EXECUTIVE SUMMARY

This report was prepared by NPL as part of the UK Airborne Particulate Concentrations and Numbers contract (AQ0604) 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 2012 and contains:

- A summary of network operation and quality procedures.
- Description of the instruments used in the Network
- A graphical presentation of all ratified network data from 2012.
- Data capture per instrument per month.
- Comparison of 2012 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.
- Summary of the main findings of the topic reports published in 2012.

The Network operated five monitoring sites for pollution measurements and one meteorological monitoring site (Rochester).

Daily measurements were performed for analysing Organic Carbon (OC) and Elemental Carbon (EC) content in the PM_{10} fraction at Harwell (rural site), London North Kensington (urban background site) and London Marylebone Road (roadside site). To comply with the European directive 2008/50/EC, weekly filters were also sampled for analysing OC/EC in the $PM_{2.5}$ fraction at two rural sites, Harwell and Auchencorth Moss.

Hourly PM_{10} ion measurements were also made at the two London sites providing concentrations of chloride, nitrate, sulphate, sodium, ammonium, potassium, magnesium and calcium in ambient air.

A provisional analysis was carried out to understand the composition of the PM, especially during pollution episodes. About 10 PM pollution episodes occurred in 2012 in South-East England, mainly in winter and spring time. Secondary components of the PM_{10}, such as nitrate, contribute up to 82% (North Kensington) and 72% (Marylebone Road) to the PM composition during episodes. However, all components increased during episode conditions and local sources still contribute, being 10-15% of the PM_{10} mass at North Kensington and 24% of the PM_{10} mass at Marylebone Road.

Total number concentrations (CPC) were measured at Harwell, Birmingham Tyburn (urban background site), North Kensington and Marylebone Road. The 2012 data was comparable with data from recent years. The concentrations at the London sites stabilised after a dramatic drop at the end of 2007, attributed to decreased sulphur content in fuel and the introduction of the LEZ (Low Emission Zones). The concentrations at Harwell were mainly influenced by meteorological conditions and long-range transport, while concentrations in urban sites were influenced by local activities, i.e. traffic and domestic heating.

Number size distributions (SMPS) were measured at Harwell, North Kensington and Marylebone Road. Nucleation events were observed at Harwell during warm months confirming previous work. These events are due to clean cool arctic and polar maritime air masses coming into the UK. At the urban sites, ultrafine particles concentrations were found to be correlated to anthropogenic activities.

A series of experiments were carried out at NPL to check the performance of the three Network SMPS instruments. The Intercomparison showed that the instruments can reliably measure size distributions over the relevant size range. Some small variations were found in the region below 40 nm but this

should not influence the total number concentrations or the characteristics of the distributions reported by the Network.

Two topic reports were published as part of this contract in 2012, one on black carbon and UV measurements (mainly from the Black Carbon network), and one on the hourly anion and cation measurements.

CONTENTS

1   INTRODUCTION

The UK Airborne Particulate Concentrations and Numbers Network (AQ0604) operates five air pollution monitoring sites and one meteorological monitoring site. The sites are arranged so as to maximise the benefit of the measurements made, in terms of drawing conclusions about the concentrations and chemical composition of particles in ambient air at these locations, and understanding more fully the sources.

The Network provides data on airborne particles by using instruments that measure number concentrations, number size distributions, Black Carbon, Organic and Elemental Carbon concentrations and anion and cation concentrations.

This report shows a summary of the 2012 data collected within this Network, along with main findings, a comparison with previous years, and a comparison with measurements carried out in other Networks.

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. Two topic reports were published in 2012 and a description of their main findings is given in Section 6.

2   NETWORK OPERATION

2.1   OVERVIEW

The operation of the Network in 2012 was structured in the same way as previous year. 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, and 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 2012 is shown in Table 2-1. Wind speed and direction are reported for the Rochester site.

Site locations are shown in Figure 2-1 and site details are available through http://uk-air.defra.gov.uk/networks/find-sites.

In accordance with the European Directive 2008/50/EC, $PM_{2.5}$ composition measurements were taken at rural sites (Harwell and Auchencorth Moss) to provide information on $PM_{2.5}$ background levels. The Leckel Sequential Samplers (model SEQ47/50) were installed at Harwell and Auchencorth Moss in September and November 2011 respectively to provide this information.
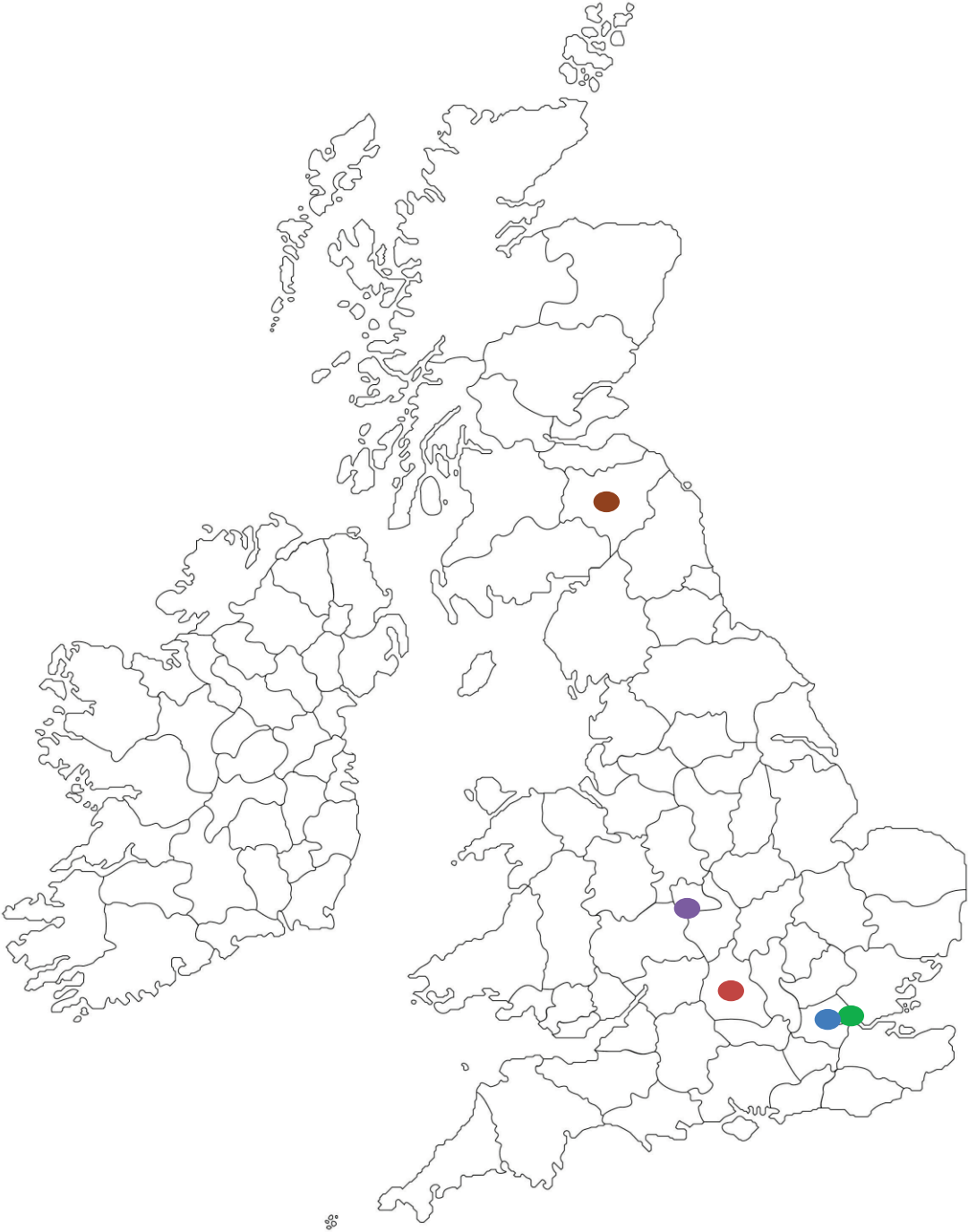
Figure 2-1 Network sites

	Site
🔵	Marylebone Road
🟢	North Kensington
🔴	Harwell
🟣	Birmingham
🟤	Auchencorth Moss

Table 2-1 Network structure during 2012

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.

2.3.1 Particle counting and size 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 (from 10^4 cm^{-3}) 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 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 (see Figure 2-2), which use Nafion driers (see Figure 2-1). Humidity sensors have been installed and are logged by the computers.
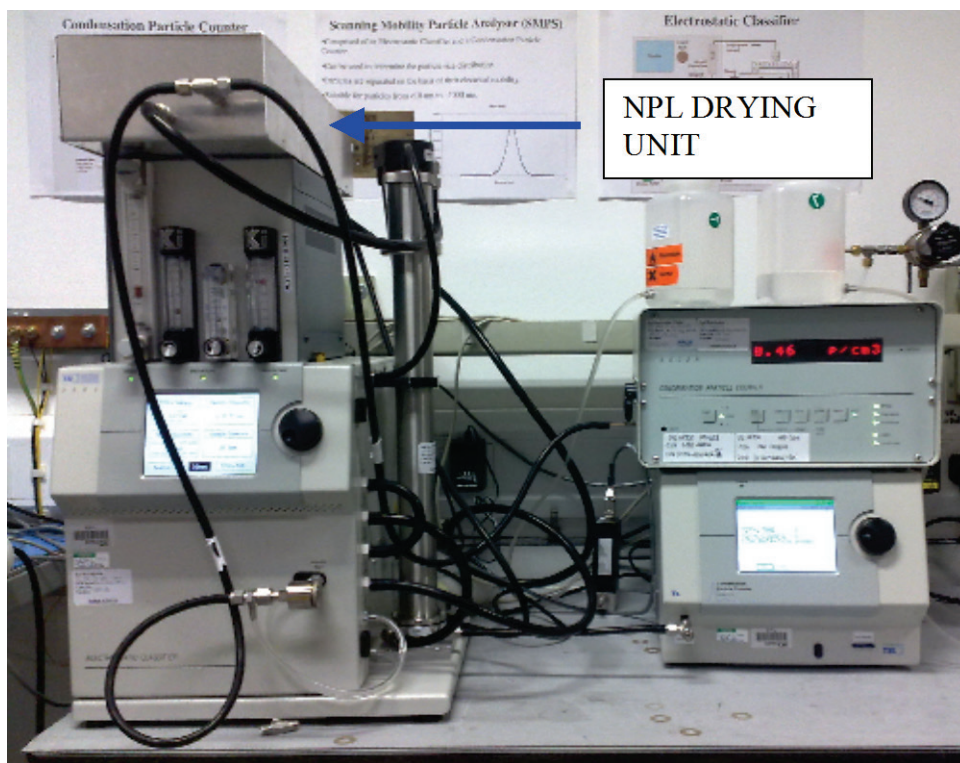

Figure 2-2 Typical configuration of CPC, SMPS and NPL drying unit at the Network sites

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} was made using a Thermo Partisol 2025 sequential air sampler (see Figure 2-3 (a)) and weekly measurements of $PM_{2.5}$ using a Leckel SEQ47/50 sequential sampler (see Figure 2-3 (b)). Ultrapure quartz filters (Pallflex Tissuquartz 2500QAT-UP) were used for the sampling.

The analysis is carried out using the Sunset Laboratory Inc. thermal/optical carbon analyser (see Figure 2-4). 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[1]. 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 870°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 890°C in the presence of oxygen and helium. The protocol used is termed Quartz, a close variation of the NIOSH protocol. Correction can be

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

made 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 5.2.2, and data from different methods is being evaluated, the results from both methods are presented in this report.

(a)

(b)
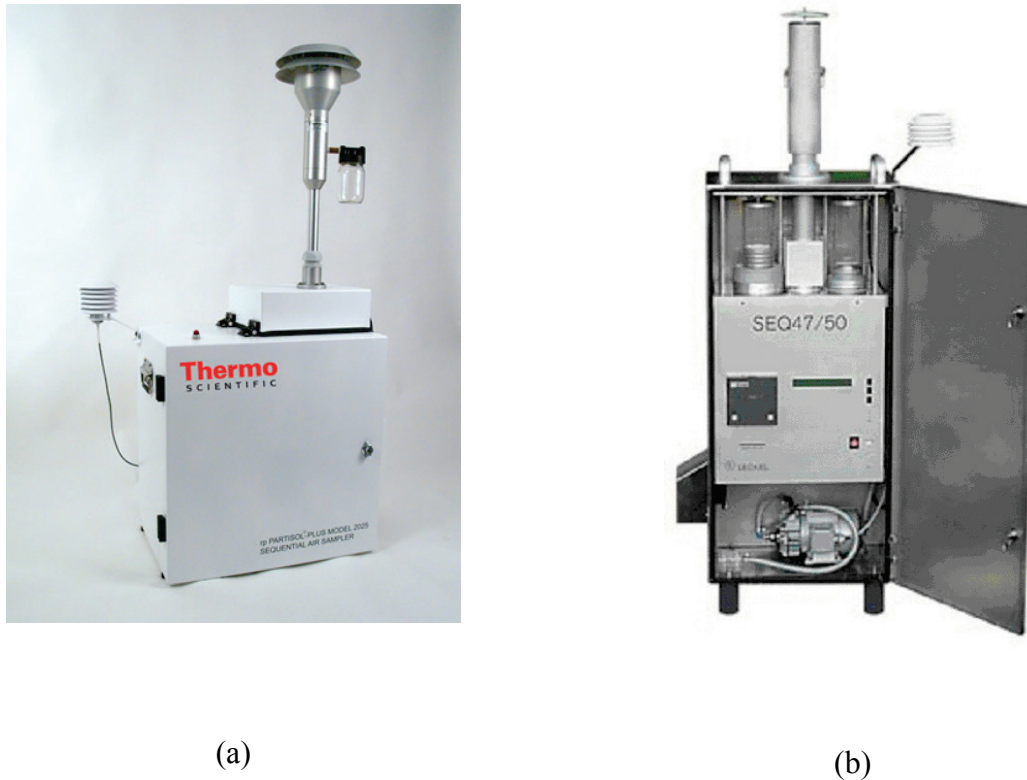
Figure 2-3 (a) Thermo Partisol 2025 sampler (b) Leckel SEQ47/50 sampler

Figure 2-4 Sunset Laboratory Inc. thermal/optical carbon analyser

2.3.4 Aethalometer (Black Carbon PM$_{2.5}$)

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 2-5) 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[2] 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 the 2012 Black Carbon Network report[3].

Figure 2-5 Magee Scientific aethalometer

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[2] 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.*

[3] NPL report "2012 Annual Report for the UK Black Carbon Network" 2013

2.3.5   URG – 9000B Ambient Ion Measurements (PM$_{10}$ anion and cation measurements)

The URG – 9000B AIM (Figure 2-6) 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 cation measurements is methanesulphonic acid (MSA) 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.

Figure 2-6 URG – 9000B Ambient Ion Measurements

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 (Local Site Operators) 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.

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 Harwell, North Kensington and Marylebone Road were serviced twice by the ESU, Air Monitors. The service procedure includes replacing old or worn parts, temperature and flow calibrations, leak tests and pump refurbishment.

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.

4 NETWORK DATA

4.1 OC/EC MEASUREMENTS (PM$_{10}$)

Daily measurements of OC (Organic Carbon) and EC (Elemental Carbon) in the PM$_{10}$ fraction collected on filters are provided in this Network at three sites: Harwell, North Kensington and Marylebone Road.

Organic carbon is present in urban environments from primary emissions and from secondary organic aerosol (SOA) formation. SOA PM dominates at rural locations, in particularly in summer, and contributes to regional episodes of high PM concentrations. Elemental carbon is usually formed by high temperature fossil fuel combustion, particularly by heavy components (such as diesel) and certain biofuels. Measurements of EC at urban and roadside locations are required to improve emission inventories and to determine the effect of diesel emissions.

Monthly data capture rates for the Partisol 2025 instruments in 2012 are given in Table 4-1.

The filter measurements of OC, EC and TC (Total Carbon – the sum of OC and EC) made in 2012 are displayed in Figures 4-1 to 4-3 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 the graphs. These are less notable in the concentrations at Marylebone Road, where local traffic and activities are the main sources, and at North Kensington where a strong seasonal pattern is shown (higher concentrations in winter and lower in summer) with only few episodes visible in summer.

Table 4-1 Monthly data capture for the Partisol 2025 Samplers during 2012

Site	Harwell	North Kensington	Marylebone Road
January	58%	100%	100%
February	79%	93%	45%
March	81%	100%	84%
April	67%	80%	83%
May	68%	100%	84%
June	90%	100%	83%
July	94%	87%	94%
August	100%	97%	97%
September	100%	90%	87%
October	100%	90%	90%
November	90%	100%	100%
December	94%	100%	74%
Average	**85%**	**95%**	**85%**

Harwell 2012
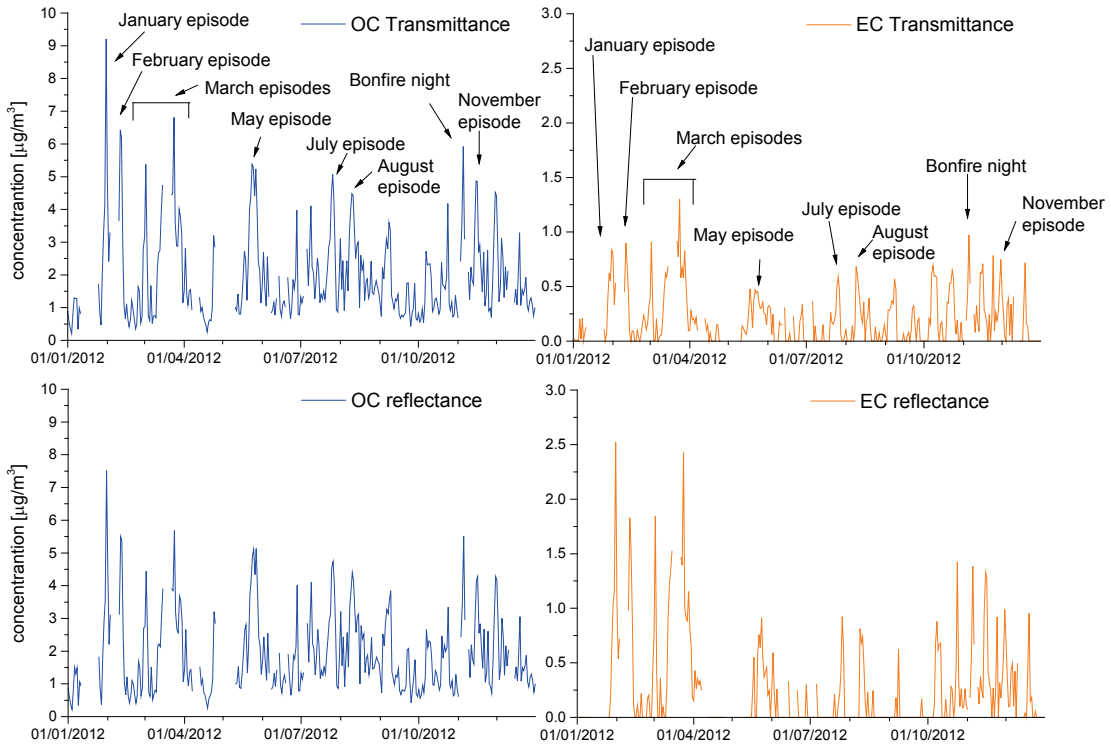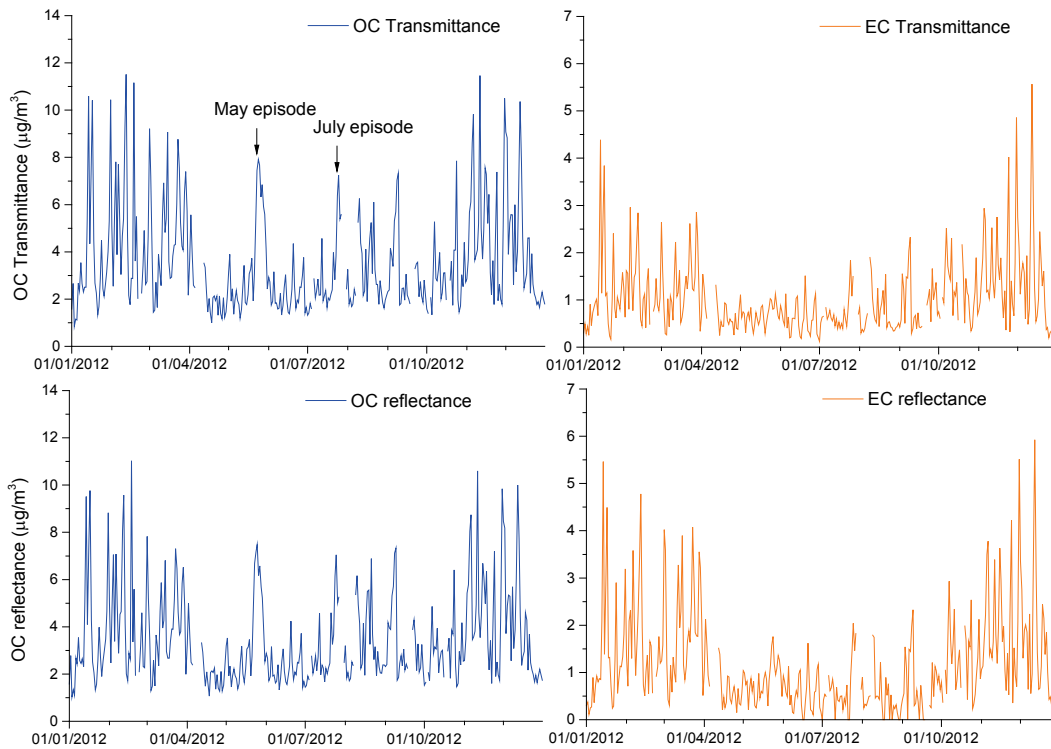

North Kensington 2012

Figure 4-1 PM₁₀ OC and EC concentrations at Harwell and North Kensington during 2012
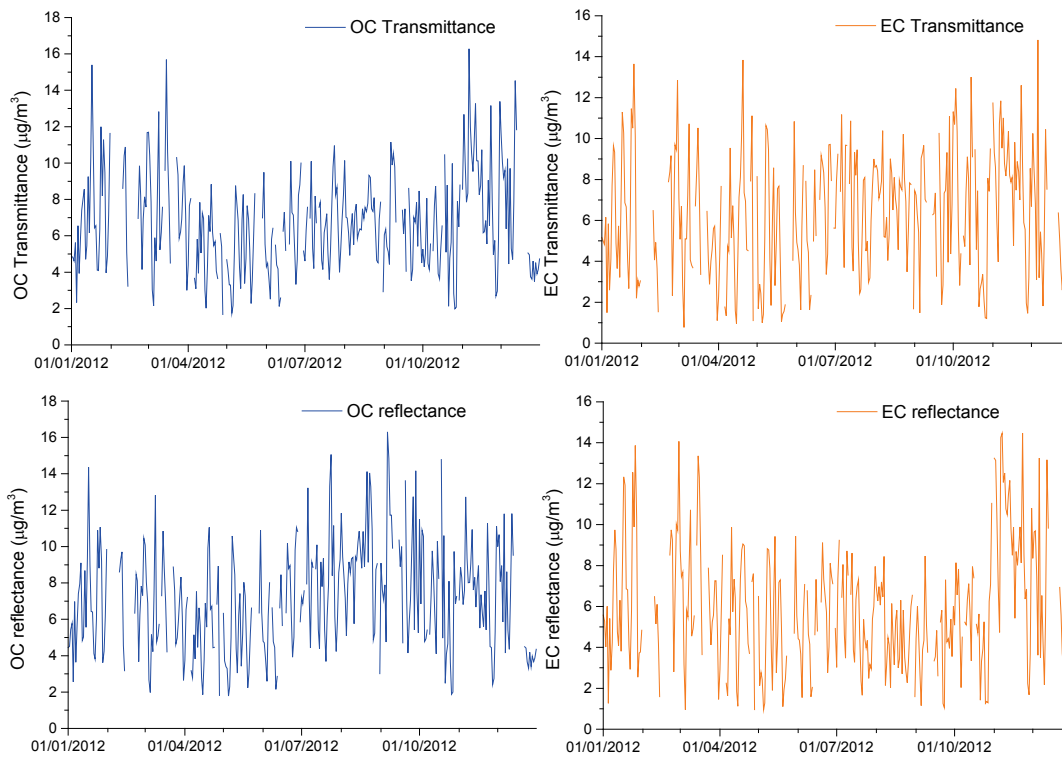
Marylebone Road 2012

Figure 4-2 PM$_{10}$ OC and EC concentrations at Marylebone Road during 2012
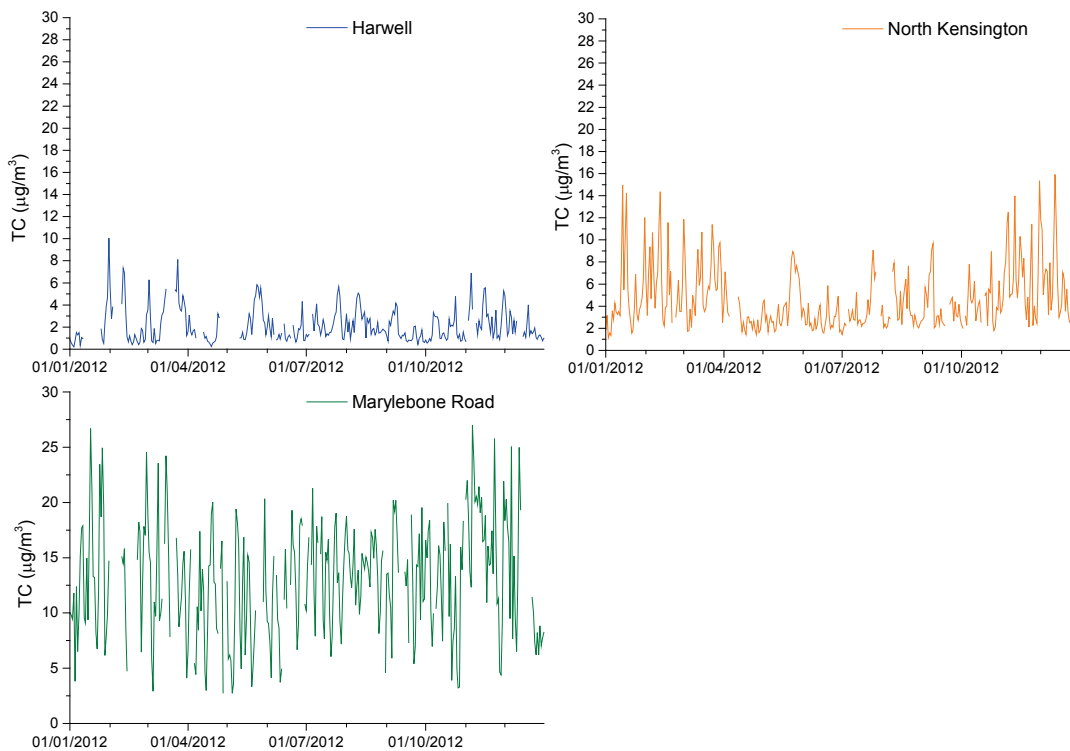
Total carbon (PM$_{10}$)

Figure 4-3 PM$_{10}$ TC concentrations at Harwell, North Kensington and Marylebone Road during 2012

4.1.1 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 scatter plots are shown in Figures 4-4, 4-5 and 4-6.

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[4].
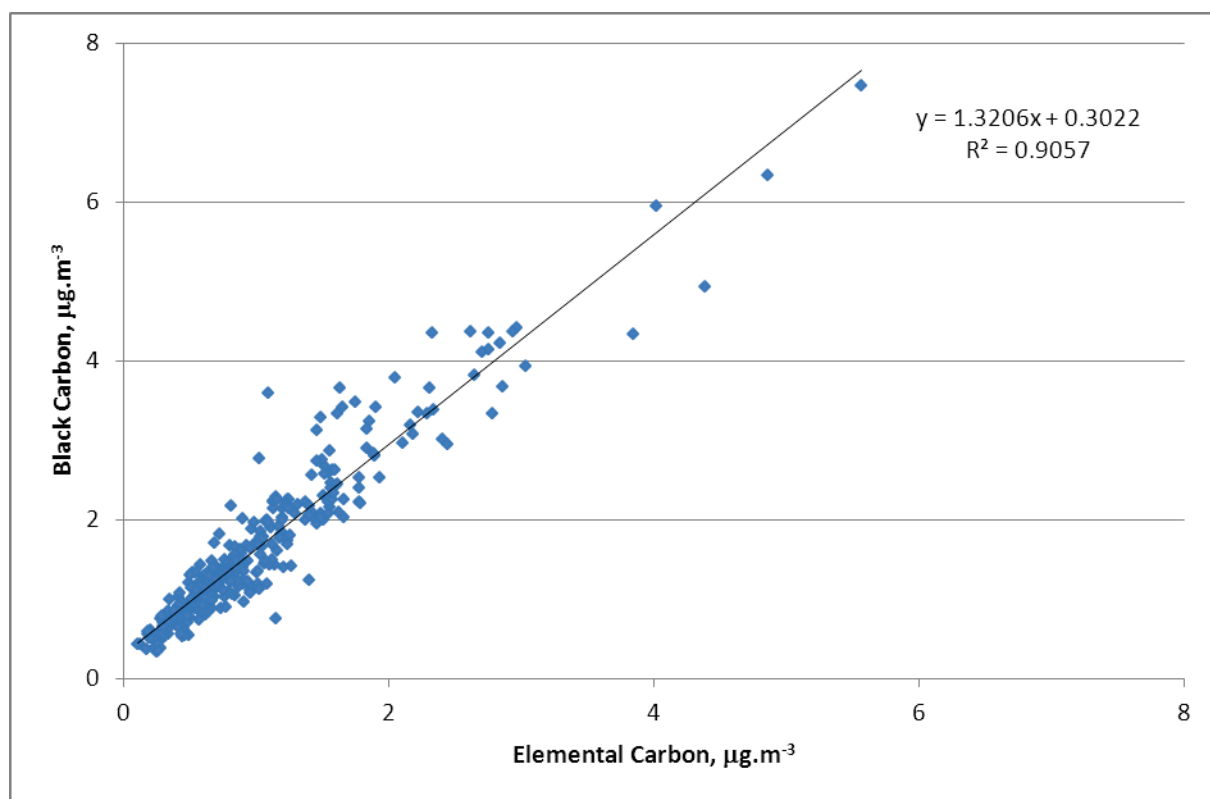
Figure 4-4 Comparison between $PM_{2.5}$ BC and PM_{10} EC (T) at North Kensington in 2012

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[4] 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 4-5 Comparison between PM$_{2.5}$ BC and PM$_{10}$ EC (T) at Marylebone Road in 2012

Figure 4-6 Comparison between PM$_{2.5}$ BC and PM$_{10}$ EC (T) at Harwell in 2012

4.2   OC/EC MEASUREMENTS (PM$_{2.5}$)

PM$_{2.5}$ weekly sampling at Harwell and Auchencorth Moss is a statutory requirement under the European Directive 2008/50/EC[5] (see Section 5.2.1) which requires measurements of OC and EC in the PM$_{2.5}$ fraction in rural background areas.

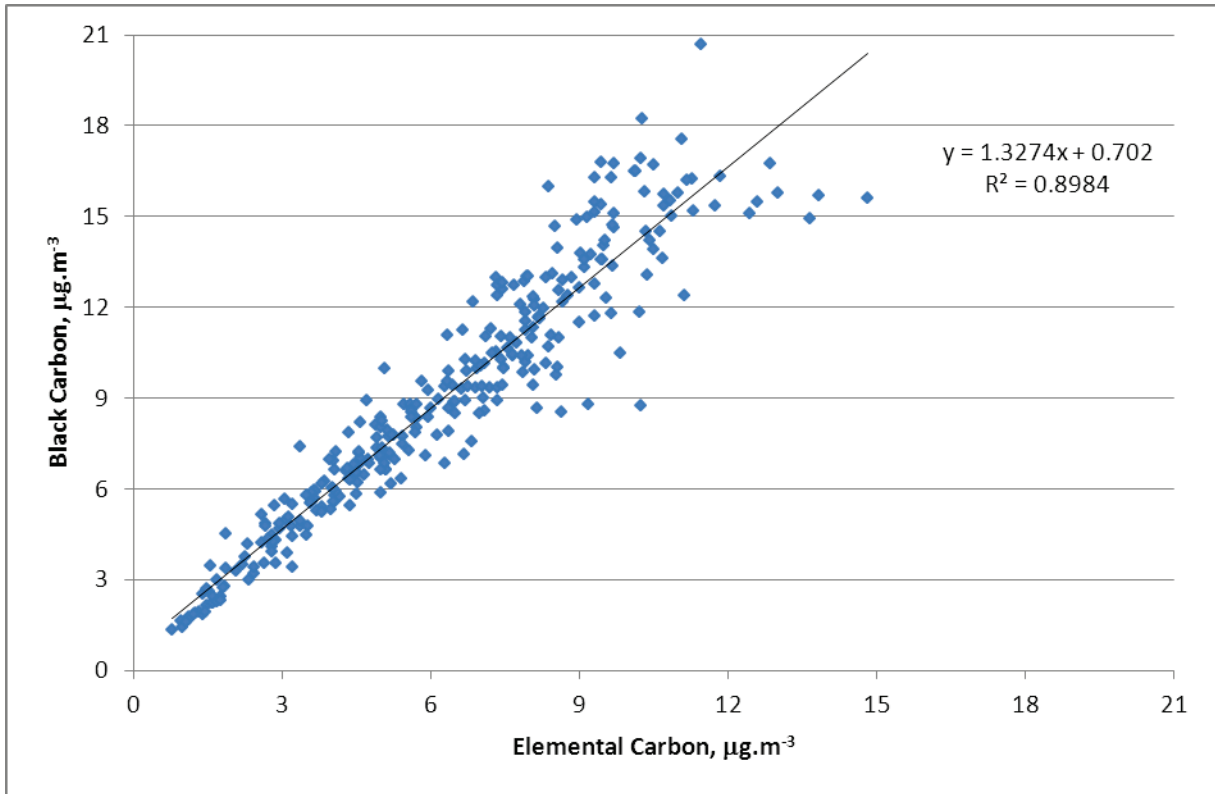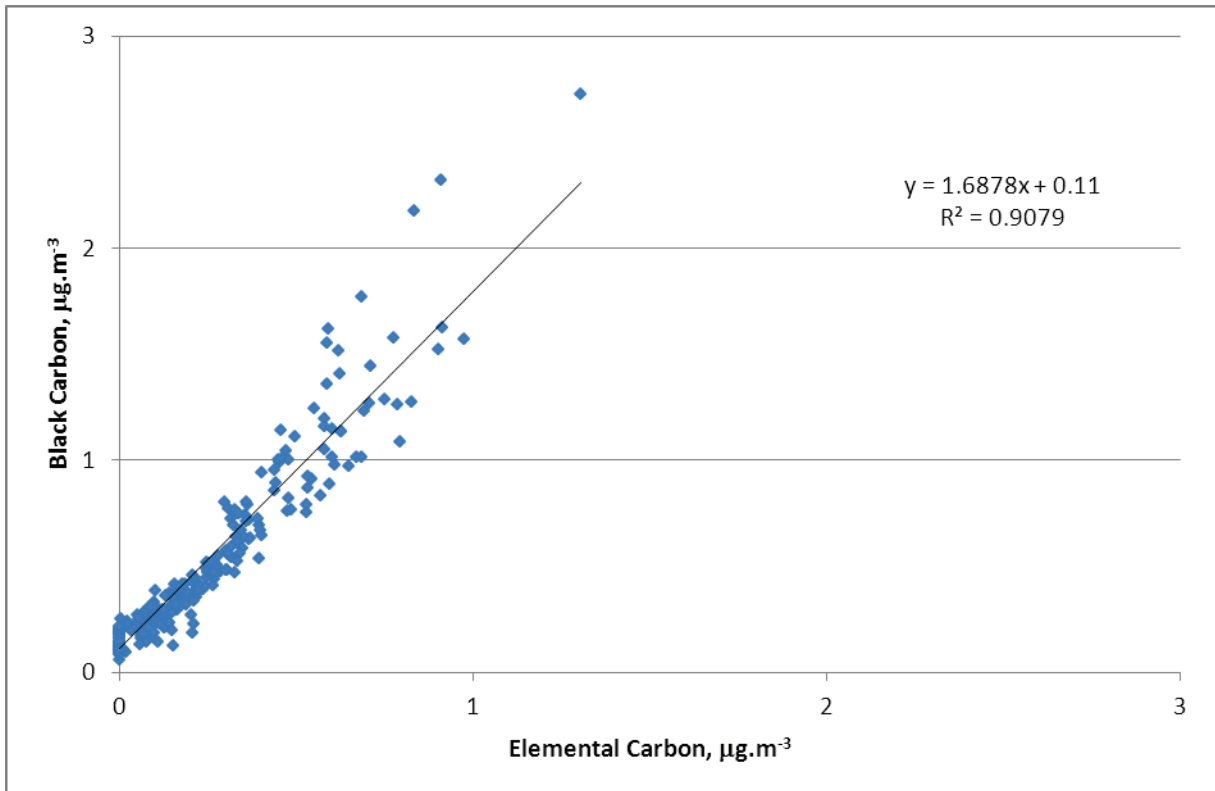The sampler at Harwell has been in operation since 1st September 2011 and the sampler at Auchencorth Moss since 17th November 2011. Data capture for 2012 was 100% for Harwell and 96% for Auchencorth Moss.

The filters were analysed by using both Quartz and EUSAAR II protocols to allow a comparison to be made. Figures 4-7 to 4-12 show the time series since the installation and the comparison between the two protocols. No significant difference could be identified in TC – a reassuring check of the analysis system. As expected, Quartz gives somewhat lower EC values than EUSAAR II (with correspondingly higher OC values). These differences are of the order of 20% for EC and 5% for OC.

Protocols that have a lower maximum temperature during the inert-gas heating phase, such as the EUSAAR II protocol with a maximum of 650°C, tend to record significantly higher EC values than protocols such as Quartz, with a maximum of 870°C, with correspondingly less OC, such that the sum of EC and OC is the same in both cases. More charring of organic material will occur in the Quartz case, which may be inadequately accounted for by the optical correction. Alternatively, the EUSAAR II protocol may not be removing all material that should be classified as OC. Ultimately the difference is because EC and OC are not objectively defined, but rather defined by the method used.

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[5] Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe
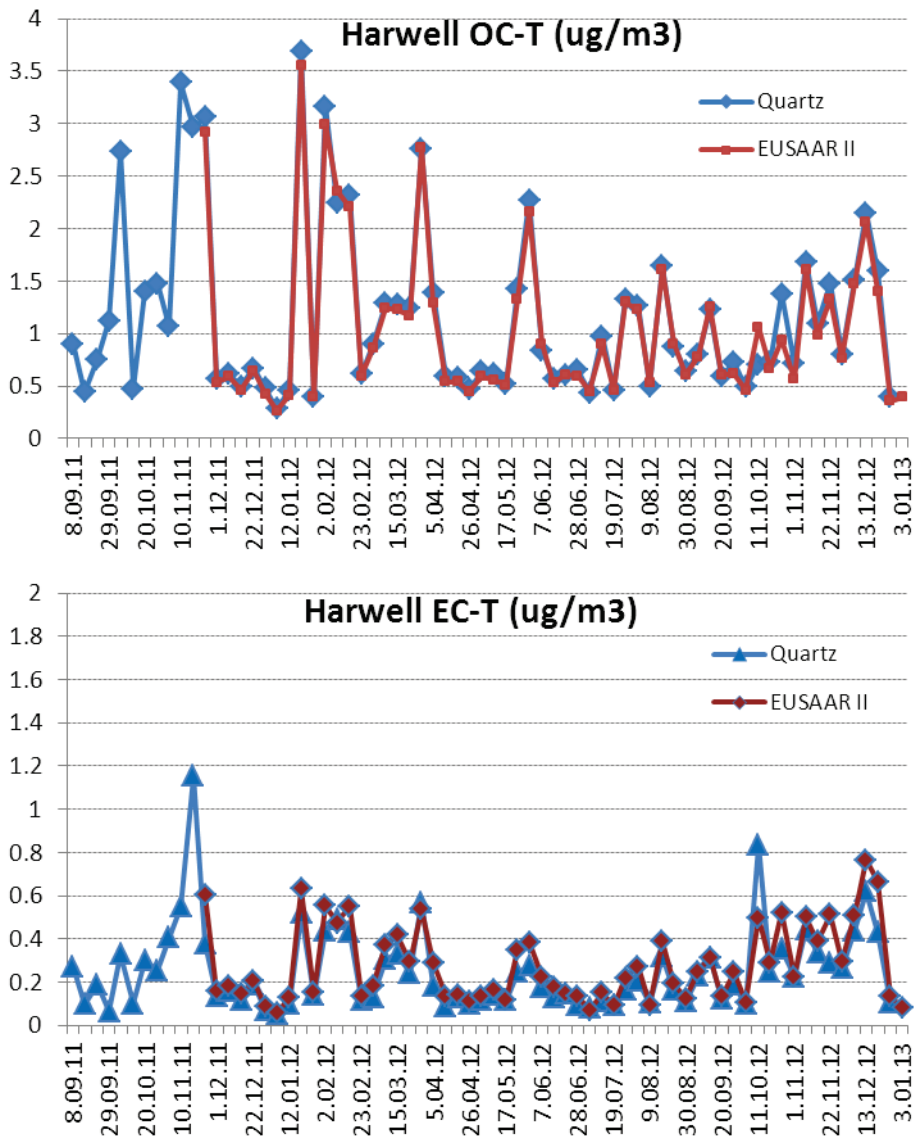
Figure 4-7 Comparison between Quartz and EUSAAR II protocol at Harwell for TOT method
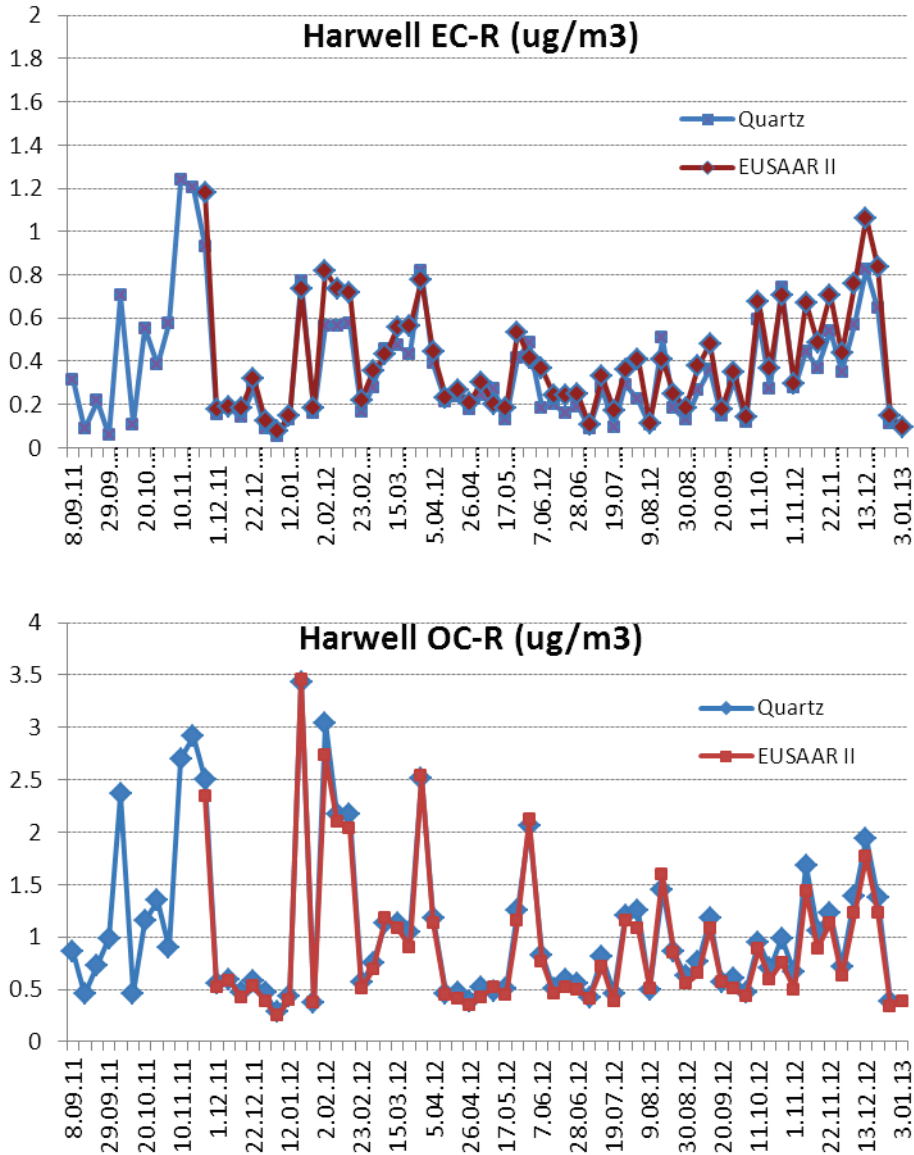
Figure 4-8 Comparison between Quartz and EUSAAR II protocol at Harwell for TOR method
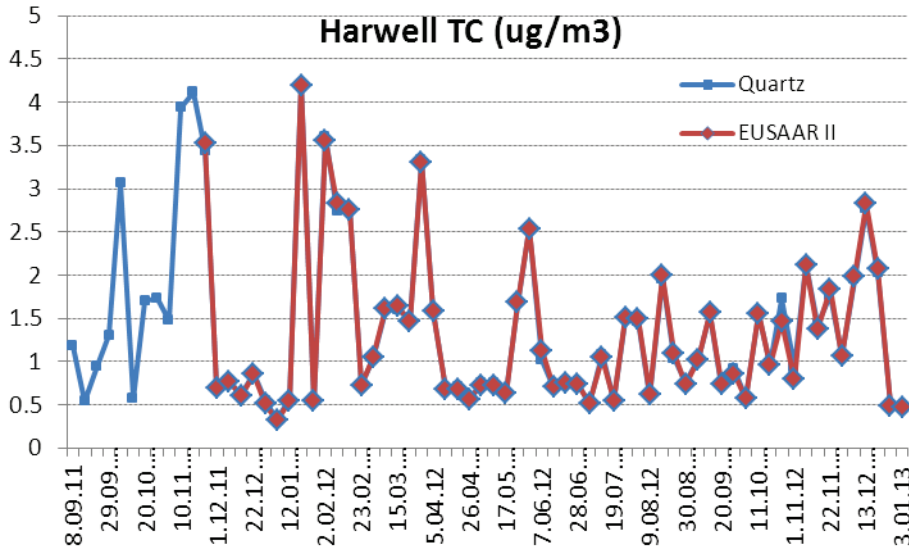
Figure 4-9 Comparison between Quartz and EUSAAR II protocols at Harwell for TC
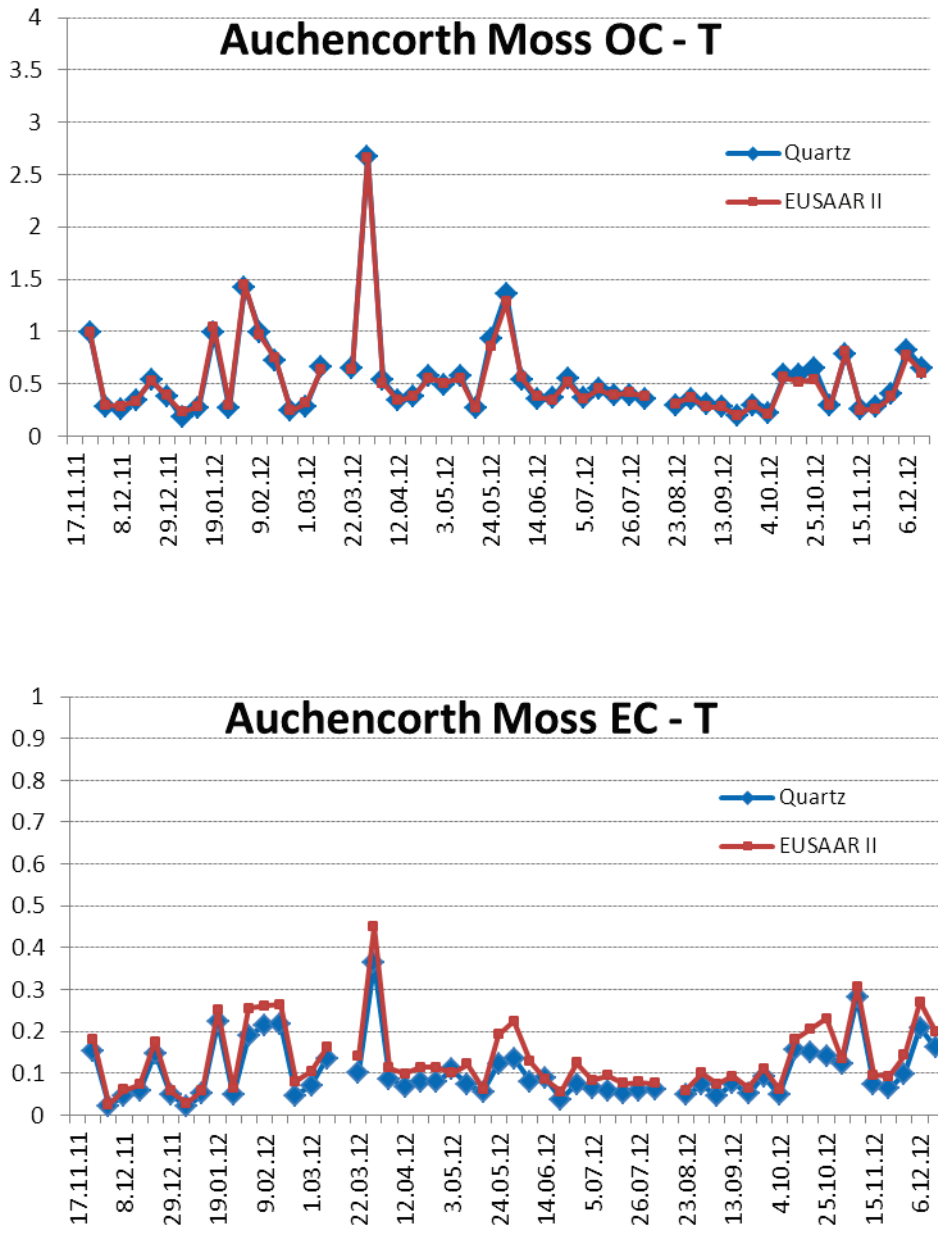
Figure 4-10 Comparison between Quartz and EUSAAR II protocols at Auchencorth Moss for TOT method
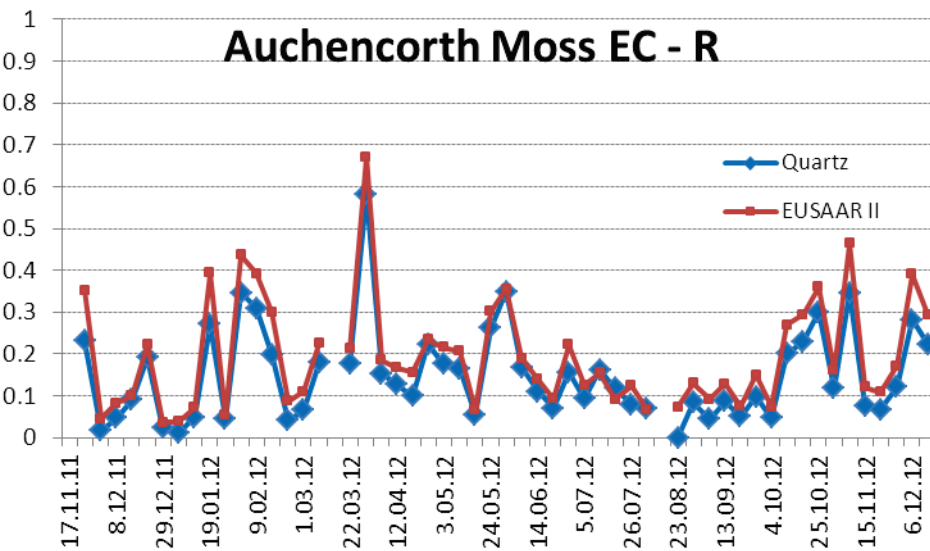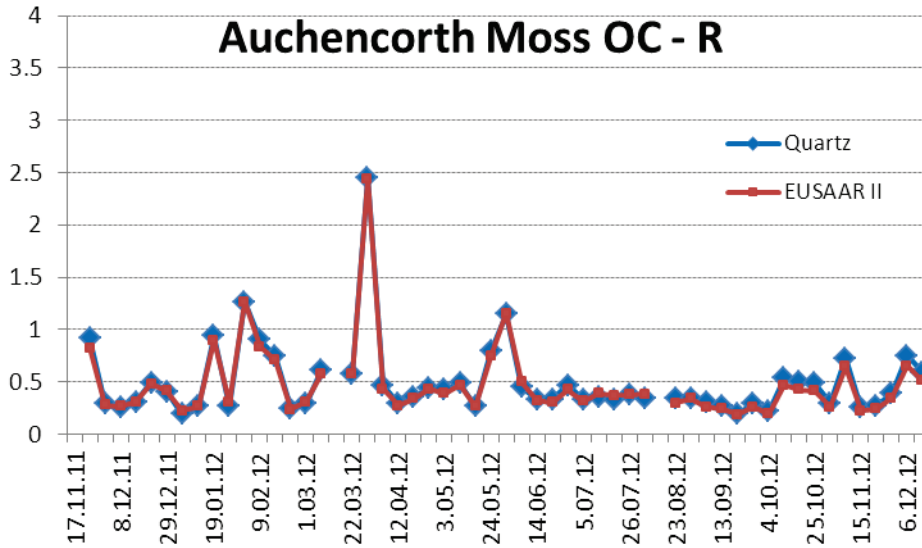
Figure 4-11 Comparison between Quartz and EUSAAR II at Auchencorth Moss for TOR method
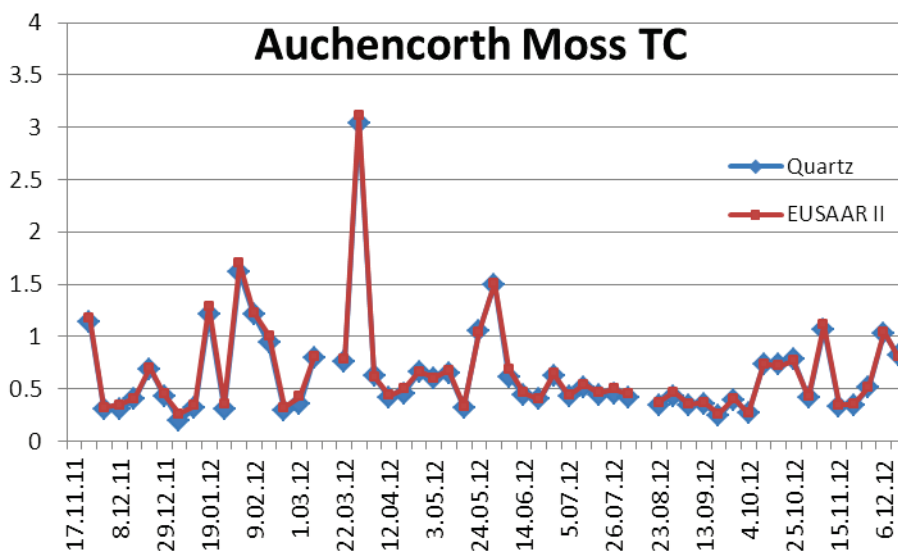
Figure 4-12 Comparison between Quartz and EUSAAR II protocols at Auchencorth Moss for TC

The $PM_{2.5}$ carbon concentrations at Harwell were compared with weekly averages from the PM_{10} filters from the Partisol (Figure 4-13). 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.
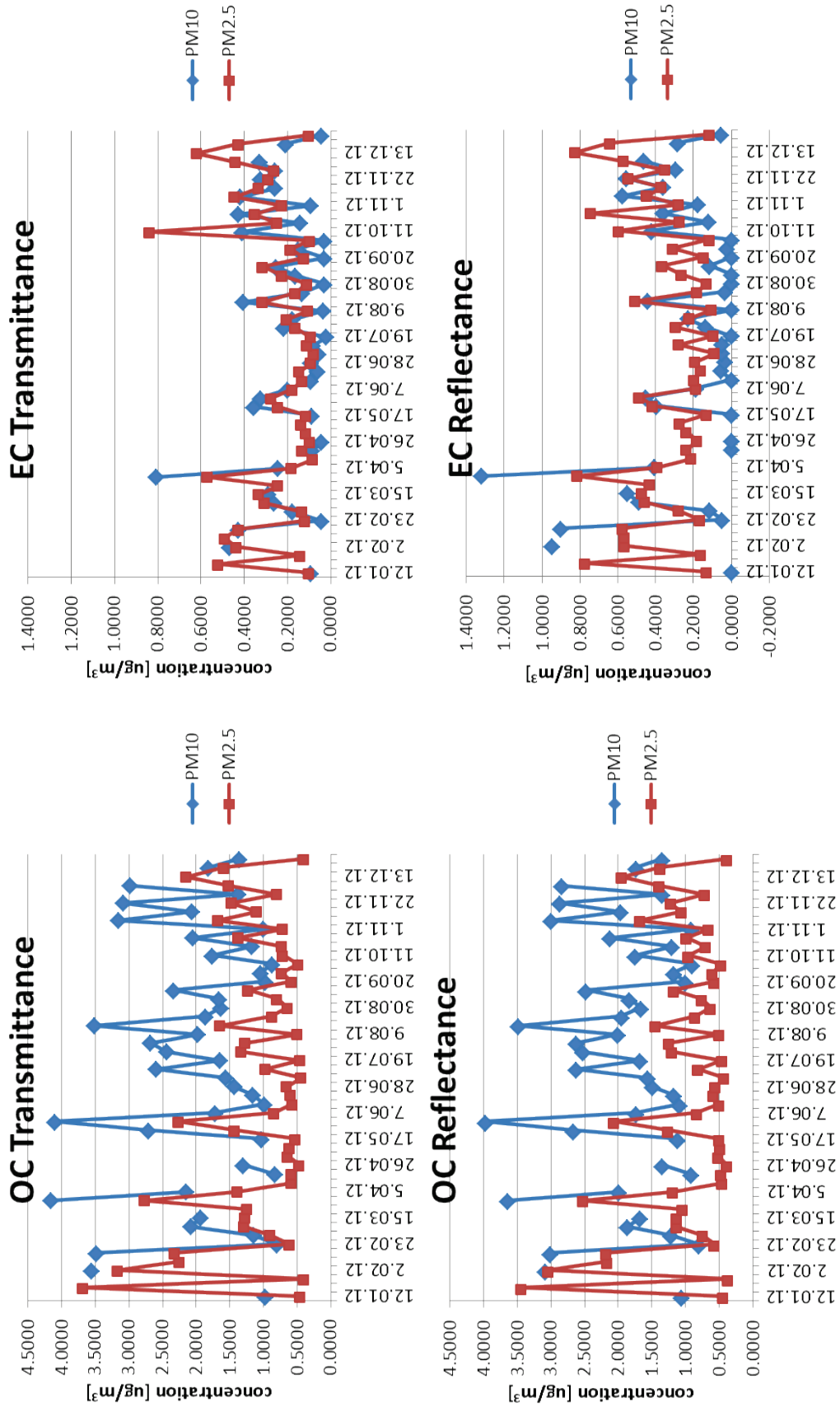
Figure 4-13 Comparison between PM₁₀ OC/EC weekly averages and PM₂.₅ OC/EC at Harwell

4.2.1   Monthly profiles

Figure 4-14 long-term monthly averages since the beginning of the PM$_{10}$ filter based measurements within this Network. No significant change over time can be seen at any of the sites.
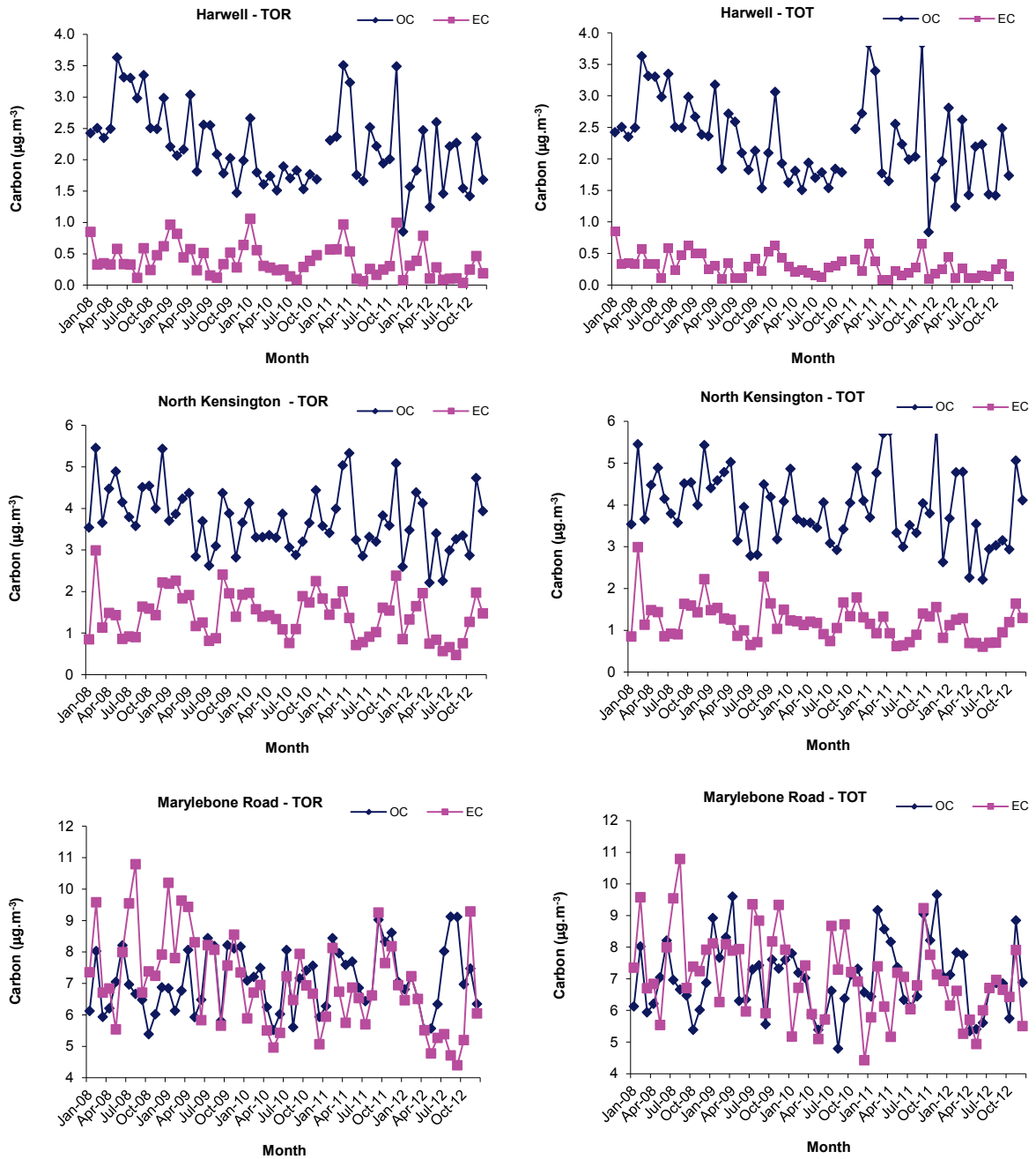
Figure 4-14 Long term monthly averages for PM$_{10}$ OC/EC concentrations at the Network sites for both TOR and TOT methods

Monthly average trends have been also produced for the PM$_{2.5}$ measurements at Harwell and Auchencorth Moss by using the Quartz protocol (Figure 4-15). It is notable that the trends at the two sites correlate well despite their very different locations.
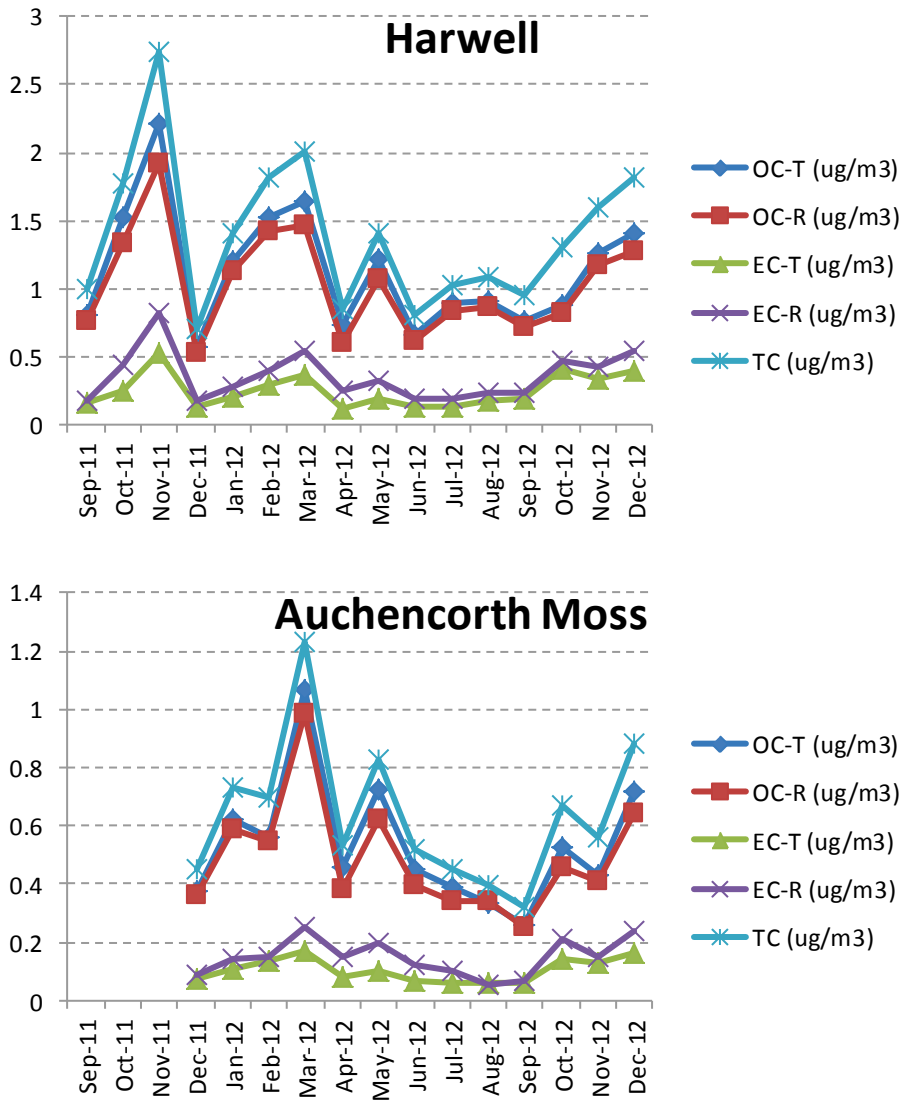
Figure 4-15 Long term monthly averages for PM$_{2.5}$ concentrations at Harwell and Auchencorth Moss

4.3 AUTOMATIC PM$_{10}$ ANION AND PM$_{10}$ CATION MEASUREMENTS

4.3.1 Anion and cation hourly measurements

The two URG 9000B – AIM instruments 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 in the PM$_{10}$ size fraction.

Prior to February 2011, daily anion measurements were made in this Network at Harwell, North Kensington and Marylebone Road using a filter based method. The two URG instruments at the London sites replaced the manual method giving a higher time resolution measurements and adding information on cation content of PM$_{10}$. At Harwell a MARGA instrument was already operative under a different Network.

Monthly data capture for each site is shown in Table 4-2 and 4-3.

The large data gap at North Kensington was due to a fault in the machine, which required the replacement of a part of the sampler, and then the breakage of one of the sample syringes. The data capture for potassium in February was 0% because of contamination in the sampler.

Table 4-2 Monthly data capture for URG analyser at North Kensington in 2012

|	Chloride	Nitrate	Sulphate	Sodium	Ammonium	Potassium	Magnesium	Calcium
January	44%	44%	44%	40%	40%	40%	61%	61%
February	71%	71%	71%	72%	71%	0%	72%	72%
March	0%	0%	0%	0%	0%	0%	0%	0%
April	0%	0%	0%	0%	0%	0%	0%	0%
May	21%	21%	21%	21%	21%	21%	21%	21%
June	86%	86%	86%	85%	85%	85%	85%	85%
July	87%	87%	87%	86%	86%	86%	86%	86%
August	96%	96%	96%	87%	87%	88%	88%	88%
September	51%	51%	51%	42%	42%	42%	42%	42%
October	72%	72%	72%	64%	62%	64%	64%	64%
November	68%	68%	68%	62%	62%	62%	62%	62%
December	75%	75%	75%	75%	75%	75%	74%	75%
Average	**56%**	**56%**	**56%**	**53%**	**53%**	**47%**	**55%**	**55%**

Table 4-3 Monthly data capture for URG analyser at Marylebone Road in 2012

	Chloride	Nitrate	Sulphate	Sodium	Ammonium	Potassium	Magnesium	Calcium
January	31%	31%	31%	31%	13%	31%	31%	31%
February	52%	52%	52%	52%	40%	50%	52%	52%
March	63%	63%	63%	62%	54%	49%	62%	62%
April	59%	63%	63%	63%	62%	63%	63%	63%
May	90%	90%	90%	90%	90%	90%	90%	90%
June	72%	73%	73%	73%	73%	73%	73%	73%
July	79%	79%	79%	79%	73%	79%	79%	79%
August	82%	88%	88%	88%	85%	88%	88%	88%
September	57%	57%	57%	58%	58%	58%	58%	58%
October	88%	88%	90%	90%	90%	90%	90%	90%
November	69%	69%	62%	69%	69%	69%	69%	69%
December	0%	0%	0%	0%	0%	0%	0%	0%
Average	**62%**	**63%**	**62%**	**63%**	**59%**	**62%**	**63%**	**63%**

In November 2012 a few changes were made to the analysers to improve the quality of the chromatography, and therefore of the data. Details of the changes can be found in Section 4.4.2. No discontinuity was found in the data.

The ion trends between the two sites correlate well, but they differ by a variable factor. Normally the concentrations at Marylebone Road are significantly higher than the concentrations at North Kensington.

A few plots are shown in Figures 4-16 to 4-18 to allow comparison between the two sites, and some findings from the data are listed below. The concentrations have been normalised to allow the comparison.

- The nitrate concentrations correlate well between the two sites and show higher concentrations at night, as expected.

- The calcium concentrations seem to follow the traffic trend at both sites, with higher concentrations during the day and lower concentrations during the weekend, suggesting that the main source of calcium could be re-suspension from the ground.

- Sodium, chloride and magnesium show the same trends suggesting they derive from the same source, possibly sea salt.
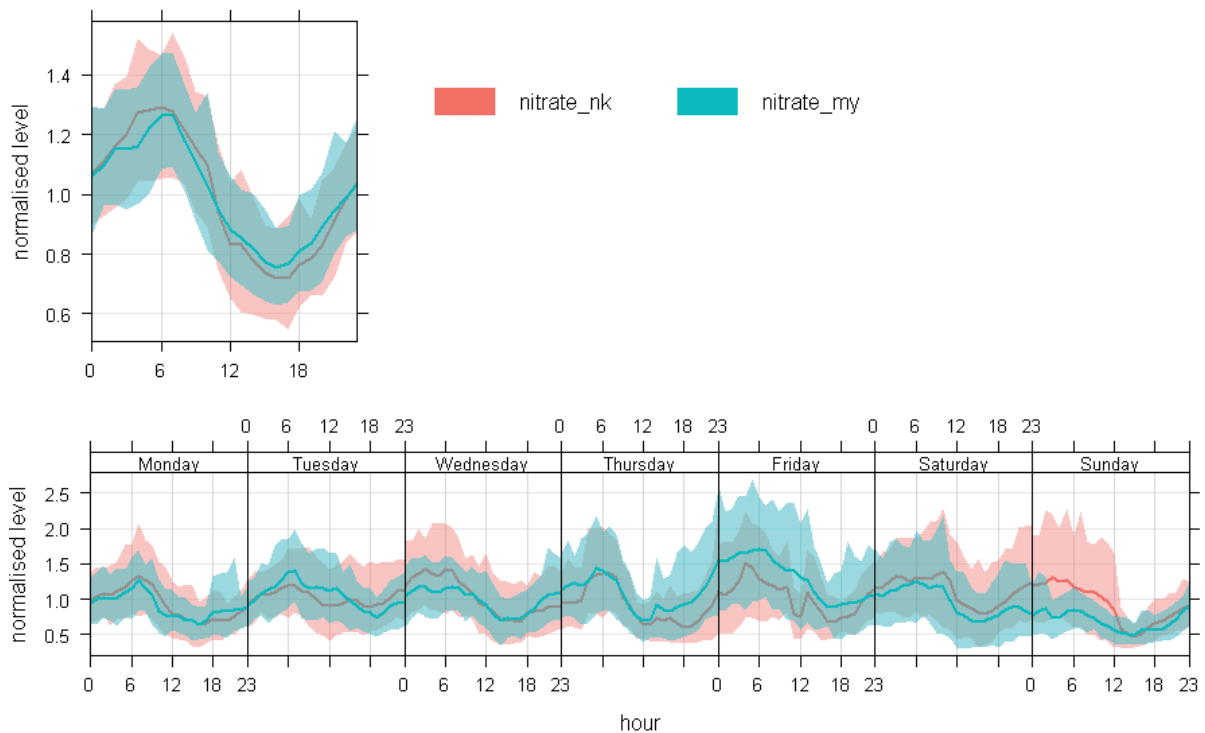

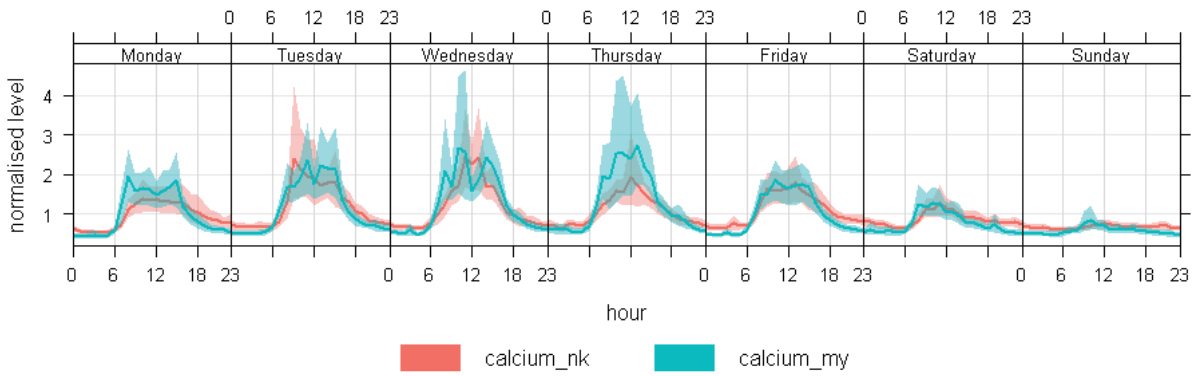**Figure 4-16 Nitrate trends during 2012 at the two London sites**

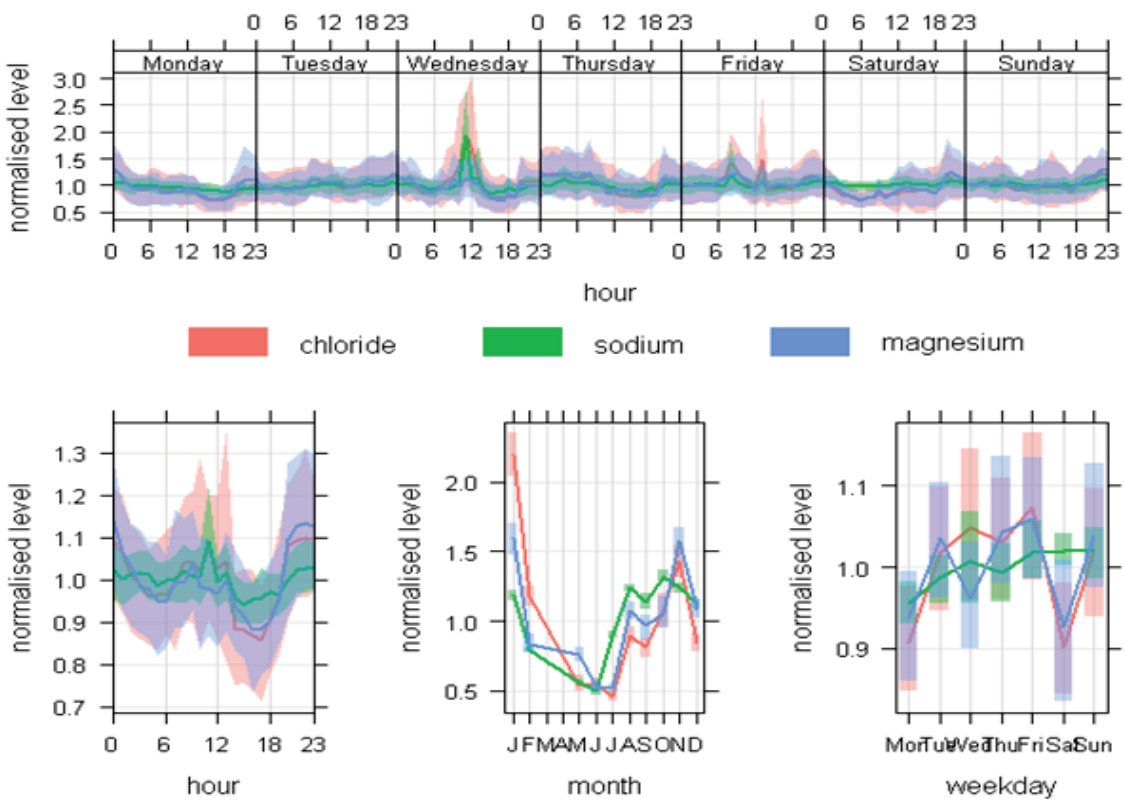**Figure 4-17 Calcium trends in 2012 at the two London sites**

Figure 4-18 Chloride, sodium and magnesium trends in 2012 at North Kensington

4.3.2   Changes to the URG analysers and improvement of the cation chromatography

During the first year of operation, a few issues arose with the cation chromatography. There was difficulty in integrating and resolving the peaks, especially during pollution episodes, which caused saturation conditions in the chromatograph. Ammonium, in particular, is known to have a non-linear calibration curve[6].

In order to resolve these issues, a different column was installed for cation analysis (CS16 instead of CS12), to improve the peak separation, and a sample loop used on both anion and cation ICs instead of a concentrator, to avoid saturation.

As an example, a comparison between the performance of the two set-ups is shown for the cation system at Marylebone Road in Figure 4-19.
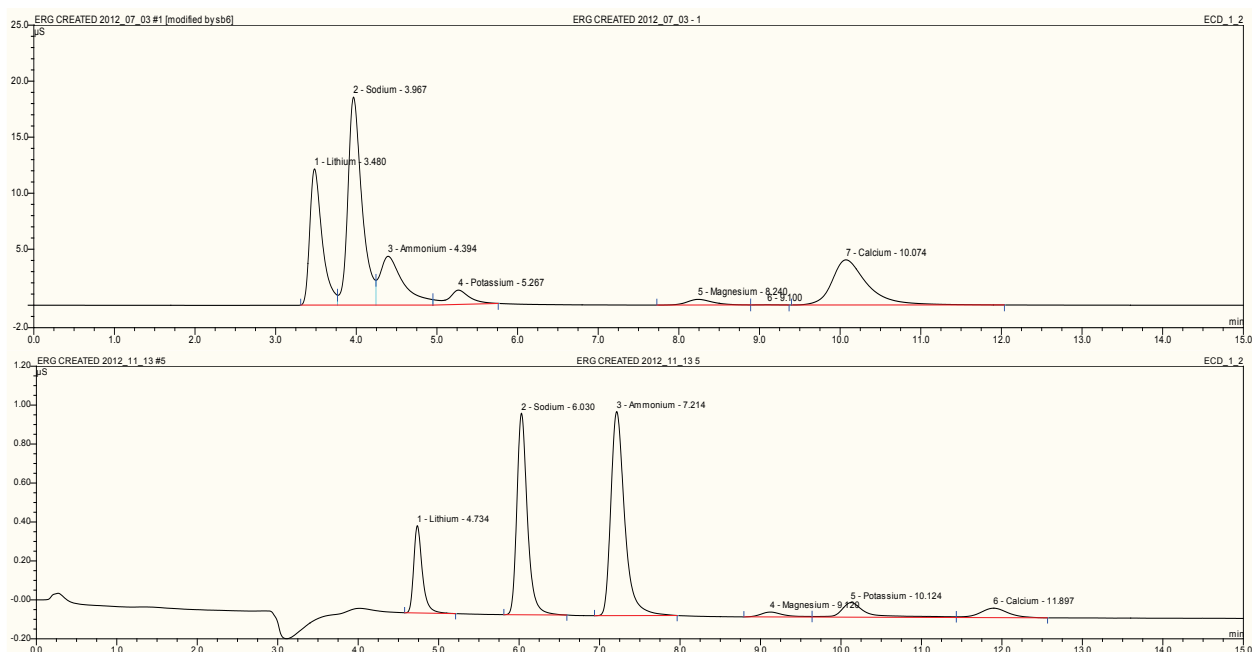
Figure 4-19 Comparison between the CS12 (upper chart) and CS16 (lower) columns at Marylebone Road

4.3.3   Anion long-term annual trends

Annual mean concentrations have been calculated for the anion species. Figure 4-20 shows the trend from 2003 to 2012. Average concentrations at Harwell in 2012 have been derived from the MARGA measurements[7].

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[6] Characterization and optimization of an online system for the simultaneous measurement of atmospheric water-soluble constituents in the gas and particle phases, Milos Z. Markovic, Trevor C. VandenBoer and Jennifer G. Murphy, *J. Environ. Monit., 2012, 14, 1872*

[7] JJN Lingard, S Ritchie, C Conolly, BJ Donovan, UK Eutrophying and Acidifying Atmospheric Pollutant project's Monitoring instrument for AeRosols and reactive Gases (MARGA), Harwell (Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v1.0, UK EMEP Supersite
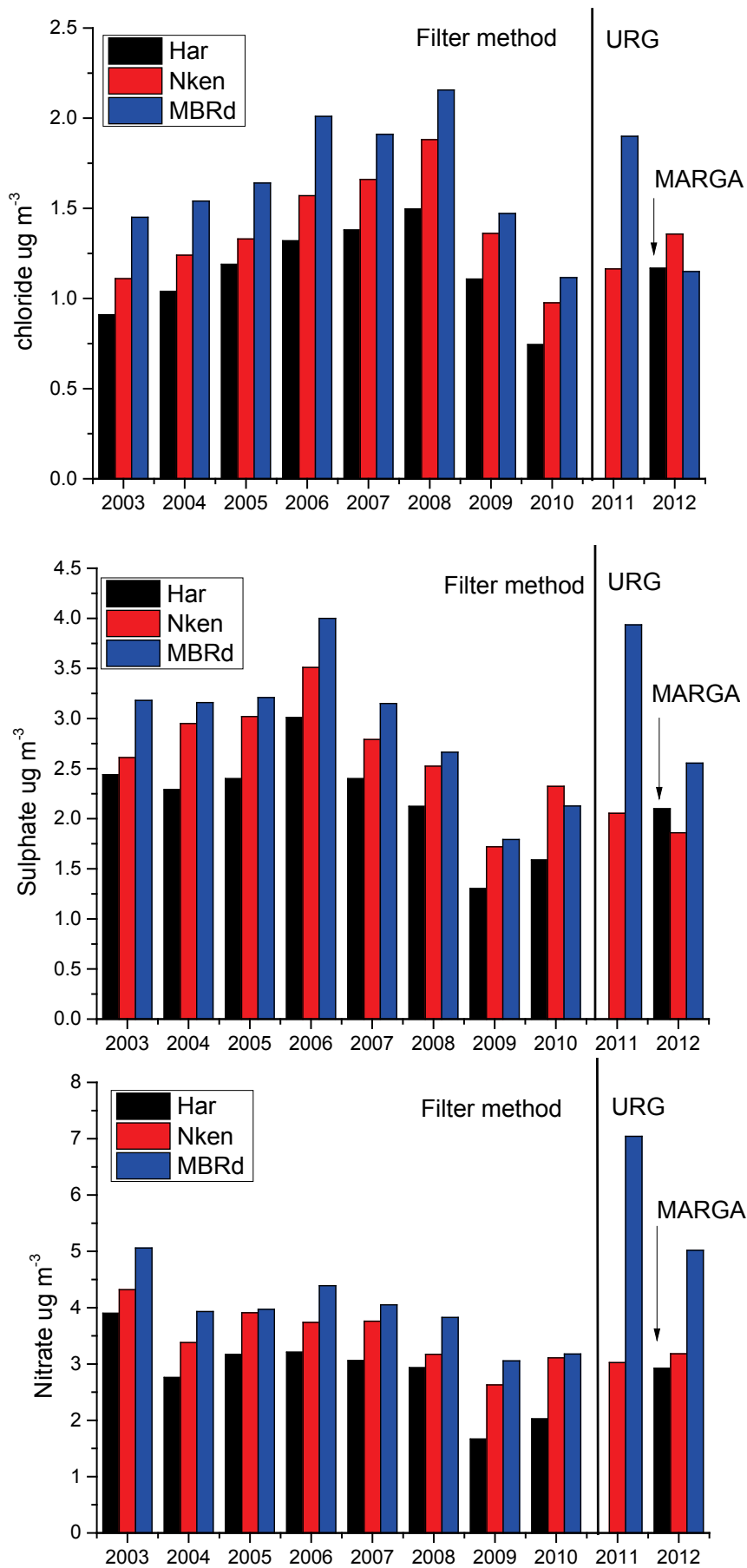
Figure 4-20 Anion long-term annual trends

4.4   PARTICLE NUMBER AND SIZE DISTRIBUTION

4.4.1   Particle number concentrations (CPC)

Time series of hourly particle number concentrations (between about 7nm and several microns in diameter) measured at network sites during 2012 are shown in Figure 4-21. The plots have been shown on the same scale.

The reasons for the main data gaps were:

- **Harwell.** The instrument was removed from site on the 7th of March for service and calibration at NPL, and re-installed on the 14th of March. On 15th July the pump failed and was replaced by NPL. The instrument was re-installed on 25th July. On 19th December the laser failed and it could not be replaced by the manufacturer or NPL.

- **Birmingham.** The instrument was removed from site on 7th March for service and calibration at NPL. Due to a technical problem with the drying unit and then the modem, the instrument could not be operative until 10th May.

- **North Kensington.** The instrument was removed from site on the 5th March for service and calibration at NPL and re-installed on the 14th March. In April the instruments failed and required a major from the manufacturer. The instrument was re-installed in June.

- **Marylebone Road.** The instrument suffered from butanol leakage in January and February. It was serviced and calibrated in March.

Monthly data capture rates for the CPC instruments during 2012 are displayed in Table 4-4. 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 4-4 Monthly data capture for CPC instruments in 2012. 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.

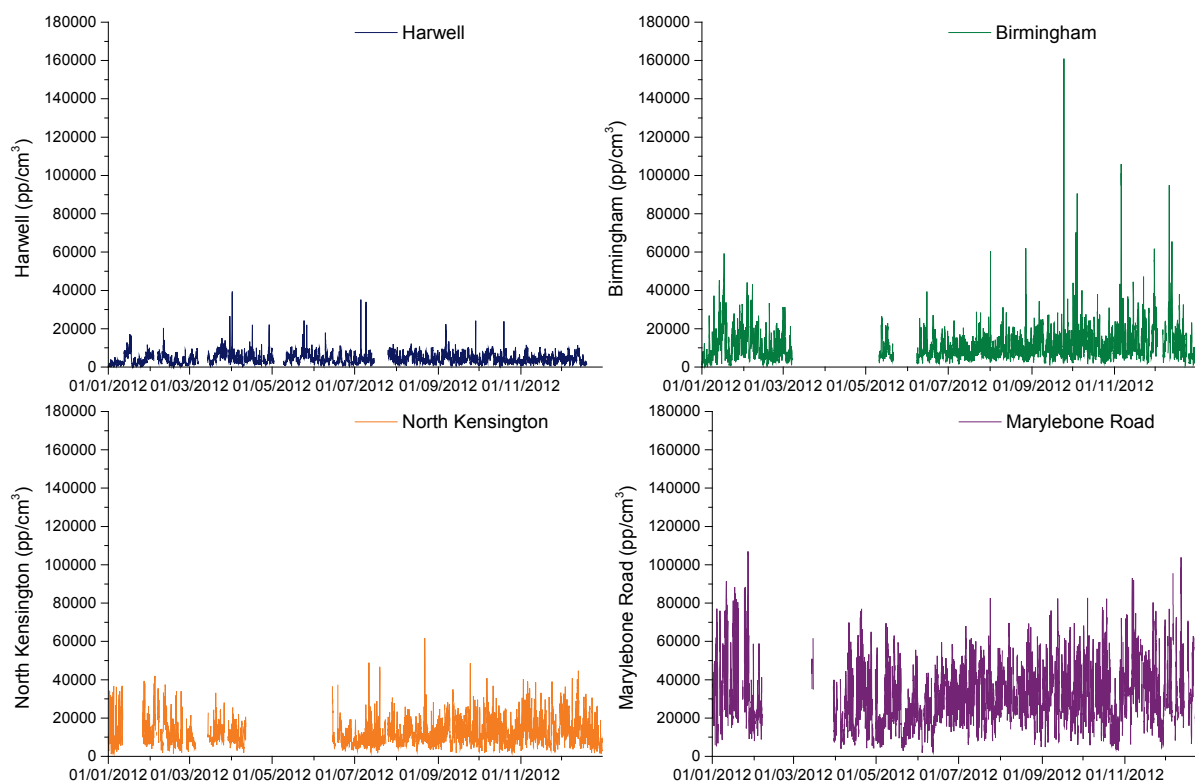| Month	Birmingham	Harwell	North Kensington	Marylebone Road
January	99%	100%	52%	76%
February	93%	83%	98%	16%
March	66%	74%	78%	51%
April	0%	94%	34%	86%
May	34%	77%	0%	99%
June	75%	97%	47%	88%
July	99%	67%	91%	96%
August	100%	100%	100%	87%
September	97%	97%	96%	89%
October	100%	100%	100%	93%
November	93%	97%	96%	83%
December	79%	60%	95%	49%
Average	**78%**	**89%**	**74%**	**76%**

Figure 4-21 Time series of number concentrations during 2012 at the Network sites

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 5.2.2).

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.

The process for defining the CEN specification has gone quite slowly in 2012, with still no final decisions, and hence no "compliant" models available. The lack of spare parts for the 3022As is becoming a problem, and a decision about whether to replace them, even if the details of the CEN specification are still not available, needs to be kept under review.

4.4.2   Particle size number distributions

The SMPS instruments generate size spectra between 16 nm and 605 nm. Table 4-5 shows the monthly data captures.

The reasons for the main data gaps were:

- **Harwell.** The instrument was removed from site on 15th February for service and calibration at NPL and put back on 7th March.

- **North Kensington.** The instrument was removed from site on the 15[h] of February for service and calibration at NPL and re-installed on the 6th of March. The CPC showed an orifice

pressure problem in December. As this problem had appeared a few times before, the CPC was sent to TSI for service and calibration and a spare CPC from NPL was installed to keep data capture high.

- **Marylebone Road.** The instrument suffered butanol leaks and unstable flow during the first months of the year. A possible leak in the system, which introduced cabin air in the sample air, interfered with the concentrations during the last two months of the year.

Table 4-5 Monthly data captures for SMPS instruments during 2012. 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	98.9%	39.4%	---
February	97.7%	82.8%	---
March	71.9%	41.9%	---
April	96.8%	93.6%	---
May	70.6%	99.2%	---
June	99.7%	89.4%	54.6%
July	84.3%	95.0%	97.3%
August	99.9%	99.2%	95.2%
September	100.0%	52.5%	95.7%
October	78.4%	99.2%	94.2%
November	99.7%	97.2%	---
December	99.7%	76.3%	---
Average	**91.3%**	**80.4%**	

The production of data from SMPS instruments is a complicated process, summarised schematically in Figure 4-22. 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 again this year, as described in Section 4.6.3.

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 4-23. 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
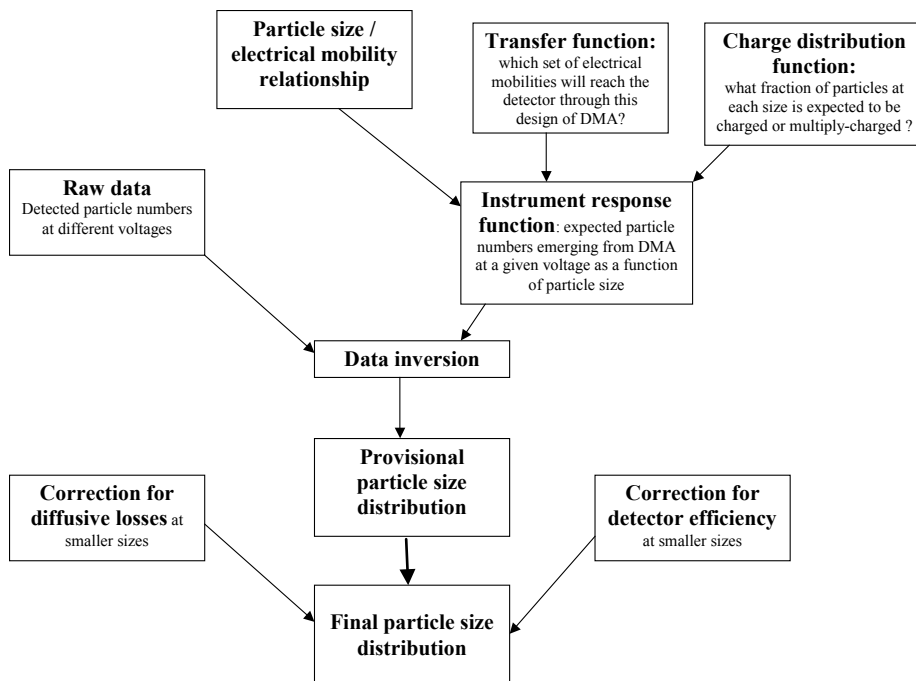
Figure 4-22 Schematic of the internal data processing of SMPS instrument in the Network
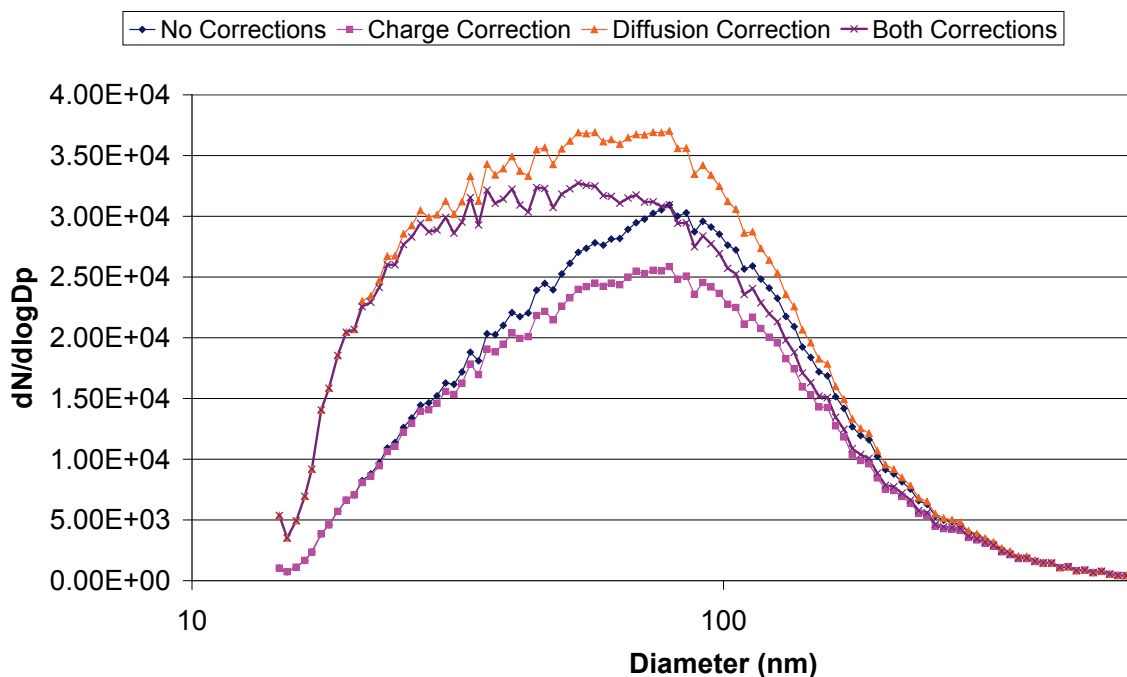
Figure 4-23 Effect of the multiple charge, the diffusion loss and their combined correction in the SMPS size spectrum.

The counts in each particle size bin measured during 2012 are presented as monthly averages in the left-hand panels of Figure 4-24 and as an annual average in the right-panel.

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].
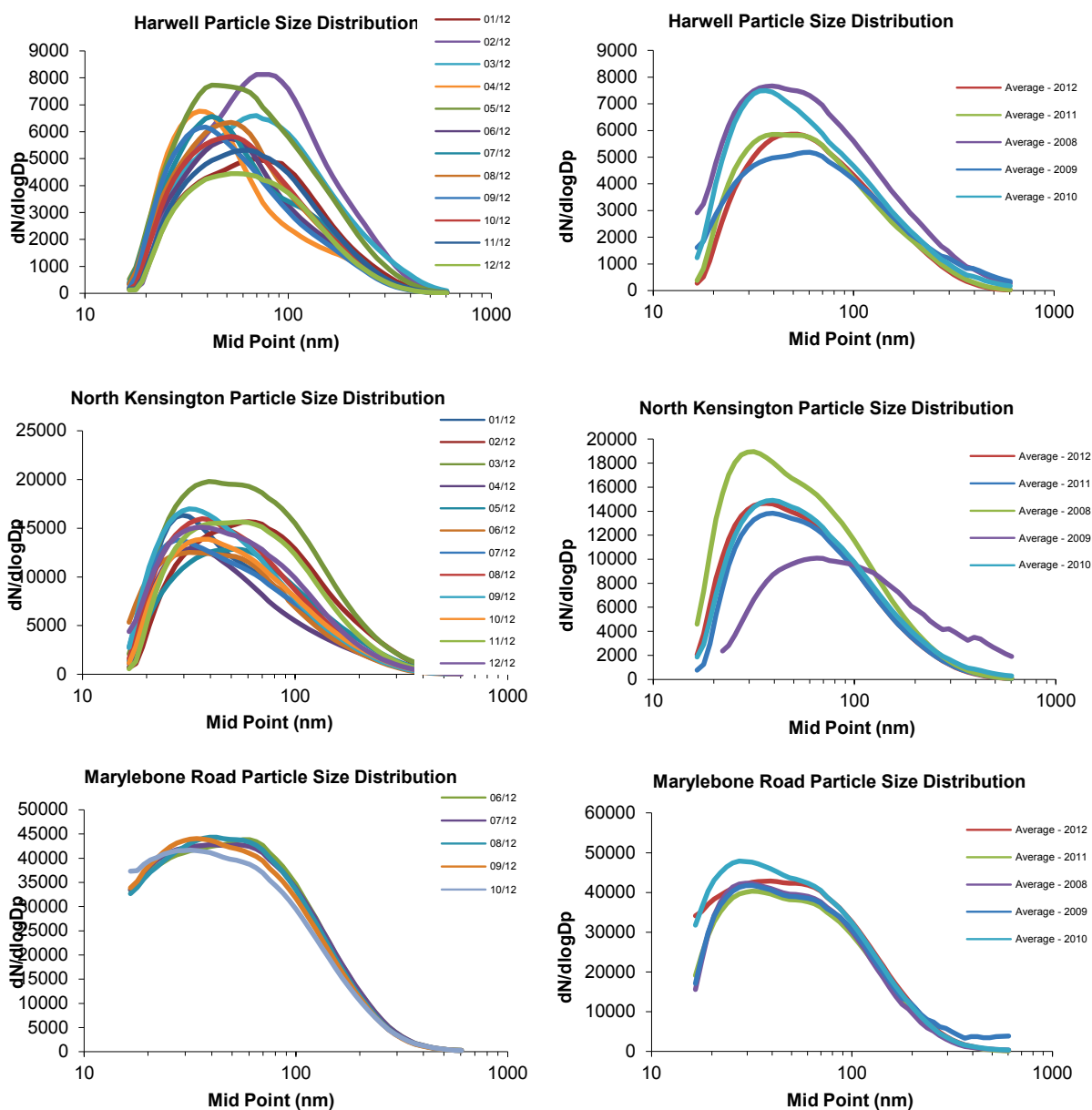
Figure 4-24 Monthly averaged particle size distributions at the Network sites during 2012 [left-hand panels] and comparison of the 2008, 2009, 2010, 2011 and 2012 annual-averaged size distributions [right-hand panels].

[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*

4.4.3   SMPS checks and Intercomparison

Introduction
To assess the performance of the network SMPSs, a series of experiments were carried out in the Airborne Nanoparticles lab at NPL (1 to 4 March 2013). The Marylebone (Mar), Harwell (Har), North Kensington (NK) and NPL SMPSs were tested in parallel, under controlled lab conditions. Similarly to last year's intercomparison (February 2012), both certified latex spheres and soot from a CAST generator were used as calibration aerosols.

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. The configuration used is shown in Figure 4-25. All three network SMPS units, plus the in-house NPL one, were tested in parallel through a simple flow splitter.
The PSL (polystyrene latex) beads aerosols generated, by means of solution nebulisation and subsequent drying, were based on NIST traceable PSLs of 59 ± 2 nm, 92 ± 3 nm, 125 ± 3 nm and 203 ± 5 nm.
In the case of soot particles, a CAST generator was used, with the respective aerosols having nominal particle sizes of 55, 117 and 156 nm, with an additional bimodal distribution also measured.
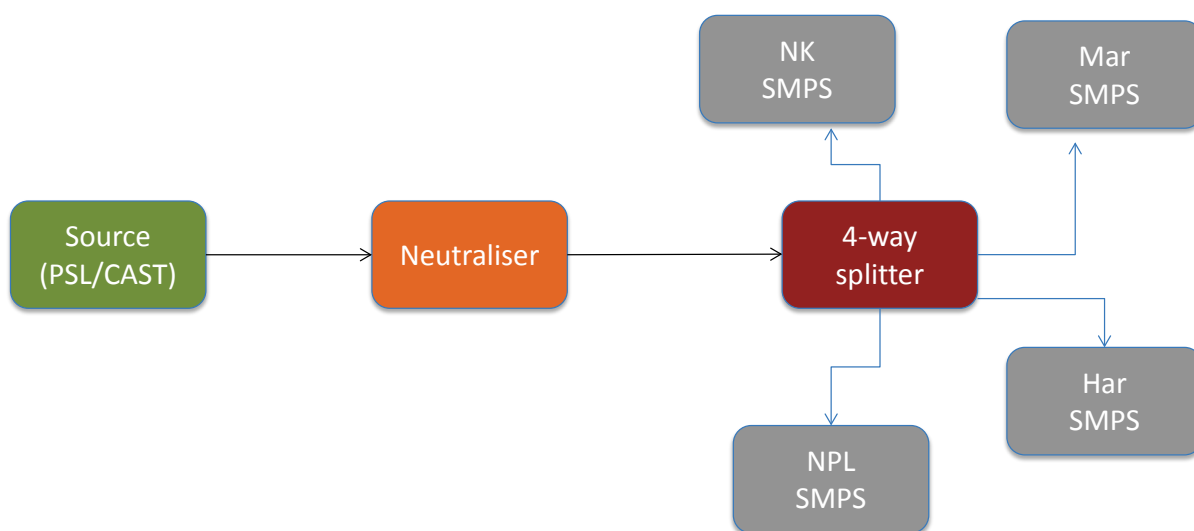
Figure 4-25 Schematic showing the parallel sampling of the four SMPS when connected to a flow splitter and fed with a single particle source (PSL or CAST soot), conditioned with a single neutraliser.

Results and Discussion

PSL
In Table 4-6 the PSL results for the four SMPS instruments are summarised and compared with the nominal diameters of the feeding polystyrene beads. In general, there is very good agreement amongst the four instruments. When compared to the nominal PSL values, there are slight deviations, 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. Also, there is an uncertainty element related to defining the appropriate peaks, since the PSL solutions tend to give non-monomodal peaks due to the presence of surfactants, double-beads etc.

CAST
An example of the bimodal distribution recorded is shown in Figure 4-26, in order to illustrate the overall picture of the four instruments' performance. The agreement is very satisfactory, especially for

the higher size bins. In the region below 40 nm the scans start deviating with respect to particle numbers recorded, revealing a higher uncertainty in the performance of the respective SMPSs in that region.

Sequential scanning of three discreet soot sizes (55, 117 and 156 nm) confirmed the very good agreement in the SMPSs' behaviour (Figure 4-27). The respective distribution modes are in line with the nominal diameters of the source aerosol. There is an indication of slight under-counting for the North Kensington SMPS, especially for the 55 and 117 nm sizes, but this is not significant in operational terms, and the respective distributions appear identical in qualitative terms.

Conclusions
An intercomparison of three network SMPS units (Marylebone, Harwell and North Kensington), and one held at NPL, was performed under controlled lab conditions. The experiments with standard PSL and soot aerosols showed that the four SMPSs can accurately and comparably measure distributions in the nanoparticle scale. Some small variations between instruments were observed in the region below 40 nm, but these are not expected to have any significant effect on the total concentrations, or the characteristics of the distributions reported by the Network.

Table 4-6 Comparison of SMPS measured distributions with polystyrene latex (PSL) nominal values.

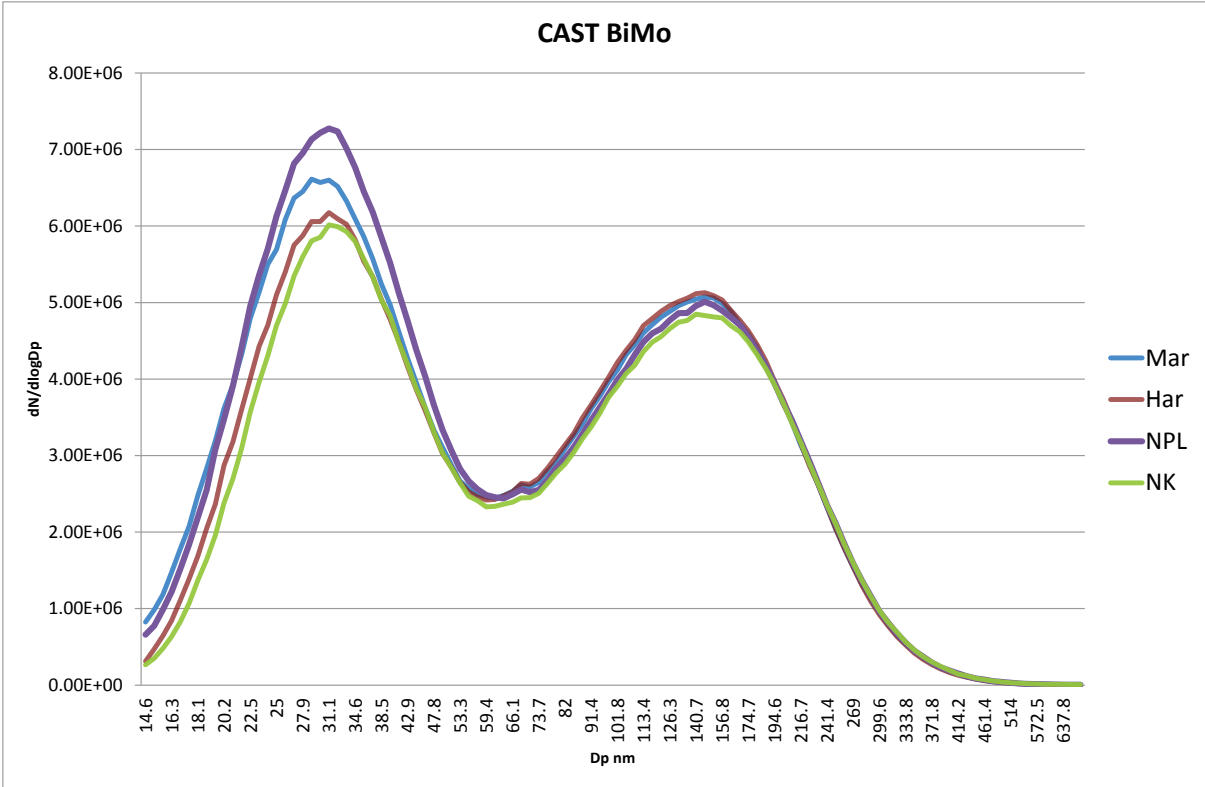| Site		PSL			
		59 ± 2 nm	92 ± 3 nm	125 ± 3 nm	203 ± 5 nm
Mar	Geometric mean	62.84	87.58	126.37	207.68
	Geometric st. dev.	1.16	1.16	1.08	1.18
Har	Geometric mean	62.73	86.95	125.40	207.14
	Geometric st. dev.	1.16	1.15	1.08	1.16
NK	Geometric mean	63.48	90.39	127.66	212.07
	Geometric st. dev.	1.16	1.17	1.07	1.16
NPL	Geometric mean	63.14	88.75	127.98	211.41
	Geometric st. dev.	1.17	1.16	1.07	1.16

Figure 4-26 CAST generated bimodal distribution as measured by the three site SMPS.
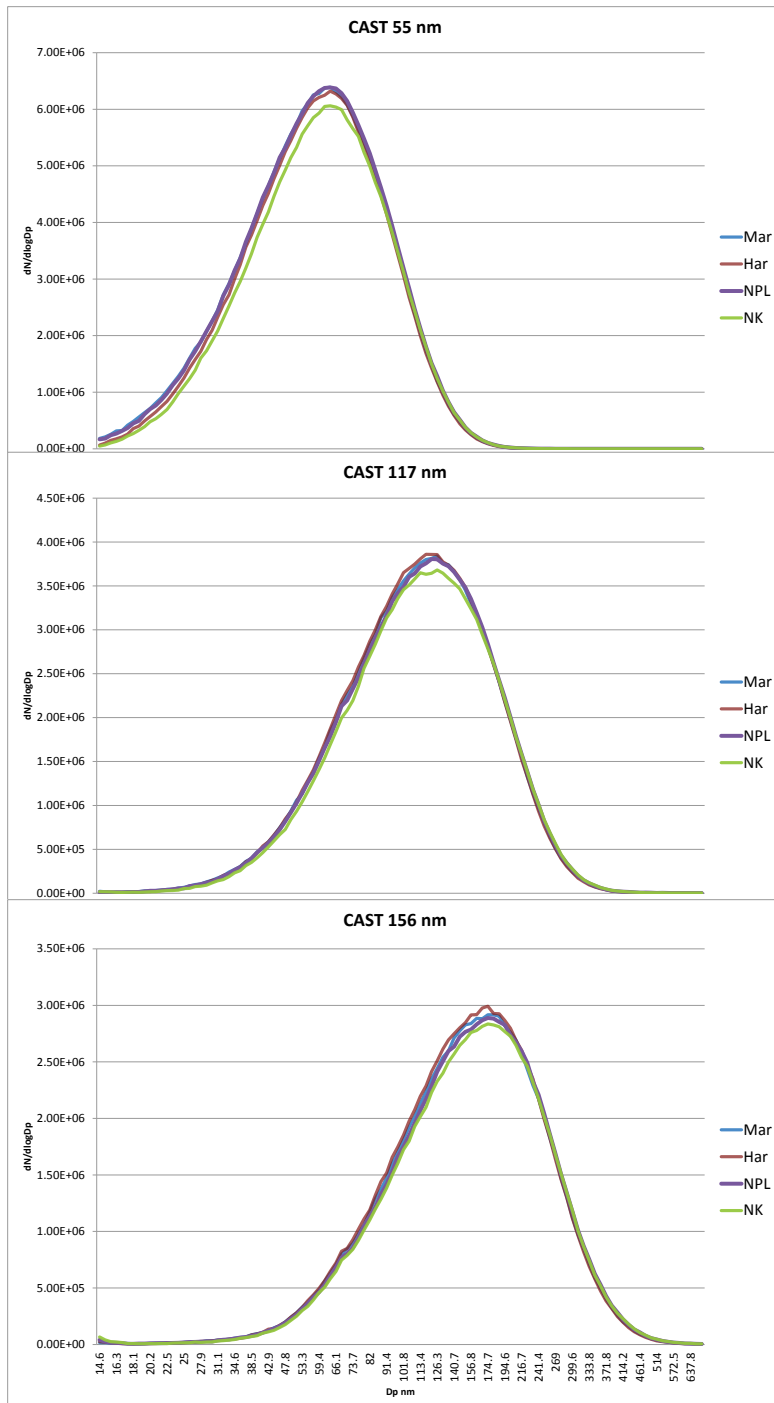
Figure 4-27 SMPS scans of the four site instruments when fed with CAST generated particles at nominal diameters of a) 55 nm, b) 117 nm and c) 156 nm.

4.4.4   Diurnal, weekly and monthly profiles

Diurnal, weekly and monthly profiles have been plotted for the 2012 particle number concentration data using the Openair tools[11,12,13]. Figures 4-28 to 4-31 show the average diurnal profiles across the year and for each day of the week, along with weekly and monthly profiles for all the four sites.

At rural sites like Harwell, the diurnal profile is similar for all days of the week. Concentrations show a minimum at 6am and an increase during the day, probably due to particle formation, which usually occurs during the day. The monthly trend shows a maximum in spring and autumn and a minimum in winter. This is in agreement with nucleation events explained in Section 4.5.2.

At urban and urban background sites, the trends show a strong correlation with anthropogenic sources, with lower concentrations during the weekend. In urban conditions, there is a minimum in summer as a combination of vertical dilution during warm months due to a higher mixing layer, and the summer break which reduces anthropogenic activities.
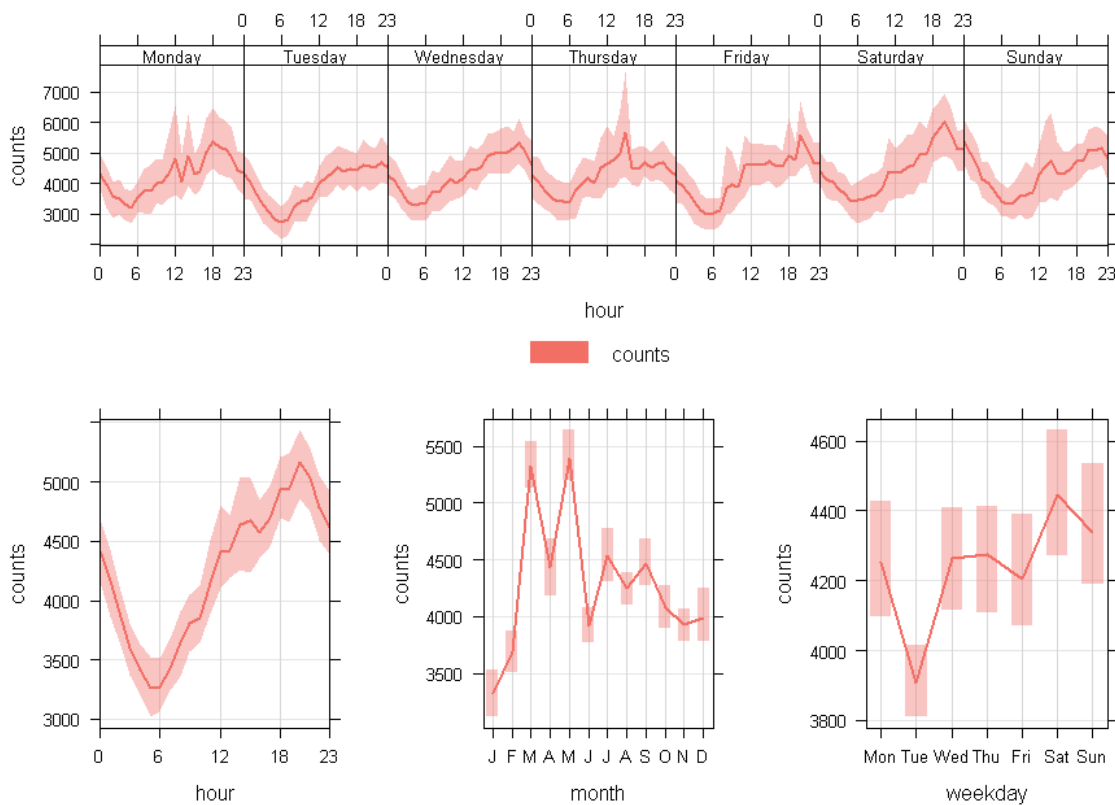
Figure 4-28 Diurnal, weekly and monthly profiles for number concentrations at Harwell in 2012

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[11] The Openair project http://www.openair-project.org/

[12] DC Carslaw and K Ropkins, (2012) OpenAir --- an R package for air   quality data analysis, Environmental Modelling & Software. Volume 27-28, 52-61.

[13] DC Carslaw and K Ropkins (2012). OpenAir: Open-source tools for the analysis of air pollution data, R package version 0.5-23.

Figure 4-29 Diurnal, weekly and monthly profiles for number concentrations at Birmingham in 2012

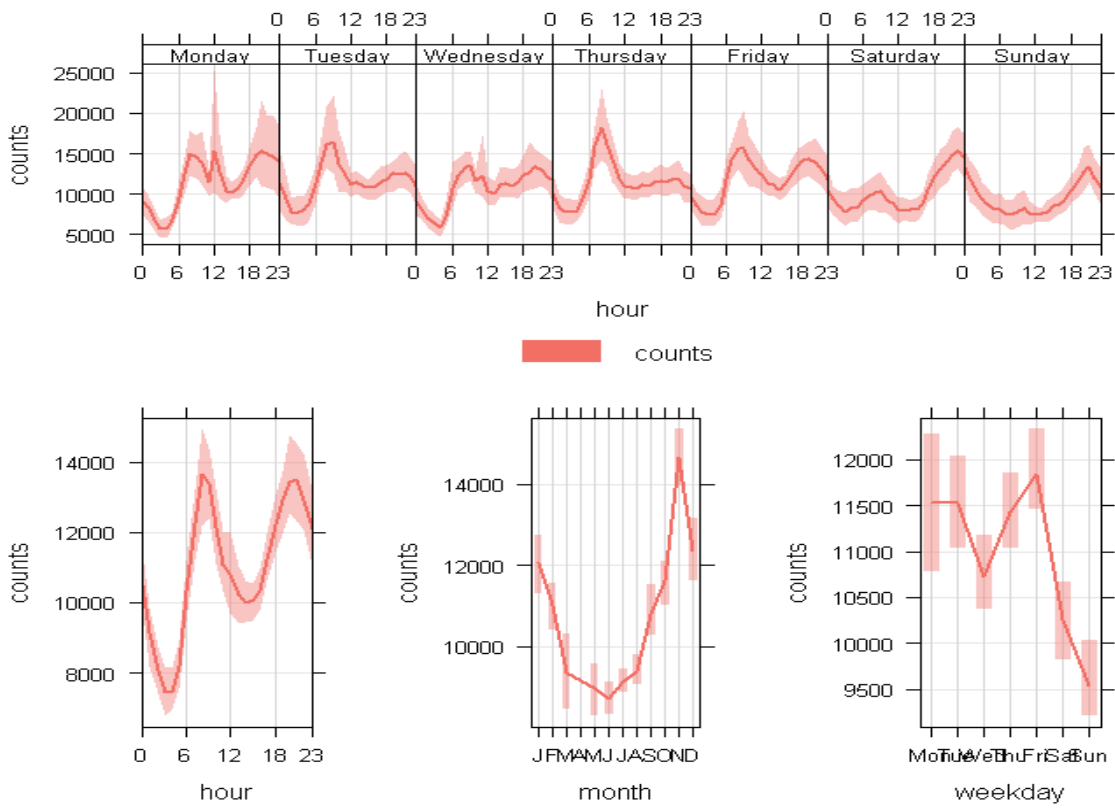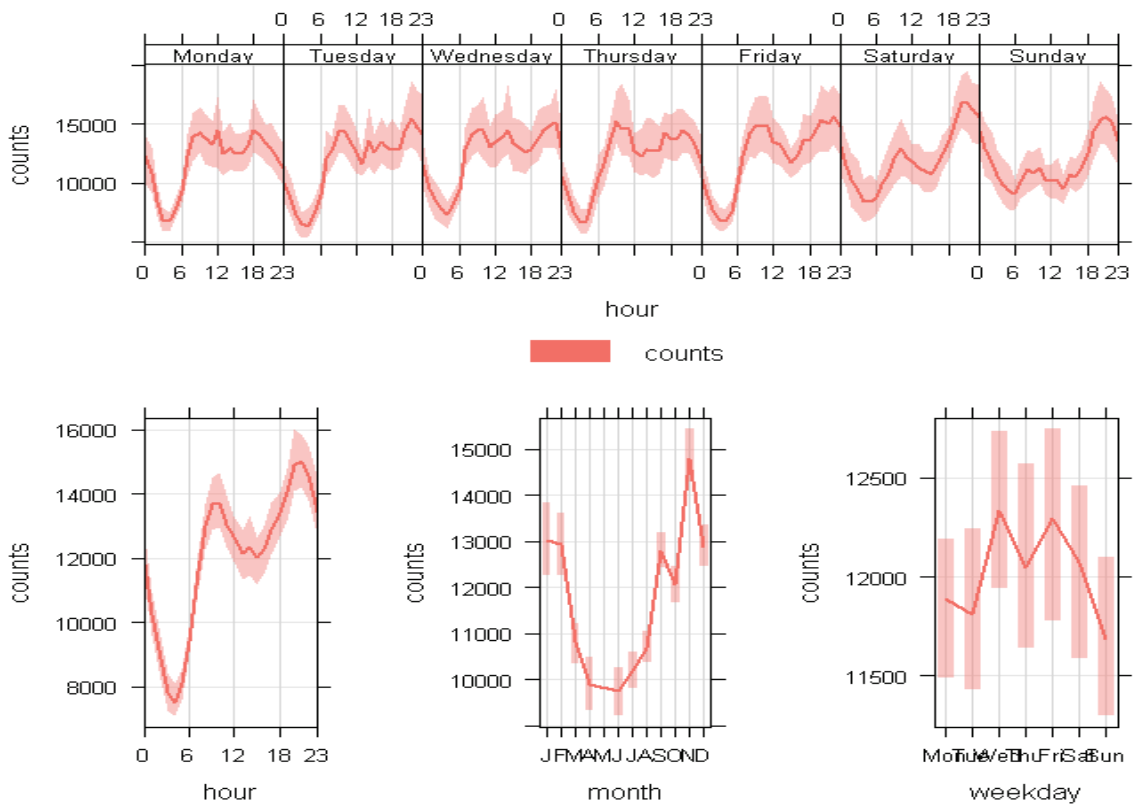**Figure 4-30 Diurnal, weekly and monthly profiles for number concentrations at North Kensington in 2012**
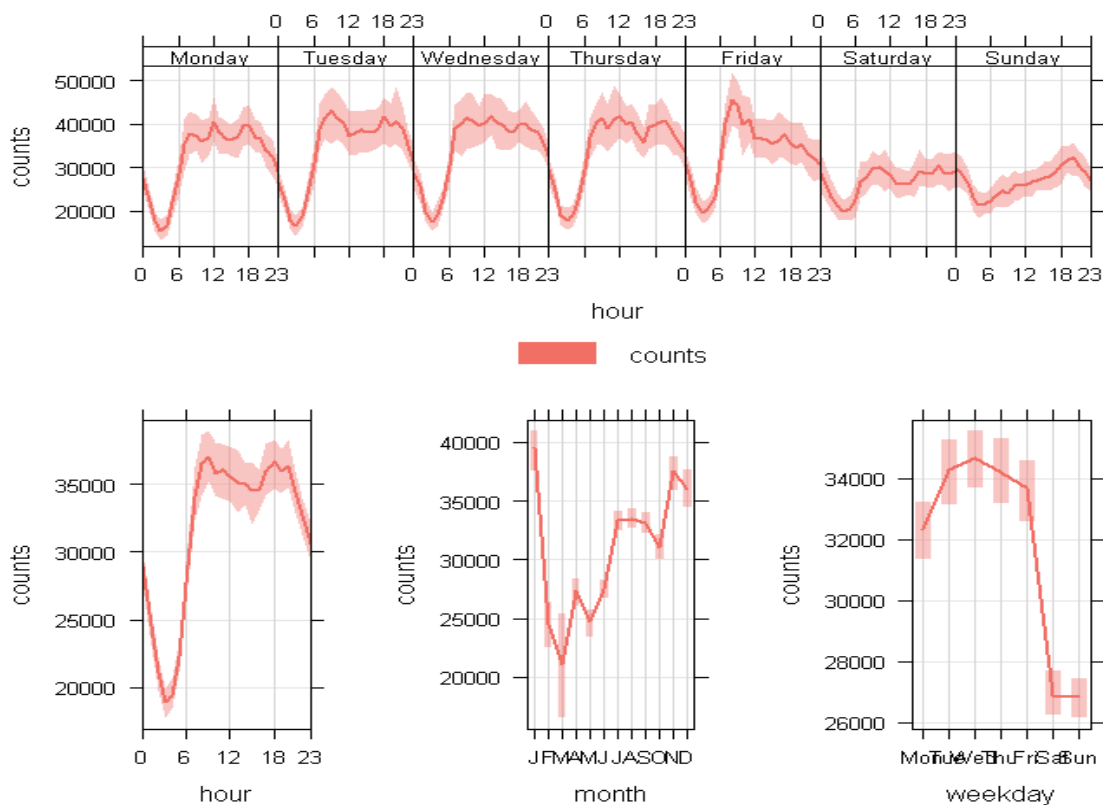
Figure 4-31 Diurnal, weekly and monthly profiles for number concentrations at Marylebone Road in 2012

Using the SMPS measurements in this Network it is possible to observe the trends from different particle sizes and also compare the three locations. Size bins around 20, 200 and 400 nm have been chosen as representatives of the size distribution modes.

It can be seen from Figure 4-32 the profiles of the three sizes at Harwell are quite different. Being a rural site, the particle concentrations are more affected by the chemistry and the physics of the atmosphere, meteorological conditions and long-range transport. For example, the 20 nm and 400 nm size bins follow opposite trends, probably depending on day/night chemistry and the height of the mixing layer.

At North Kensington, the 200 and 400 nm size bin trends show the typical rush hours in the morning and evening, along with domestic heating. Particles with 20 nm diameter seem to have different sources but are possibly connected to domestic heating at night.

At Marylebone Road, in contrast, the trends for the different sizes are strongly correlated, indicating that traffic is the dominant source of particles at this roadside site.

This simple analysis gives a clear indication of differing site characteristics relating to sources of particles at different sizes.

Figure 4-32 Diurnal, weekly and monthly profiles for 3 SMPS size bins at Harwell in 2012

Figure 4-33 Diurnal, weekly and monthly profiles for 3 SMPS size bins at North Kensington in 2012

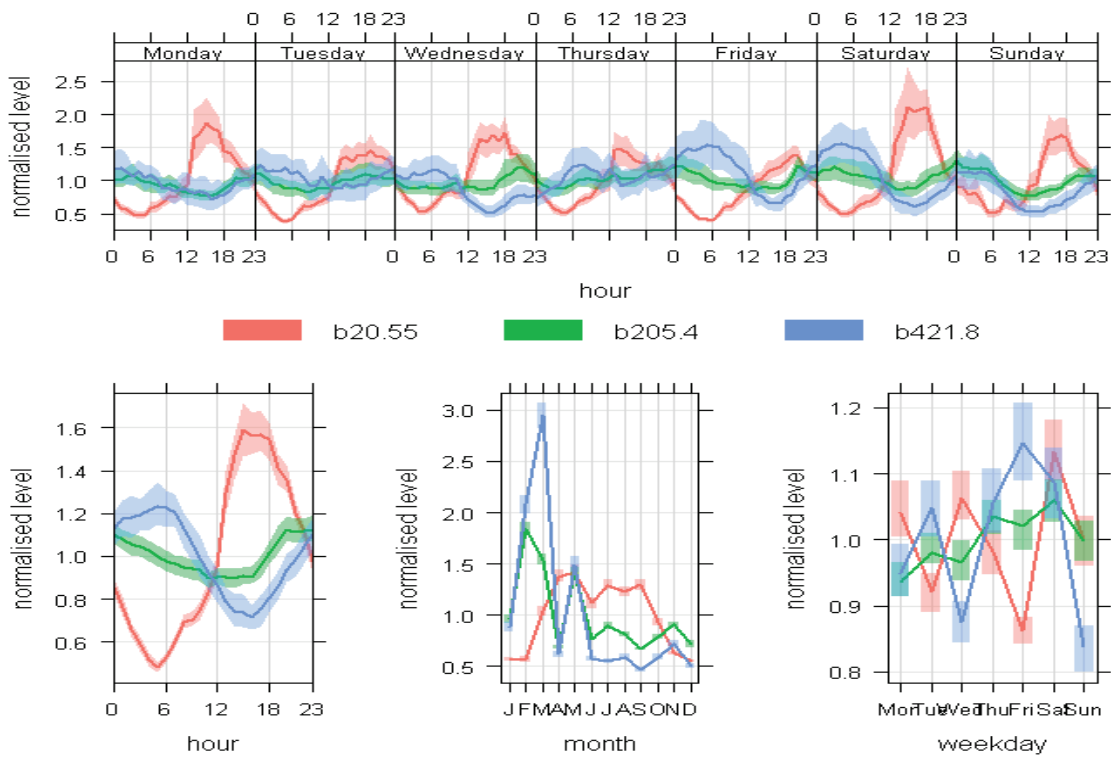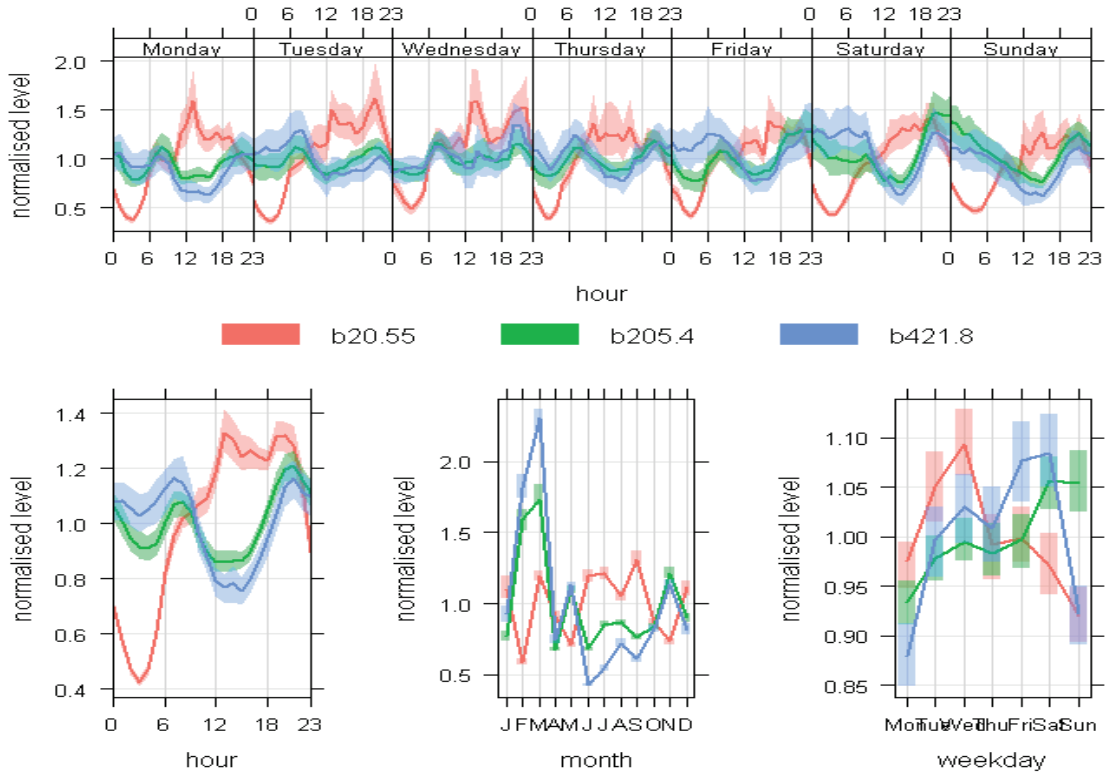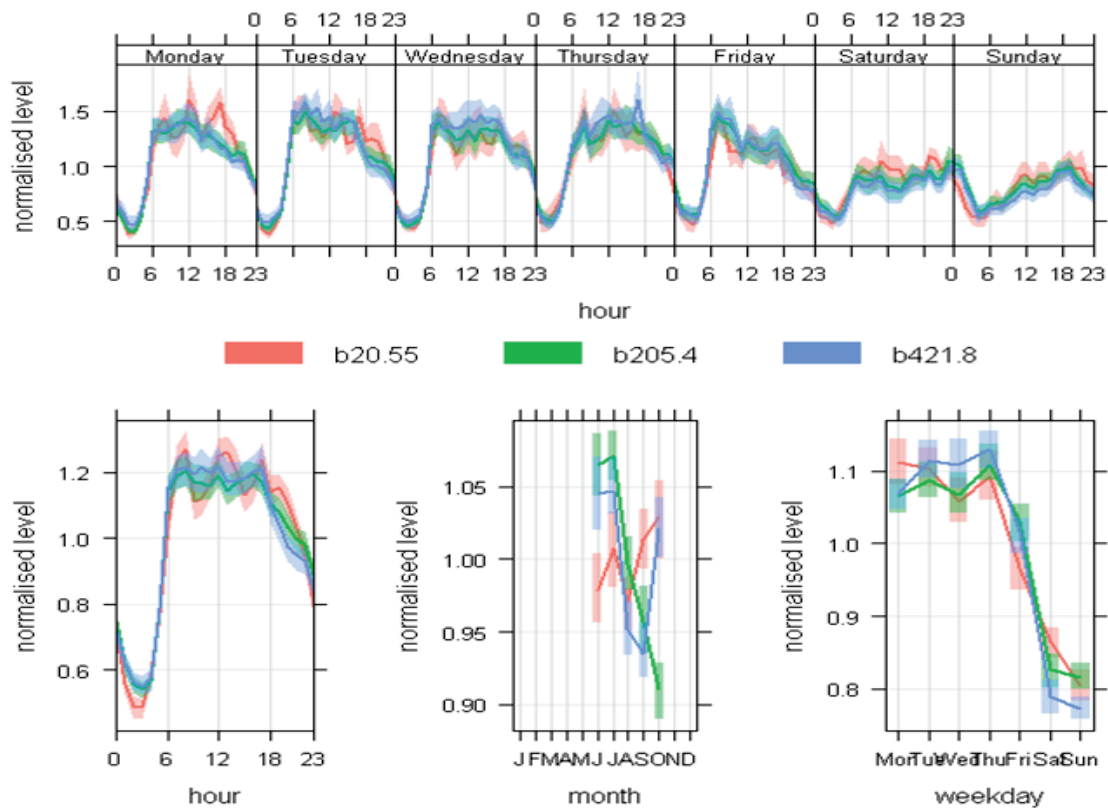**Figure 4-34 Diurnal, weekly and monthly profiles for 3 SMPS size bins at Marylebone Road in 2012**

Figure 4-35 shows long-term monthly trends for CPC measurements. The particle number concentrations at Marylebone Road and North Kensington have been stable after the dramatic drop at the end of 2007 due to the introduction of sulphur-free diesel fuel and of the LEZ (Low Emission Zone)[14].

Legislation enacted in June 2007[15] required that diesel and super-unleaded petrol sold by retailers in the UK for use in road vehicles should be "sulphur free" (less than 50 ppm sulphur)[16] from 4th December 2007, with all UK road vehicle fuel being "sulphur free" (less than 10 ppm sulphur) by 1st January 2009.

The LEZ, which covers the area of Greater London, was confirmed in May 2007[17] and was enforced for heavy goods vehicles (HGVs) greater than 12 tonnes from February 2008, and for other goods vehicles, buses and coaches greater than 3.5 tonnes from July 2008. The London LEZ applies to vehicles using diesel and biodiesel fuels and requires HGVs to comply with EURO III emission standard for particulate matter. The EURO III standard for HGVs does not require the fitting of a particle trap. However, for pre-EURO III vehicles, the most effective form of compliance is likely to have been the retro fitting of a particle trap.

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[14] 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*

[15] SI, 2007. The Motor Fuel (Composition and Content) (Amendment) Regulation 2007. Statutory Instruments 2007 No. 1608. Public Health.

[16] TRL, 2009. Emission factors 2009: report 5 – a review of the effects of fuel properties on road vehicle emissions. In: Boulter, P.G., Latham, S. (Eds.), TRL Published Project Reports 358. TRL, Berkshire, UK.

[17] GLA, 2007. Greater London Low Emission Zone Charging Order, 2006.

Hourly measurements of airborne particle number concentrations at the two sites in London and the site in Birmingham show over a period of few months in late 2007 concentrations were reduced by between 30% and 59 %[18].

The reduction in particle number concentrations occurred immediately prior to the requirement for all diesel fuel for use in highway vehicles to be "sulphur free" and the commencement of enforcement of the London LEZ. No similar change was seen in the particle number concentrations associated with the later removal of "sulphur free" from sale or with the enforcement of the LEZ on lighter vehicle. Given the simultaneous drop of concentration at Birmingham centre, it is probable that the reduction is due to change in fuel rather than the introduction of the London LEZ. Although, the greater reduction in particle number concentration in comparison to NOx at Marylebone Road than at Birmingham means that it is not possible to exclude a minor influence of the LEZ at the two London sites[18].

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[18] 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*
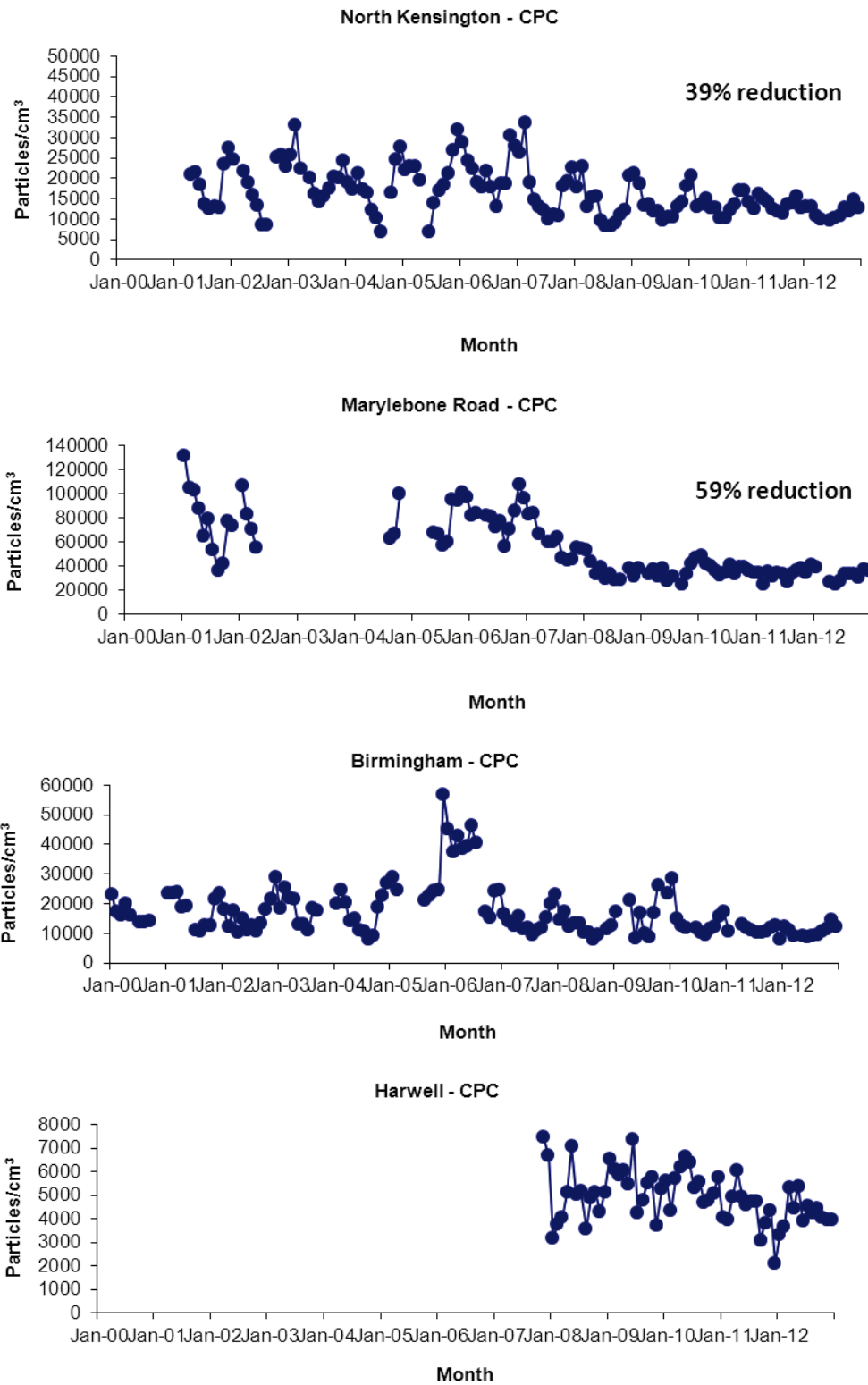
Figure 4-35 Number concentration long-term monthly trends

5   ANALYSIS OF PM$_{10}$ POLLUTION EPISODES

5.1   POLLUTION EPISODES

The measurements made on this network allow a more detailed examination of the composition and causes of pollution episodes. Analysis is provided here, highlighting the key points and drawing some conclusions regarding the sources of pollution episodes at the stations in the network which measure chemical composition (Harwell, North Kensington and Marylebone Road). For the purpose of this analysis, an episode is defined as a day when the mean PM$_{10}$ concentration breached the European Air Quality Directive Limit Value of 50 µg m^{-3}.

Several pollution episodes were identified in 2012, which occurred mainly in London and the South East of England. A list of the episodes which affected the network measurements with a brief description is given below.

- A high pressure system over the country led to cold settled conditions and a low altitude easterly air flow, bringing pollution in from the continent to combine with local emissions. This resulted in widespread 'moderate' PM$_{10}$ and PM$_{2.5}$ on **31st January**.

- The episode started on **3rd February** and continued until a change in air mass on the afternoon of **12th February**. Widespread 'moderate' PM$_{10}$ and PM$_{2.5}$ levels were recorded across the region on most days over this period, along with occasional 'moderate' NO$_2$ in some busy roadside locations.

- 'Moderate' PM$_{10}$ and PM$_{2.5}$ particulate levels were recorded across much of London and the south east from 29th February until 3rd March. 'High' PM$_{2.5}$ particulate levels, and to a lesser extent 'high' PM$_{10}$ levels, were also recorded in heavily trafficked roadside locations across London on **1st and 2nd March**.

- South-East England suffered a severe fine particulate pollution episode between **12th and 15th March**. PM$_{2.5}$ concentrations in London on 15th March were at their greatest since measurements with EU reference equivalent instruments began in late 2008.

- The third particulate pollution episode of March was widespread and prolonged, peaking on **23rd March** with widespread 'very high' PM$_{2.5}$ being recorded across London. Only isolated 'moderate' particulate was recorded on **26th and 27th March**. Rising levels of PM$_{10}$ and PM$_{2.5}$ from **early 28th March** resulted in widespread 'moderate' PM$_{10}$ and PM$_{2.5}$ through until **30th March,** with some 'high' PM$_{10}$ at busy roadside and industrial locations.

- Widespread 'moderate' PM$_{2.5}$ and PM$_{10}$ particulates were measured in London between **22nd May** and **24th May** after the change to warm weather. This was caused by the combination of polluted air from outside London and London's own emissions.

- Widespread moderate ozone affected London and South-East England on **24th July**. The moderate ozone was caused by the action of sunlight and high temperatures on pollution emitted from vehicles and industry. High PM$_{10}$ was measured at Shepherds Bush (North Kensington area) due to the combination of traffic and local construction works.

- 'Moderate' ozone affected London during the **last three days of the 2012 Olympic Games in August**. This pollution episode resulted from a period of calm sunny conditions with air circulating over the UK and the near continent.

- Elevated particulate was measured across London and South-East England from **22nd October** as calm and foggy conditions led to a build-up of local emissions and combined with an easterly airflow that brought pollution from the continent. PM_{10} and $PM_{2.5}$ reached 'moderate' at a small number of sites. A further rise in particulate levels occurred on the afternoon and evening of 23rd October, continuing into the morning of the 24th October.

- Widespread 'moderate' PM_{10} was measured at several busy roadside sites on **15th November**, including sites in central and outer London, and in Reading. 'Moderate' $PM_{2.5}$ was also measured at several roadside sites and a small number of background sites. The elevated particulate levels were caused by calm, foggy conditions with light winds leading to poor dispersion of local emissions.

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

5.1.1 PM$_{10}$ pollution episodes

Firstly, an analysis of the frequency and magnitude of the pollution episodes during 2012 and previous years was undertaken. To provide maximum data capture across all sites, a composite data set was constructed. This was firstly populated with the results of the measurements made using the FDMS, gaps in the data were then filled with mass concentrations from filter measurements (AURN network). The days with mean PM$_{10}$ concentration at each site greater than 50 µg m^{-3} during 2012 are listed in Table 4-7. Unsurprisingly, Marylebone Road measured PM$_{10}$ concentrations greater than 50 µg m^{-3} on the largest number of days (27), followed by North Kensington (12) and Harwell (3). The magnitude of the PM$_{10}$ concentrations also differed markedly; the maximum at Harwell was 54 µg m^{-3}, at North Kensington 76 µg m^{-3} and at Marylebone Road 87 µg m^{-3}. On days when Harwell measured PM$_{10}$ concentrations greater than 50 µg m^{-3}, the other two sites also measured concentrations greater than 50 µg m^{-3}. On these days the difference between all the sites was <20 µg m^{-3} and between the London sites it was <10 µg m^{-3}.

Date	Harwell	Marylebone Road	North Kensington
16/01/2012		55	
17/01/2012		63	
31/01/2012		58	51
04/02/2012		53	
06/02/2012		56	
09/02/2012		52	
10/02/2012		58	
11/02/2012		66	58
12/02/2012		66	56
29/02/2012		63	
01/03/2012		78	52
02/03/2012	51	70	61
09/03/2012		53	
14/03/2012		62	52
15/03/2012		87	69
16/03/2012		59	
22/03/2012	54	68	63
23/03/2012		80	76
24/03/2012	54	65	62
29/03/2012		61	
30/03/2012		58	56
01/08/2012		53	
24/10/2012		67	65
06/11/2012		56	
16/11/2012		54	
12/12/2012		59	
13/12/2012		62	
Total	**3**	**27**	**12**

Table 4-7 date and daily mean concentration measured at each site when greater than 50 ug m^{-3}

During 2012, PM$_{10}$ pollution episodes predominantly occurred in the winter and spring time; with the majority occurring during February and March, and only one in August at Marylebone Road. This distribution is typical of PM$_{10}$ concentrations in the UK[19] and is compared to 2009-2011 in Figure 4-36. The number of pollution episodes during the winter at Marylebone Road was were lower than the

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[19] Green, D.C. and G.W. Fuller, *Characterising the PM climate in the UK for Equivalence Testing*, 2012, King's College London.

average in previous years; this may be due to a reduction in primary emissions as suggested by some studies[20] or fewer days when meteorological conditions favoured the build-up of locally emitted PM.
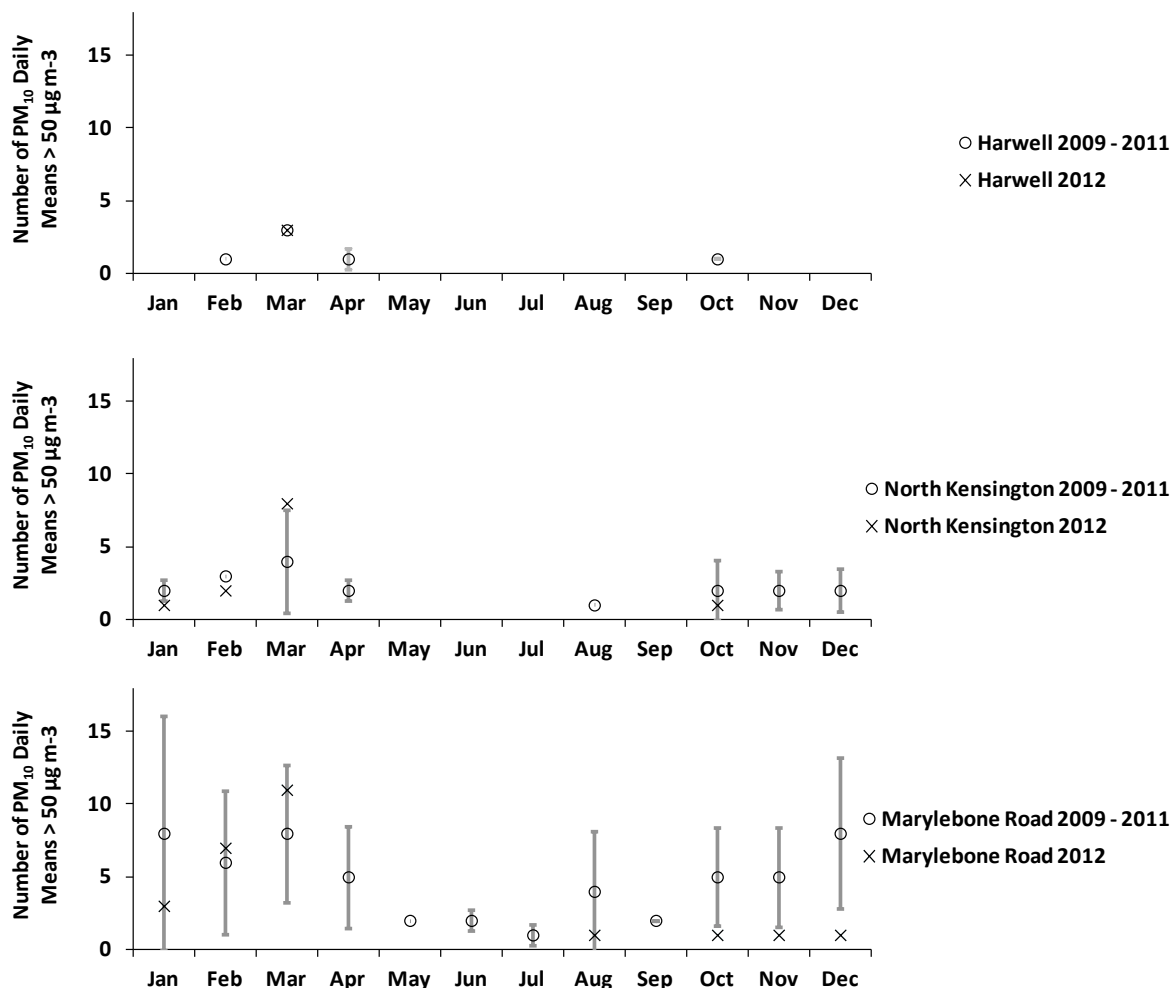

Figure 4-36 Comparison of days where PM10 > 50 μg m^{-3} during 2012 compared to average of 2009-2011. Error bars show standard deviation.

5.1.2   Average PM$_{10}$ composition

The measurements from this network are able to characterise many of the bulk chemical components that constitute PM$_{10}$ in the UK at a daily time resolution or higher. These include inorganic ions measured using the URG ion monitor (Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, NO$_3^-$, SO$_4^{2-}$), elemental carbon and organic carbon. Unfortunately, the concentrations of other elements, (e.g. Fe, Si, Ba, Cu) typical of the mineral components found in PM$_{10}$ and non-exhaust emissions, which contribute substantially to the mass concentration[21], are not available. Nevertheless, the available measurements can be analysed to gain insight into the sources of PM$_{10}$ mass through a mass closure analysis, whereby the individually measured components are combined along with enrichment factors to reconstruct the PM$_{10}$ mass. As only EC and OC measurements are available from this network for Harwell, this analysis is limited to North Kensington and Marylebone Road.

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[20] Jones, A.M., et al., *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, 2012. **50**(0): p. 129-138.

[21] Harrison, R.M., et al., *Estimation of the Contributions of Brake Dust, Tire Wear, and Resuspension to Nonexhaust Traffic Particles Derived from Atmospheric Measurements.* Environmental Science & Technology, 2012. **46**(12): p. 6523-6529.

Mass closure methodology

Many of the chemical components (e.g. EC, inorganic ions) can be summed directly; however the sources of organic aerosol are more complex; it can be emitted directly into the atmosphere or result from gas-to-particle conversion processes. Once in the atmosphere it ages through oxidation and the addition of low and semi-volatile products of photochemical reactions; this results in the molecular weight per carbon weight for the organic aerosol increasing with aerosol age. To enable the measured OC concentration to reflect this, it was differentiated into source categories: Primary Organic Aerosol (POA) and Secondary Organic Aerosol (SOA) using the EC tracer method[22]. In this case, an increment-based approach was used to calculate the $(OC/EC)_{fossil\ fuel}$ by subtracting the North Kensington OC and EC concentrations from those measured at Marylebone Road. For 2012, this resulted in a mean $(OC/EC)_{fossil\ fuel}$ value of 0.63, which is higher than the 0.3-0.4 range reported using a similar approach in Birmingham[18]. However, the Birmingham measurements date from 2005-6 and there is evidence of an increasing trend in the mean $(OC/EC)_{fossil\ fuel}$ in London which has risen from 0.38 in 2008 as shown in Figure 4-37; though more data would be required to confirm any trend.
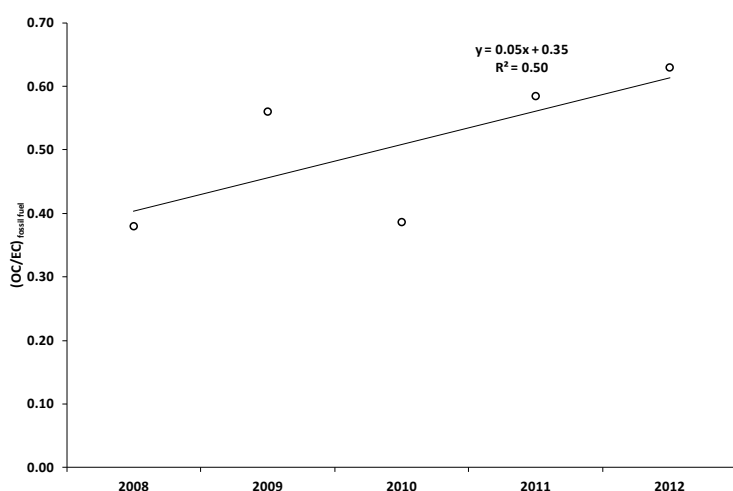

Figure 4-37 London (OC/EC) fossil fuel 2008 – 2012.

The POA and SOA at each site was calculated by using the equation originally derived by Turpin et al[23]

$$POA = EC \times (OC/EC)_{minimum}$$
$$SOA = OC\text{-}POA$$

An increment approach[24] is then taken to apportion the total SOA between Regional Secondary Organic Aerosol (RSOA) and Urban Secondary Organic Aerosol (USOA). The SOA calculated at North Kensington (3.37 μg m^{-3}) is a similar magnitude to the SOA at Marylebone Road (3.34 μg m^{-3}) and shows a reasonable agreement in Figure 4-38 (left). The USOA was calculated as the difference between SOA measured at the Harwell rural site and the SOA measured at the sites in London. The OC measured at Harwell was simply split into POA and RSOA while OC at North Kensington and Marylebone Road was partitioned into POA, USOA and RSOA. The USOA should be uniform over London, the USOA at North Kensington (1.27 μg m^{-3}) is a similar magnitude to the USOA at Marylebone Road (1.25 μg m^{-3}) and shows a reasonable agreement in Figure 4-38 (right). Given the

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[22] Pio, C., et al., *OC/EC ratio observations in Europe: Re-thinking the approach for apportionment between primary and secondary organic carbon.* Atmospheric Environment, 2011. **45**(34): p. 6121-6132.
[23] Turpin, B.J. and J.J. Huntzicker, *Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS.* Atmospheric Environment, 1995. **29**(23): p. 3527-3544.

[24] Lenschow, P., et al., *Some ideas about the sources of PM10.* Atmospheric Environment, 2001. **35, Supplement 1**(0): p. S23-S33.

geographical distance between Harwell and London (approx 90 km) and the diversity of sources of OC in both the urban and rural environment, these results demonstrate that this method is robust for apportioning organic aerosol into different classes.
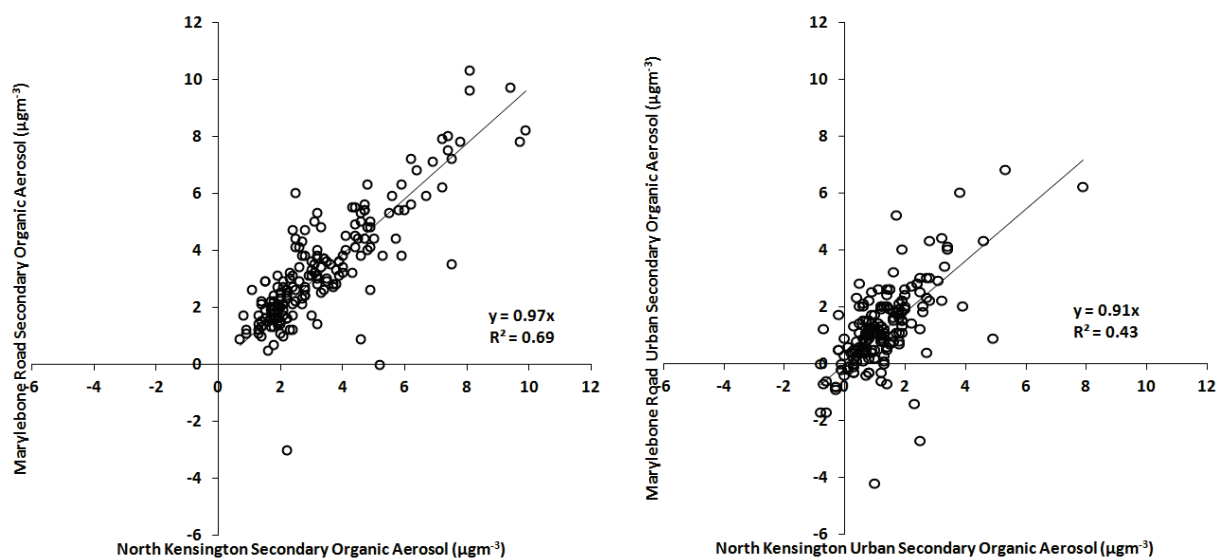

Figure 4-38 Relationship between total SOA (left) and USOA (right) calculated at North Kensington and Marylebone Road

The concentrations of the remaining measured chemical components were used in the analysis with the exception of Na. The concentrations of Na were found to be much larger than would be expected from a predominantly marine aerosol. They also did not correlate well with Cl or ICPMS measurements of Na^+ from the NERC ClearfLo study. This is most probably due to the chromatography issues discussed in Section 4.4.2. Na^+ concentrations were therefore substituted with a value of Cl*0.61 to provide a mass of Na^+ in NaCl. No factors were applied to the organic aerosol measurements to account for the associated O and H atoms in the organic aerosol. Factors in the literature are predominantly based on measurements made in the USA[25] and when applied here, these were found to lead to large organic mass values which, when combined with the other measured chemical components, resulted in a PM_{10} mass greater than that measured directly despite the absence of concentrations of mineral and abrasion sources of PM_{10} in our analysis. Further work is therefore required to identify accurate factors which account for the mass of organic matter in current UK conditions.

The reconstructed mass of PM_{10} was compared to the measured mass of PM_{10} for North Kensington in Figure 4-39 (left) and for Marylebone Road in Figure 4-39 (right). This comparison was restricted to days when all measurements were available for North Kensington (n=77) and for Marylebone Road (n=98). The measured mass is a combination of FDMS PM_{10} measurements supplemented by filter measurements on any missing days. It is clear that chemical components measured by the network make up the majority of the measured mass concentration; this missing mass can be attributed to the organic mass (unaccounted for here), mineral and abrasion sources.

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[25] Turpin, B.J. and H.-J. Lim, *Species Contributions to PM2.5 Mass Concentrations: Revisiting Common Assumptions for Estimating Organic Mass.* Aerosol Science and Technology, 2001. **35**(1): p. 602-610.
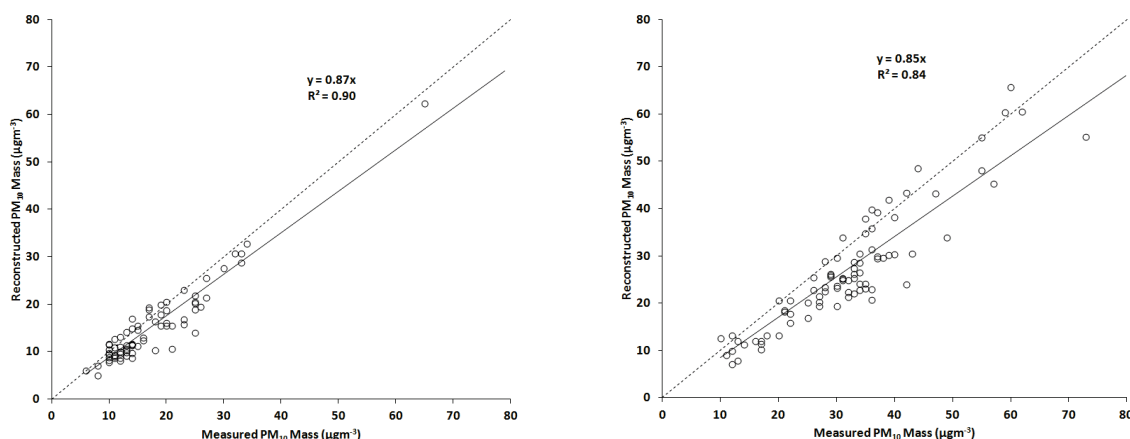
Figure 4-39 Correlation between measured mass and reconstructed mass for North Kensington (left) and Marylebone Road (right). The dotted line represents 1:1 correlation.

The chemical composition as a percentage of the PM_{10} measured using all available data is shown as pie charts in Figure 4-40 for North Kensington (left) and Marylebone Road (right); the mass concentrations are also shown in Table 4-8. All available days were used, as contemporaneous days resulted in a small and unrepresentative dataset, while using only days when all parameters were available at each site led to distinctly different atmospheric conditions being compared.

Table 4-8 Measured chemical composition of the PM_{10} for North Kensington, Marylebone Road and the calculated roadside increment

	North Kensington	Marylebone Road	Roadside Increment
PM_{10} (µg m^{-3})	20.2	30.8	10.5
Elemental Carbon (µg m^{-3})	1.0	6.3	5.3
Primary Organic Aerosol (µg m^{-3})	0.7	3.7	2.9
Local Secondary Organic Aerosol (µg m^{-3})	1.3	1.3	0.0
Regional Secondary Organic Aerosol (µg m^{-3})	2.1	2.1	0.0
Chloride (µg m^{-3})	1.4	1.1	-0.2
Nitrate (µg m^{-3})	3.1	5.0	1.8
Sulphate (µg m^{-3})	1.8	2.5	0.7
Ammonium (µg m^{-3})	1.4	1.9	0.6
Sodium (µg m^{-3})	0.8	0.7	-0.1
Potassium (µg m^{-3})	0.5	0.5	0.1
Magnesium (µg m^{-3})	0.1	0.1	0.0
Calcium (µg m^{-3})	0.2	0.4	0.2
Particle Bound Water (µg m^{-3})	0.8	1.1	0.3
Unidentified Mass (µg m^{-3})	2.3	5.1	2.7

Figure 4-40 shows that the chemical components that are associated with traffic sources (elemental carbon, POA) are elevated as a percentage of the PM_{10} mass at Marylebone Road compared to the other sites. Conversely, the non-traffic components contribute a lower percentage to PM_{10} mass at Marylebone Road than they do at North Kensington. There is a larger percentage of unidentified mass at Marylebone Road, which is consistent with the stronger mineral and abrasion sources at this location[26].

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[26] Harrison, R.M., et al., *Estimation of the Contributions of Brake Dust, Tire Wear, and Resuspension to Nonexhaust Traffic Particles Derived from Atmospheric Measurements.* Environmental Science & Technology, 2012. **46**(12): p. 6523-6529.
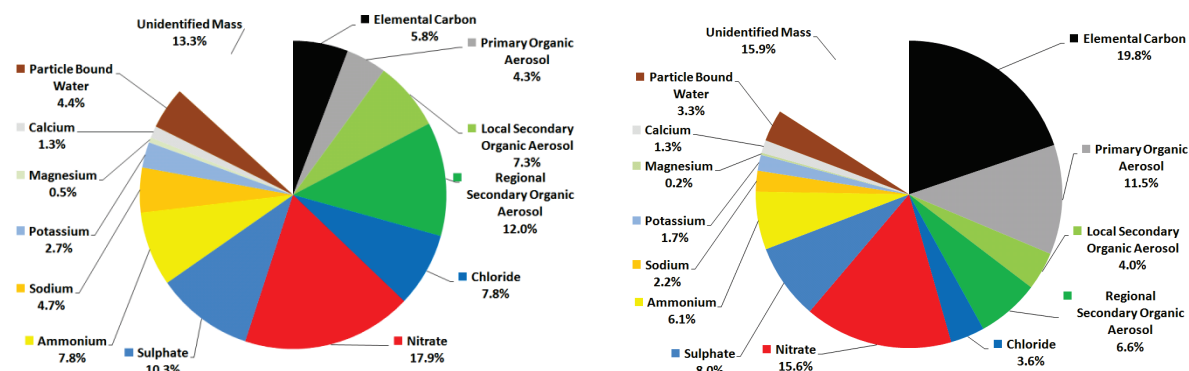
Figure 4-40 Chemical composition as a percentage of the PM$_{10}$ for North Kensington in (left) and Marylebone Road in (right)

Table 4-8 shows the chemical composition of the PM$_{10}$ for North Kensington and Marylebone Road, and the calculated roadside increment, reported as concentrations. As in Figure 4-40, this shows the elevated concentrations associated with traffic sources (elemental carbon, POA and unidentified mass), however, it also highlights increments in nitrate, sulphate and ammonium. This roadside increment in nitrate may be a result of the rapid oxidation of NO$_X$ by OH to form HNO$_3$ and then neutralisation by any excess ammonia present, alternatively at night NO$_2$ and ozone can react to form N$_2$O$_5$. The increment in sulphate concentrations may be a result of local soluble mineral sources. Alternatively, the difference between the nitrate and sulphate measurements at the two locations may be a simple artifact of the experimental uncertainty.

5.1.3   PM$_{10}$ composition during episodes

The analysis of when pollution episodes occurred demonstrated that they happen at different times and for different reasons, whether due to a build-up of local emissions or the transport of secondary aerosol from more distant sources. A detailed analysis of each individual episode is beyond the scope of this report, nevertheless, the relationship between the chemical components and PM$_{10}$ mass concentrations can be examined to help understand which components, and therefore sources, are most important during episode conditions.

To achieve this, the PM$_{10}$ mass concentration was grouped into 10 µg m^{-3} bins (0-10, 10-20 etc) and the corresponding concentrations of each chemical component were averaged for each bin. The results of the five most important chemical components by mass are shown for North Kensington in Figure 4-41 (top) and for Marylebone Road in Figure 4-41 (bottom). To allow an interpretation of the importance of the organic aerosol mass, the factors recommended by Turpin et al[27] have been applied; these are 1.4 for POA, 1.6 for LSOA and 2.1 for RSOA. These factors were found to increase the mass of organic aerosol beyond the mass of measured PM$_{10}$ when all measured components were summed, so should be considered with some caution.

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[27] Turpin, B.J. and H.-J. Lim, *Species Contributions to PM2.5 Mass Concentrations: Revisiting Common Assumptions for Estimating Organic Mass.* Aerosol Science and Technology, 2001. **35**(1): p. 602-610.
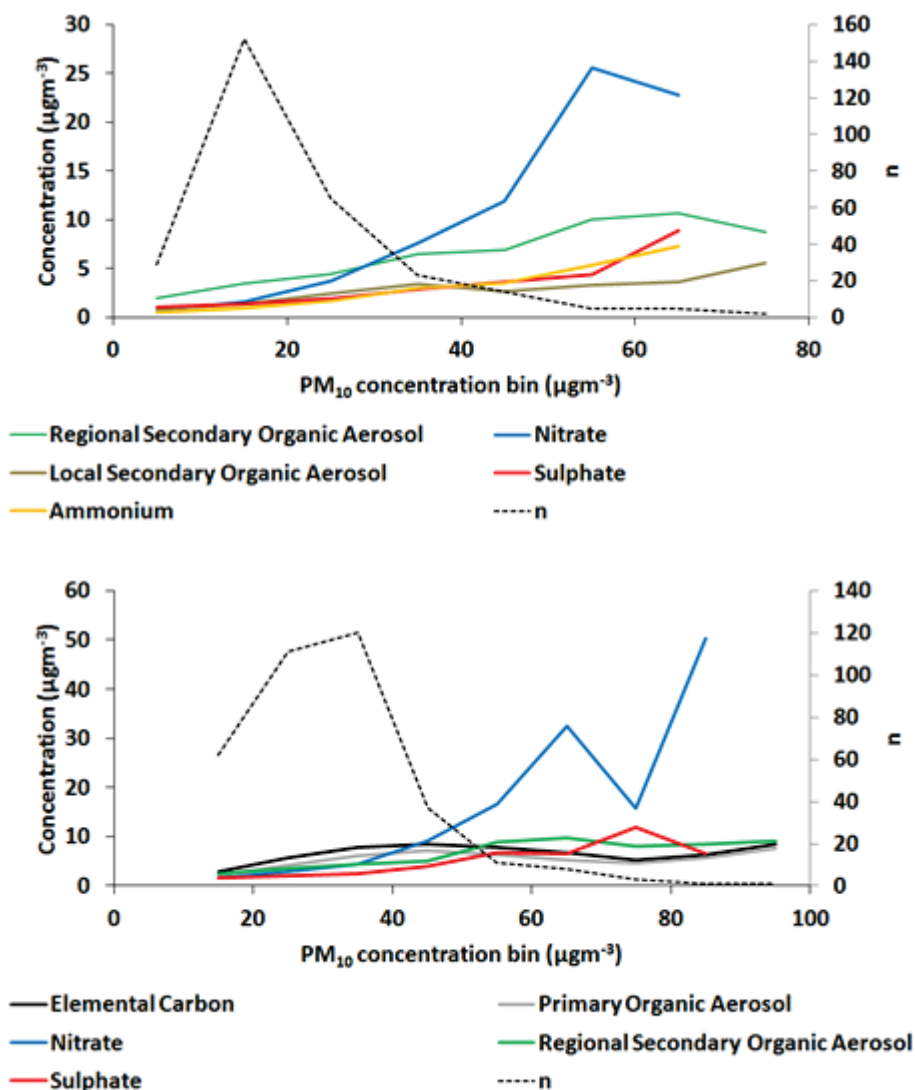
Figure 4-41 Top five contributors to PM$_{10}$ mass at North Kensington (top) and Marylebone Road (bottom) grouped by 10 μg m^{-3} increments in mass

It is clear that some components contribute a greater percentage of the PM$_{10}$ mass during episodes than during periods when concentrations are lower. At North Kensington, the secondary components of PM$_{10}$ (nitrate, sulphate, ammonium, RSOA, LSOA) are the most important during episodes, making up 41%, 11%, 10%, 16% and 6% of the daily mean concentrations over 50 μg m^{-3} respectively. At Marylebone Road, both the primary (EC, POA) and secondary components (nitrate, sulphate, RSOA) of PM$_{10}$ are important during episodes making up 10%, 8%, 40%, 11% and 12% of the daily mean concentrations over 50 μg m^{-3} respectively.

At both North Kensington and Marylebone Road, nitrate is the dominant component during episodes, however, the measurements available here are not capable of differentiating between sodium and ammonium nitrate. A previous study in London[28] found that approximately 60 % of nitrate was found in the fine fraction and could therefore be assumed to be ammonium nitrate, the remainder being sodium nitrate; however, during episode conditions nitrate is expected to be found predominantly as

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[28] Harrison, R.M., A.M. Jones, and R.G. Lawrence, *A pragmatic mass closure model for airborne particulate matter at urban background and roadside sites.* Atmospheric Environment, 2003. **37**(35): p. 4927-4933.

ammonium nitrate. This ammonium nitrate has been shown to originate from local and more distant sources[29].

It is essential to consider that although nitrate and other some of the secondary components are the most important components during episodes, contributing approximately 82% of the PM_{10} mass at North Kensington and 72% of the PM_{10} mass at Marylebone during these periods, the concentration of all components of PM_{10} increases during episode conditions. The components of PM_{10} that can be considered local (EC, POA, USOA although not including any locally generated nitrate) still contribute significantly during episode conditions; 10-15% of the mass of PM_{10} at North Kensington and 24% of the PM_{10} mass at Marylebone Road. Furthermore, the predominately locally generated abrasion sources of PM_{10} are not considered here; these would also add to the mass of PM_{10} that could be considered to be generated locally.

5.2   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 2012 are displayed in Table 4-9. A summary of the data is given in Annex 1.

Table 4-9 Monthly data capture for meteorological instruments at Rochester in 2012

	Data capture
January	100%
February	100%
March	100%
April	94%
May	100%
June	97%
July	100%
August	98%
September	100%
October	99%
November	99%
December	91%
Average	98%

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[29] Dall'Osto, M., et al., *Real time chemical characterization of local and regional nitrate aerosols.* Atmospheric Chemistry and Physics, 2009. **9**(11): p. 3709-3720.

6   UPDATE 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 compare with the measurements made in this network or (b) to assist the interpretation of the measurements.

6.1   UPDATE ON RELATED UK ACTIVITIES

6.1.1   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.

The London 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, required 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.

6.1.2   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 continued throughout 2012, complemented by more detailed Intensive Observation Periods (IOPs) during January/February and July/August. 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 were centred on the London PM network sites. Both sites were 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.

6.1.3   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 14 sites in the Black Carbon Network optically measuring particulate matter collected on filters, using aethalometers operating at two wavelengths. The infrared wavelength metric is designed to approximate to Elemental Carbon. There are strong links to this Network through NPL and KCL'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.

- Black Carbon by aethalometry, with supplementary analysis of filter samples for EC and OC (which is explicitly performed within this network).

6.2   UPDATE ON EUROPEAN ACTIVITIES

6.2.1   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, through the REVIHAAP process looking at health effects evidence, and through stakeholder meetings. There is input from the operators of this network through AQUILA, and though EU projects such as AirMonTech. The review was originally scheduled to be completed in 2013, but this timescale has apparently been extended.

6.2.2   CEN standards
2012 has seen considerable CEN activity in the areas covered by this Network.

CEN TC 264 WG 15 has nearly completed 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 standard has been through formal enquiry.
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 been through formal enquiry.

Validation work is necessary, especially in the areas of filter selection and performance characteristics of automatic instruments. The bidding process for this work has been completed. The work is expected to start later in 2013. 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 revised EN 12341 designates one sampler design (at 2.3 m^3/hr) as the reference, and attempts to clarify the status of other "established" samplers such as the Digitel (at 30 m^3/hr) and the Partisol (at 1 m^3/hr) by giving them special status (in Annex B of the standard).

There has been close involvement in this Working Group from the AURN operators, and there should be no major or unexpected implications for the running of the AURN or other UK networks.

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 likely to be silver. Although this has no environmental relevance, it is the only material that can be readily formed as particles with a narrow size spread in the range 5 nm to 10 nm, using evaporation/condensation generation.

   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. Other likely specifications are that maximum allowed sample line losses are to be 30% at 7 nm (these can be calculated from theoretical diffusive losses), and the sample line RH is to be kept below 40%.

   These changes would have minor changes on the infrastructure of the sites and calibration procedures.

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 has not been started yet, but the SMPS guidelines are likely to be based on procedures that came out of the EUSAAR project that were published as *Mobility particle size spectrometers: harmonization of technical standards and data structure to facilitate high quality long-term observations of atmospheric particle number size distributions*, A. Wiedensohler et al, Atmos. Meas. Tech., 5, 657-685, 2012.   .

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.

Validation work has been outlined and contracts are being set up. 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 the influential EUSAAR project) has looked at rural background samples rather than roadside samples like those from Marylebone Road.

It is likely that the chosen EC/OC protocol will be a modified version of EUSAAR_2. This would have a minor effect on the operation of the network (the analysis protocol takes about 5 minutes longer per sample). The parallel analyses, shown earlier in this report, suggest that there would be no significant step change in the data.

The proposed WG34 validation programme will result in a validated standard method which may be adopted by the EC as a reference method. It is very likely that this standard will specify a manual method, whereas the current measurements of anions and cations in $PM_{2.5}$ at the two background sites at which the UK is required to measure are made using automatic methods. In future, using historical or new field comparison data of these instruments against manual measurements may provide enough confidence that the data currently produced by the automatic method is consistent with the method proposed in the new standard.

7   MAIN FINDINGS OF TOPIC REPORTS IN 2012

Work was carried out on two Topic Reports during the course of 2012:

- Black Carbon and UV Particulate Matter (June 2012)
- Analysis of Hourly data from continuous anion and cation (URG) measurements in London (March 2013)
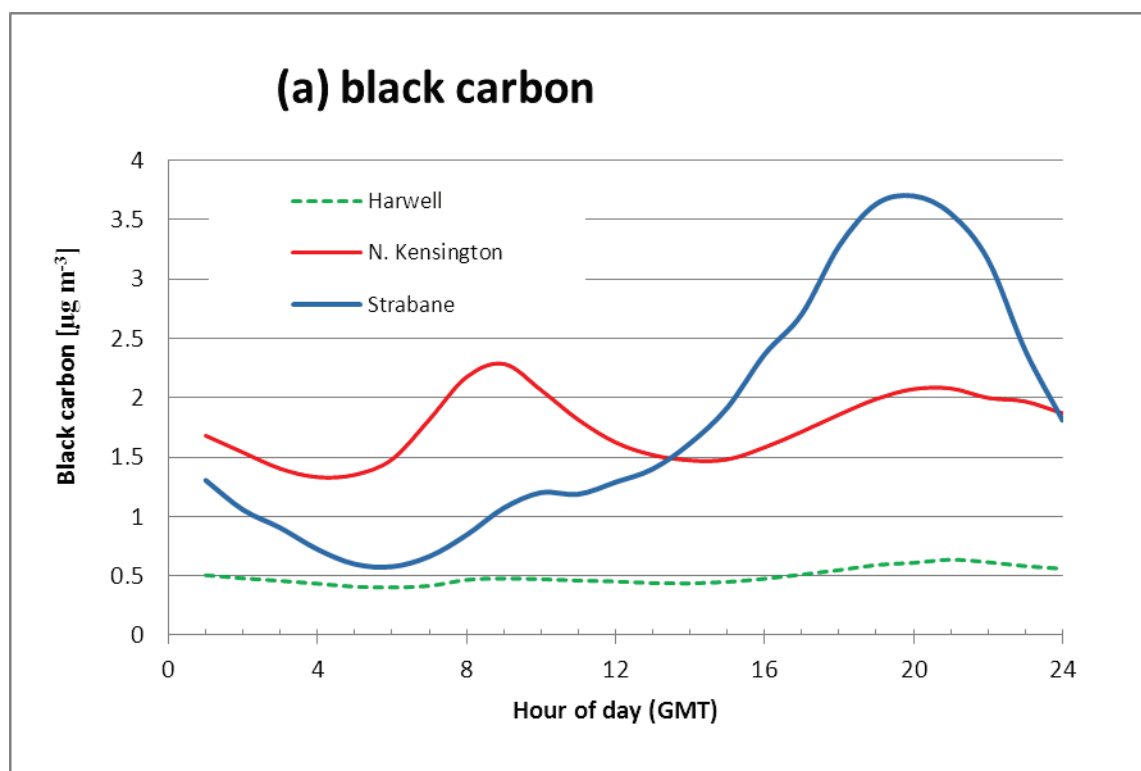
7.1   BLACK CARBON AND U.V. PARTICLE MATTER

Data from the aethalometers in the UK black carbon network for the period up to 31 December 2010 were examined. The instruments report carbon as black carbon, measured by absorption at 880 nm and expected to correspond approximately to elemental carbon, and "UV Particulate Matter" estimated from absorption at 370 nm due to components of the particles which have an enhanced absorption in the ultraviolet compared to that in the visible and infra-red ranges. A small literature currently exists suggesting that the UV Particulate Matter measurement may be used as a surrogate for wood smoke.

Data from sites such as Marylebone Road with very high concentrations of traffic-generated black carbon are liable to show negative concentrations of UV Particulate Matter at certain times suggesting weaknesses in the aethalometer algorithm used to estimate concentrations of UV Particulate Matter.

The diurnal variations of black carbon and UV Particulate Matter are markedly different. At most sites in Great Britain, black carbon shows a diurnal profile typical of that of a traffic-generated pollutant, while UV Particulate Matter typically shows a small increase in the morning followed by a minimum during the afternoon and a broad nocturnal maximum (Figure 6-1). Ratios between black carbon and UV Particulate Matter are highly variable between sites but are largely explicable in terms of a major traffic source of black carbon. The seasonal patterns of black carbon and UV Particulate Matter have been compared. Both show enhanced winter concentrations at sites in Great Britain with winter to summer ratios broadly similar for the two metrics. Measurements of inter-site correlations as a function of separation distance between sampling sites reveal a negative exponential decline in the coefficient of determination (r^2) for both black carbon and UV Particulate Matter (Figure 6-2), although the rate of decline of correlation with distance is less for UV particulate.

The wind speed dependence of black carbon and UV Particulate Matter has been compared, and for most sites, the two metrics behave broadly similarly with typically a decline in concentration with wind strength. Analysis of the data as a function of both wind speed and wind direction shows local directional effects upon black carbon at urban sites, probably relating to the local traffic source, whereas the data for UV Particulate Matter give a less clear indication of sources and include wind sectors where concentration maxima are observed at medium wind strengths consistent with advective area sources. Five-day airmass back trajectories to Harwell for periods of high black carbon and UV particulate matter suggest an important contribution of mainland European sources to advected black carbon and UV Particulate Matter. At two sites in Northern Ireland (Strabane and Dunmurry) black carbon and UV Particulate Matter show similar trends and appear to arise from the same source, probably coal burning.

Data for black carbon and UV Particulate Matter determined during two one-month sampling campaigns at London North Kensington show generally rather weak correlations of UV Particulate Matter with the wood smoke markers, levoglucosan and fine particle potassium. While some aspects of the data for UV Particulate Matter are consistent with a wood smoke source, other aspects, particularly the seasonal variation in concentrations suggest that wood smoke is not the only contributor. There are possibilities that other UV-absorbing components of the particulate matter make a contribution to UV Particulate Matter concentrations.
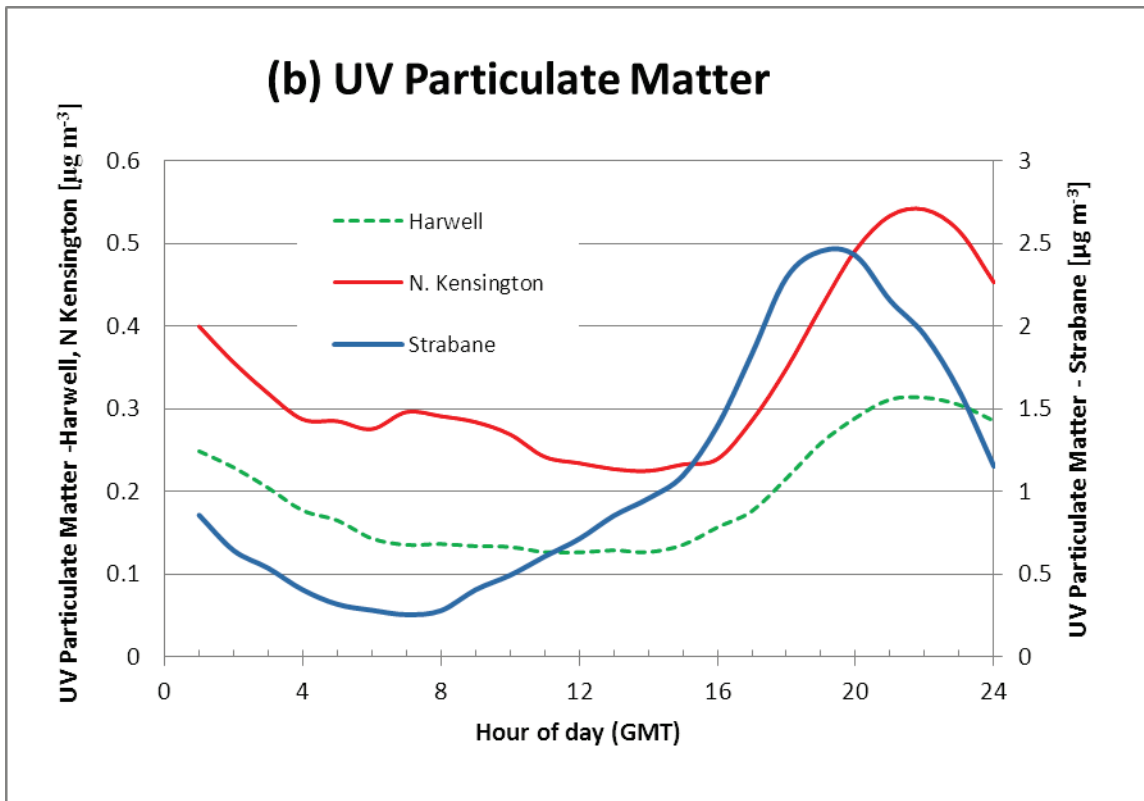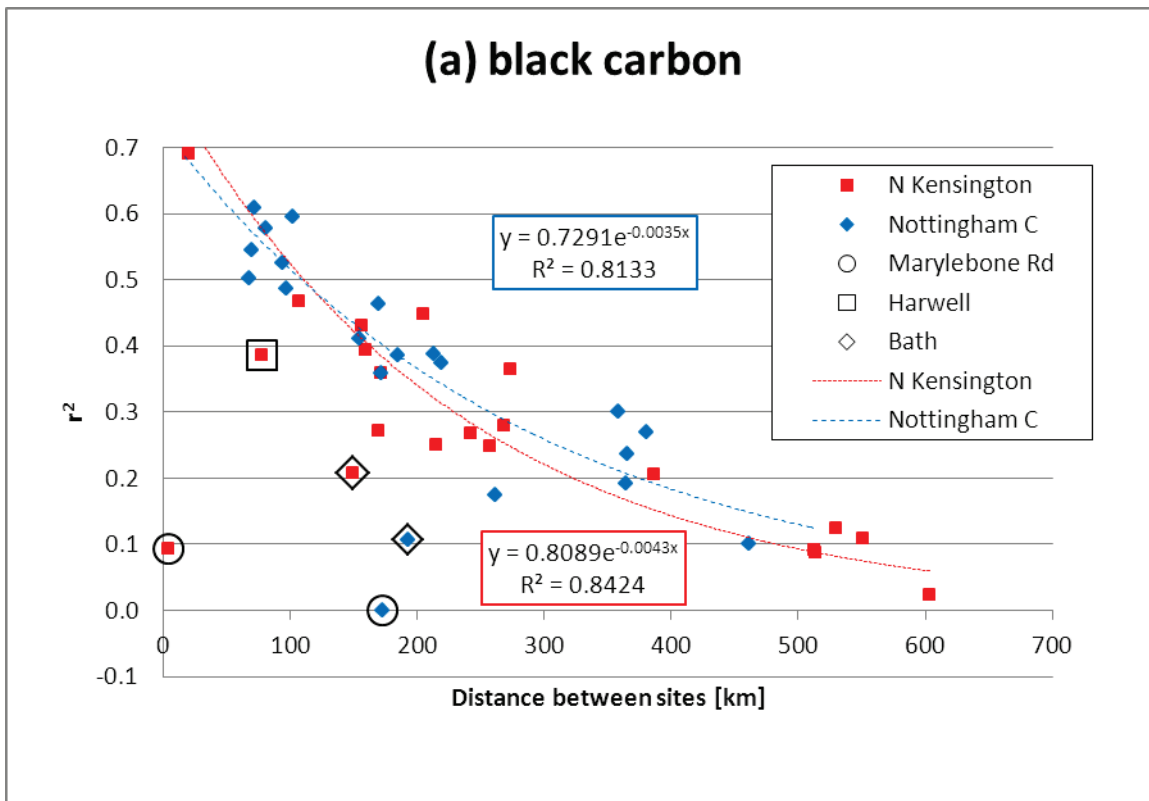
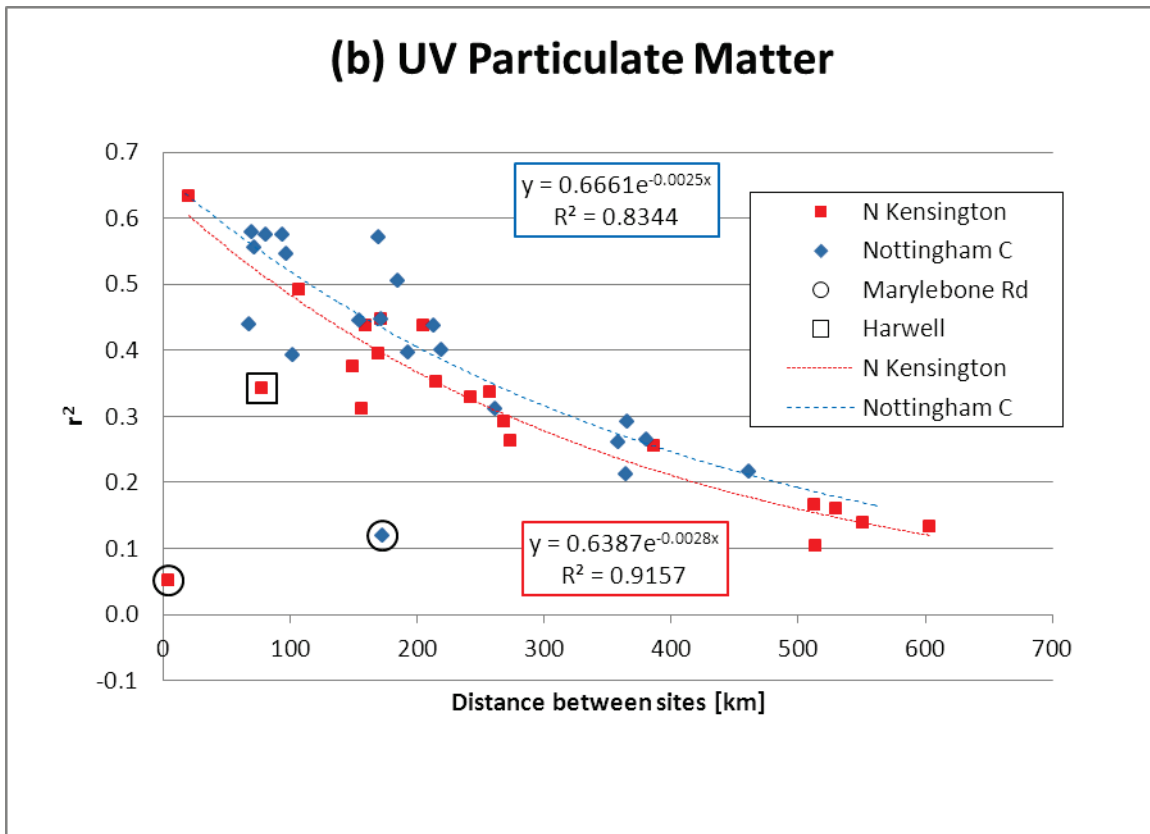**Figure 6-1 Typical diurnal profile: (a) Black Carbon; (b) UV Particle Matter**

Figure 6-2 Regression coefficient between concentrations at different sites versus distance between sites: (a) black carbon; (b) UV Particulate Matter

7.2   ANALYSIS OF HOURLY DATA FROM CONTINUOUS ANION AND CATION (URG) MEASUREMENTS IN LONDON

Preliminary data was obtained from two URG-AIM instruments located at the North Kensington and Marylebone Road sites in London of the concentrations of maritime (chloride and magnesium) and secondary (sulphate, nitrate and ammonium) species, and calcium, within the PM_{10} fraction of particulate matter. Although initial operational issues prevented reliable comparisons between the absolute concentrations of different species, and between the two sites, the hourly data was successfully used to examine the relative differences in concentration over time, and under different meteorological conditions.

Differences between the diurnal normalised concentration profiles of the species, and those of black carbon measured by co-located instruments, were compared showing calcium to have a significantly different diurnal profile, with maximum concentrations during the day, compared to the profiles of the maritime and secondary species (Figure 6-3). Weekly normalised concentration profiles were similar between the species and may have been influenced by differences in the mean meteorological conditions on different days of the week, which may not be present if a longer period of data was considered.

Previous work examining the relationship between the concentration of different particulate species and wind speed, related to the likely sources of the different species, was extended. The concentrations of most species were found to increase with wind speed at higher wind speeds (> 10 m s^{-1}) – a result that was attributed to local wind induced resuspension.

Examination of the normalised concentrations with respect to wind direction showed a maximum in the concentrations of maritime species and a local minimum in the concentrations of secondary species at a measured (10 metre) wind direction of 60^0. Taking into account the backing of the 10 metre wind direction compared to the direction of geostrophic flow this was interpreted as the effect of the presence of the Thames Estuary.

The availability of hourly, as opposed to daily, species concentration data allows the examination of how these species behave over the diurnal period, and in response to meteorological variables which can themselves vary over relatively short periods of time. The accumulation, over time, of additional data will make it possible to further refine this analysis, for example by looking at the relationship between concentration and wind speed at specific wind directions or times of day.
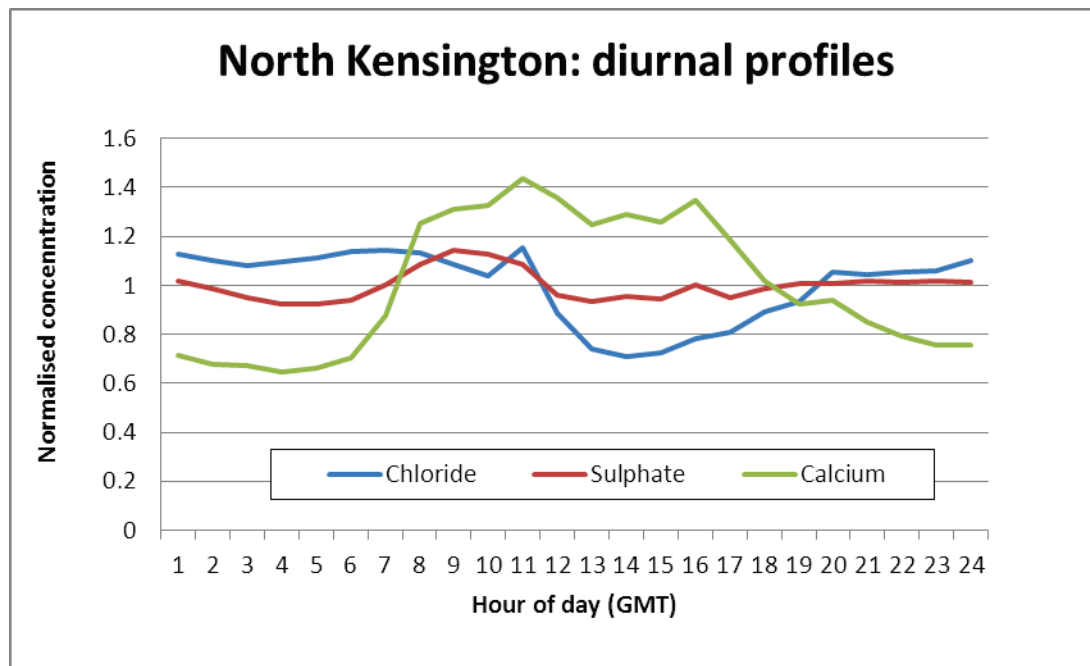
Figure 6-3: Normalised diurnal profiles of chloride, sulphate and calcium at North Kensington

8   CONCLUSIONS

The primary purpose of this report is to summarise both the operational history of the Network in 2012 and the data collected. The Network is evolving in line with improvements in instrumentation, and with international scientific and policy developments.
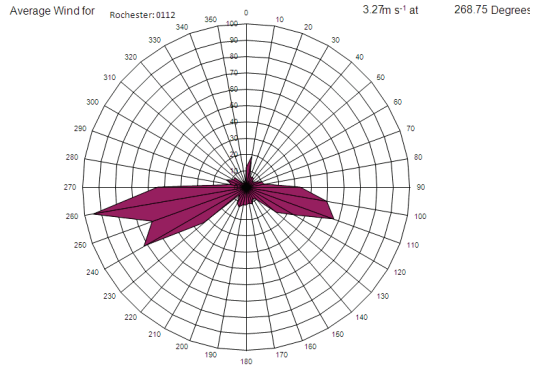
Additional data analysis provides important information on the chemical composition of the PM at the location sites, and the dynamics of PM pollution episodes that occurred in London in 2012. Possible sources could be identified, but further investigation is required.
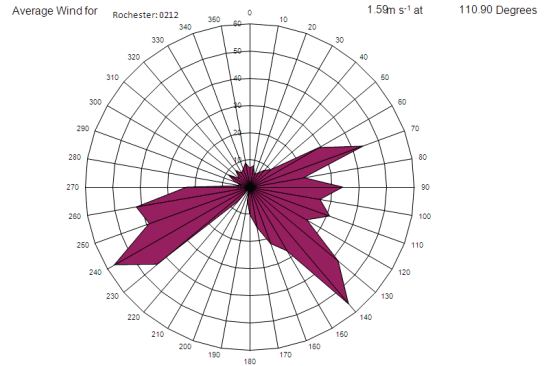
9   ACKNOWLEDGEMENTS

ANNEX 1. WIND ROSES AT ROCHESTER
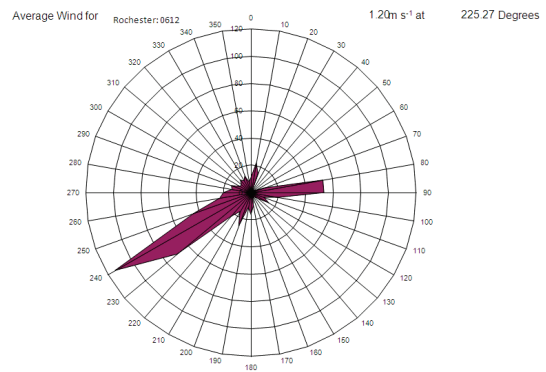
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February 2012

March 2012
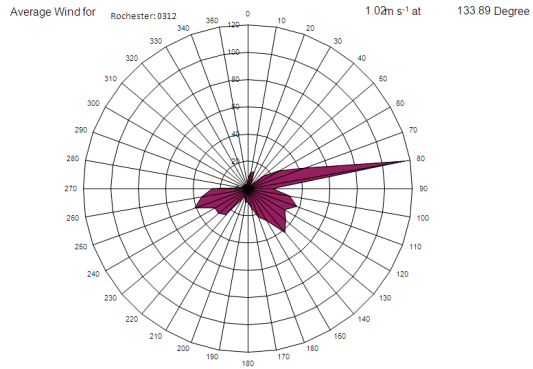
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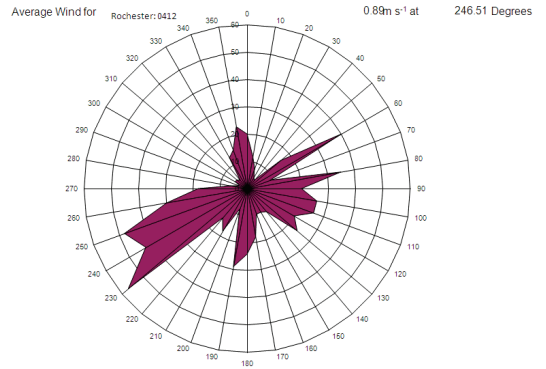
May 2012
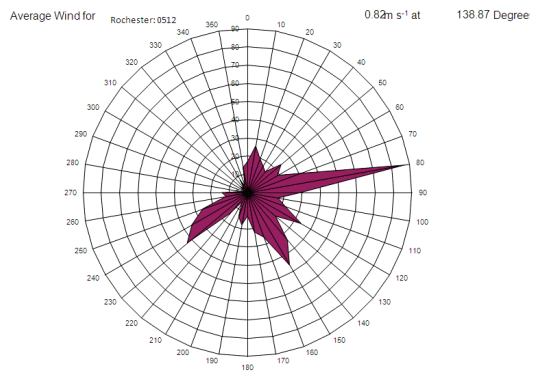
June 2012

July 2012
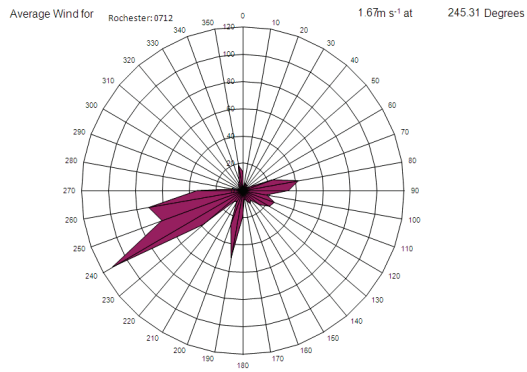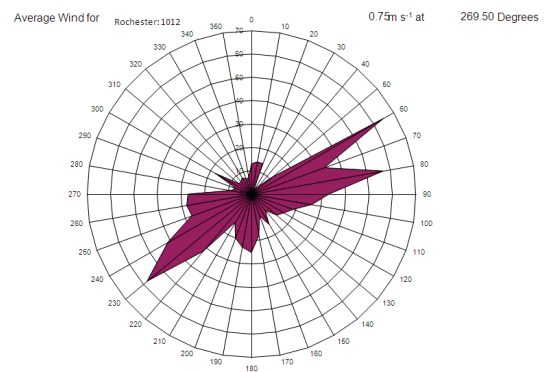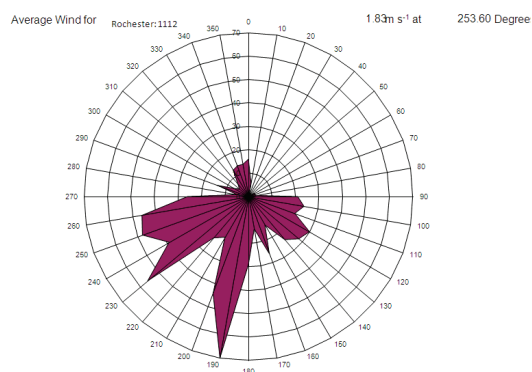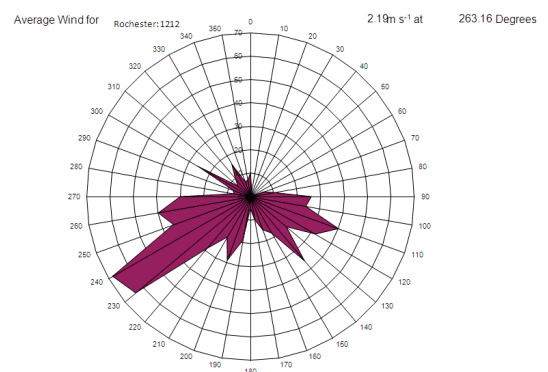

August 2012
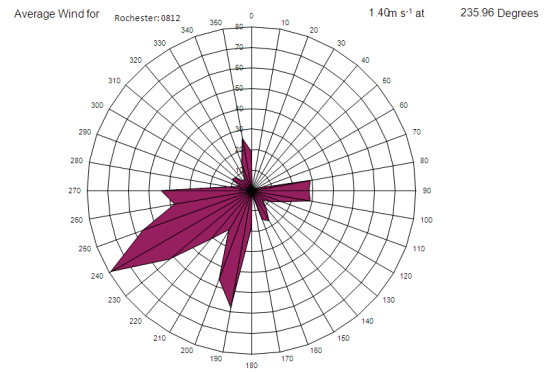
September 2012
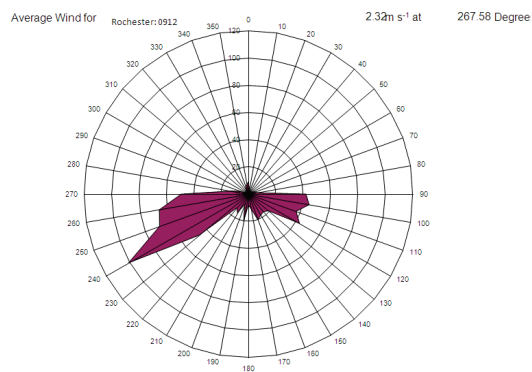
October 2012

November 2012

December 2012

ANNEX 2. TOPIC REPORTS AND PUBLICATIONS

Reports and papers produced or published since the start of the contract are listed below.

Topic reports and projects

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

May 2011 – June 2013

CPEA 28: Airborne Particulate Concentrations and Numbers in the UK (phase 3),
 Annual Report 2011.

Black Carbon and UV Particulate Matter (Brown Carbon) Alan M. Jones and Roy M. Harrison

Analysis of Hourly Data from Continuous Anion and Cation (URG) Measurements in London Alan M. Jones and Roy M. Harrison

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).

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

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

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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.

Cluster Analysis of Rural, Urban and Curbside Atmospheric Particle Size Data, D.C.S. Beddows, M. Dall'Osto and R.M. Harrison, Environ. Sci. Technol., **43**, 4694-4700 (2009).

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, Atmos. Environ., **43** (2009) 5085-5091

The Wind Speed Dependence of the Concentrations of Airborne Particulate Matter and NO$_x$, A.M. Jones, R.M. Harrison and J. Baker, Atmos. Environ., **44**, 1682-1690 (2010).

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