

**Airborne Particulate Concentrations and Numbers in the United Kingdom (phase 3)
Annual report 2013**

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Approved on behalf of NPLML by Martyn Sené, Operations Director

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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 2013 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 2013.
- Data capture per instrument per month.
- Comparison of 2013 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 2013.

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 PM₁₀ 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 PM₁₀ 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.

Total number concentrations (CPC) were measured at Harwell, Birmingham Tyburn (urban background site), North Kensington and Marylebone Road. The 2013 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 2013, one on anion and cation measurements and one on Elemental and Organic Carbon.

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 2013 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 2013 and a description of their main findings is given in Section 6.

2 NETWORK OPERATION

2.1 OVERVIEW

The operation of the Network in 2013 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 2013 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.

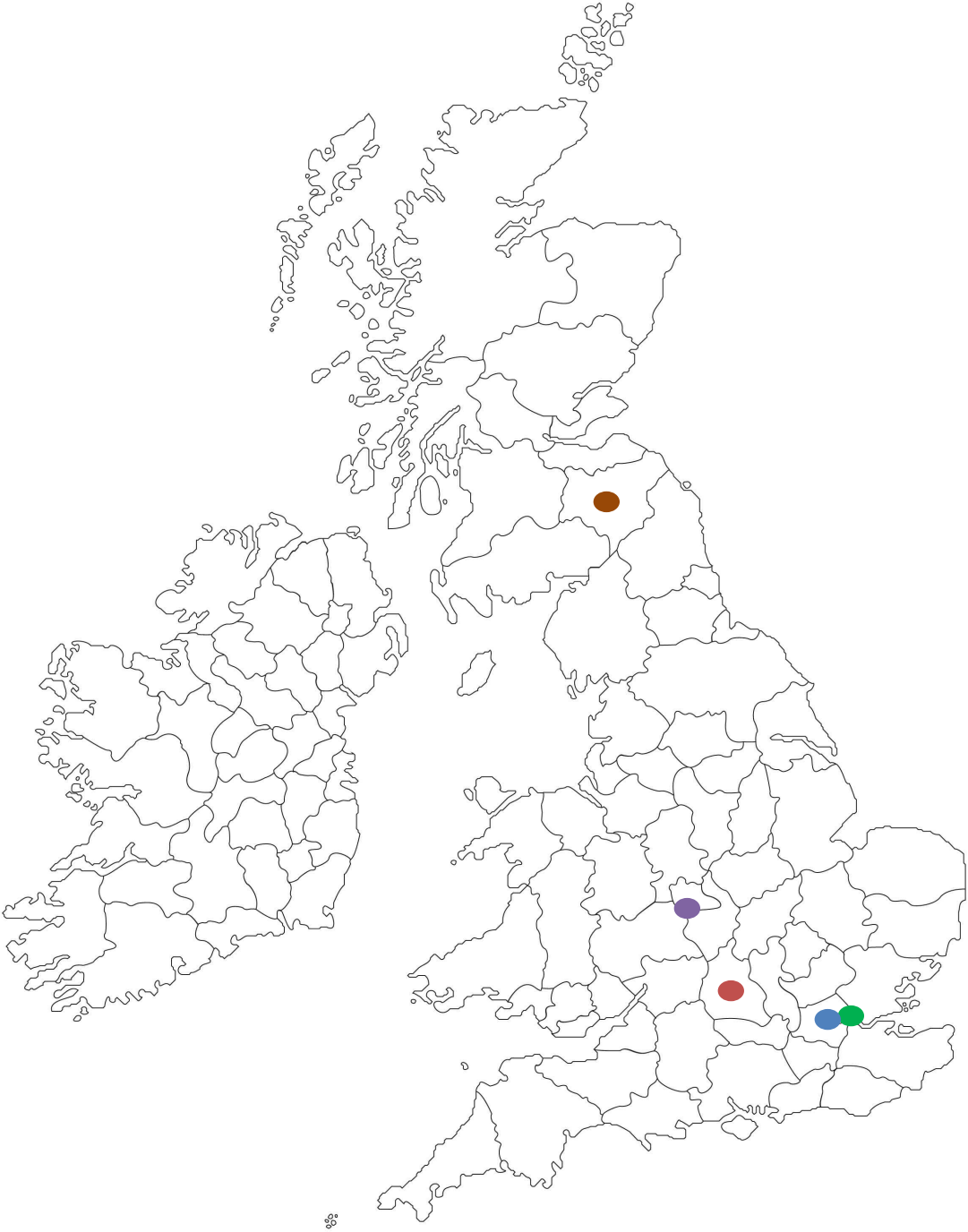


Figure 2-1 Network sites

	Site
●	Marylebone Road
●	North Kensington
●	Harwell
●	Birmingham
●	Auchencorth Moss

Table 2-1 Network structure during 2013

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 μm 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 unit

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 PM₁ 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.

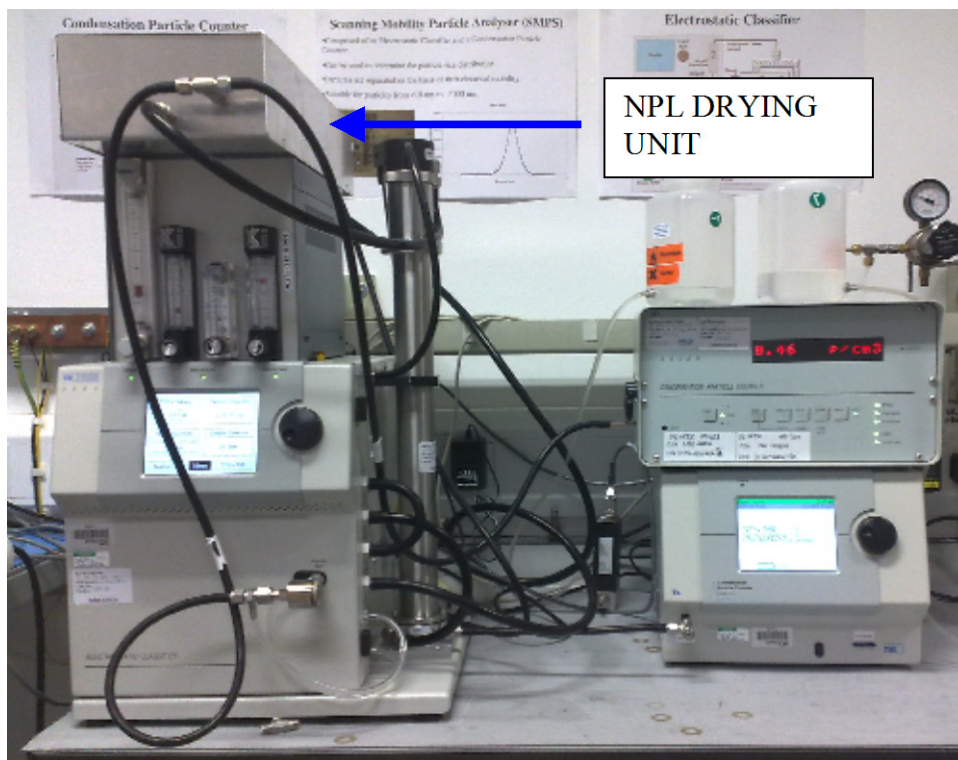


Figure 2-2 Typical configuration of CPC, SMPS and NPL drying unit at the Network sites

2.3.3 Organic Carbon and Elemental Carbon (PM₁₀ and PM_{2.5})

Sampling for daily measurements of OC/EC components of PM₁₀ 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 cm² 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 pyrolytically converted to elemental carbon. Measuring the transmission and reflection of a laser beam through the filter continuously monitors this pyrolytic 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 made using either the transmitted or reflected signal, often giving significantly different results. The temperatures have been calibrated using the Sunset Laboratories calibration kit since July 2012. 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 [$16.6 \text{ m}^2 \text{ g}^{-1}$] 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 Magee Scientific aethalometers (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 $\text{BC}_{\text{corrected}} = (1+k \cdot \text{ATN}) \text{BC}_{\text{uncorrected}}$, 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 $\text{PM}_{2.5}$ 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 2013 Black Carbon Network report [3].

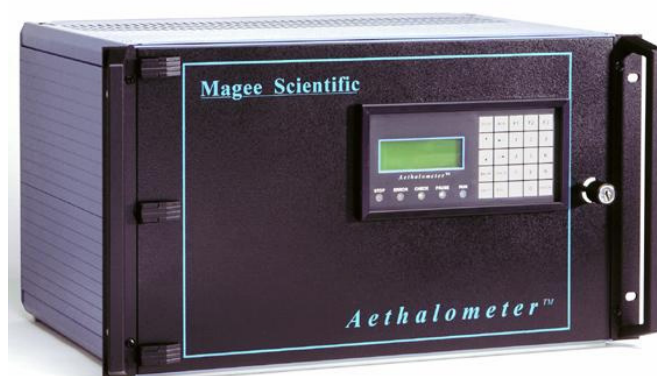


Figure 2-5 Magee Scientific aethalometer

2.3.5 URG – 9000B Ambient Ion Measurements (PM₁₀ anion and cation measurements)

The URG – 9000B AIM (Figure 2-6) provides time-resolved direct measurements of anion particulate (Cl⁻, NO₃⁻ and SO₄²⁻) and cation particulate (Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺).

The sampler 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 PM₁₀ 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 (PM₁₀)

Daily measurements of OC (Organic Carbon) and EC (Elemental Carbon) in the PM₁₀ 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, 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 2013 are given in Table 4-1.

The filter measurements of OC, EC and TC (Total Carbon – the sum of OC and EC) made in 2013 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.

A PM pollution episode that occurred on 11th and 12th December is visible at the London sites. This was due to a high pressure system centred over near Europe that brought calm and at times foggy

conditions with light south/south easterly winds bringing polluted continental air. This imported pollution combined with local emissions and led to a build-up of particulate pollution.

Table 4-1 Monthly data capture for the Partisol 2025 Samplers during 2013

Site	Harwell	North Kensington	Marylebone Road
January	100%	94%	81%
February	97%	97%	90%
March	100%	100%	90%
April	70%	100%	90%
May	100%	100%	74%
June	90%	73%	87%
July	71%	100%	100%
August	100%	100%	100%
September	100%	100%	93%
October	90%	94%	94%
November	93%	100%	100%
December	26%	97%	97%
Average	86%	96%	91%

Harwell

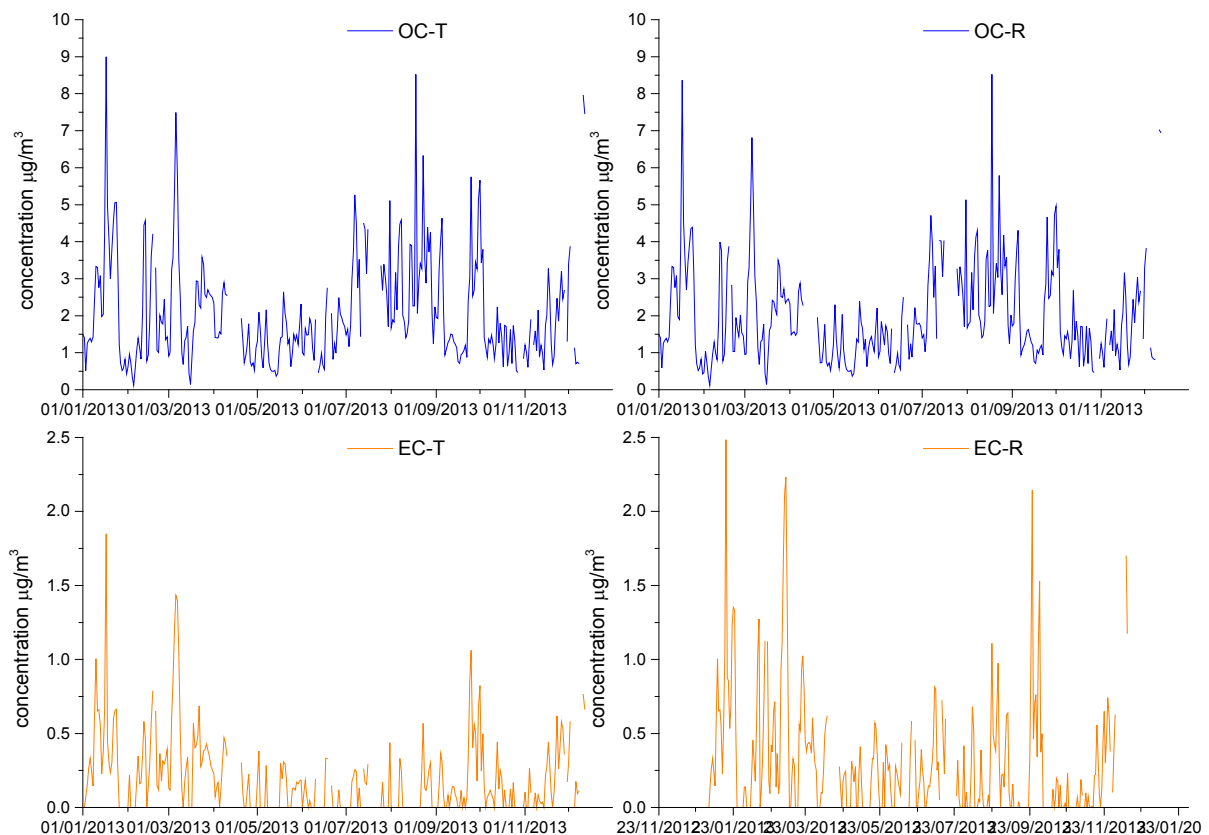
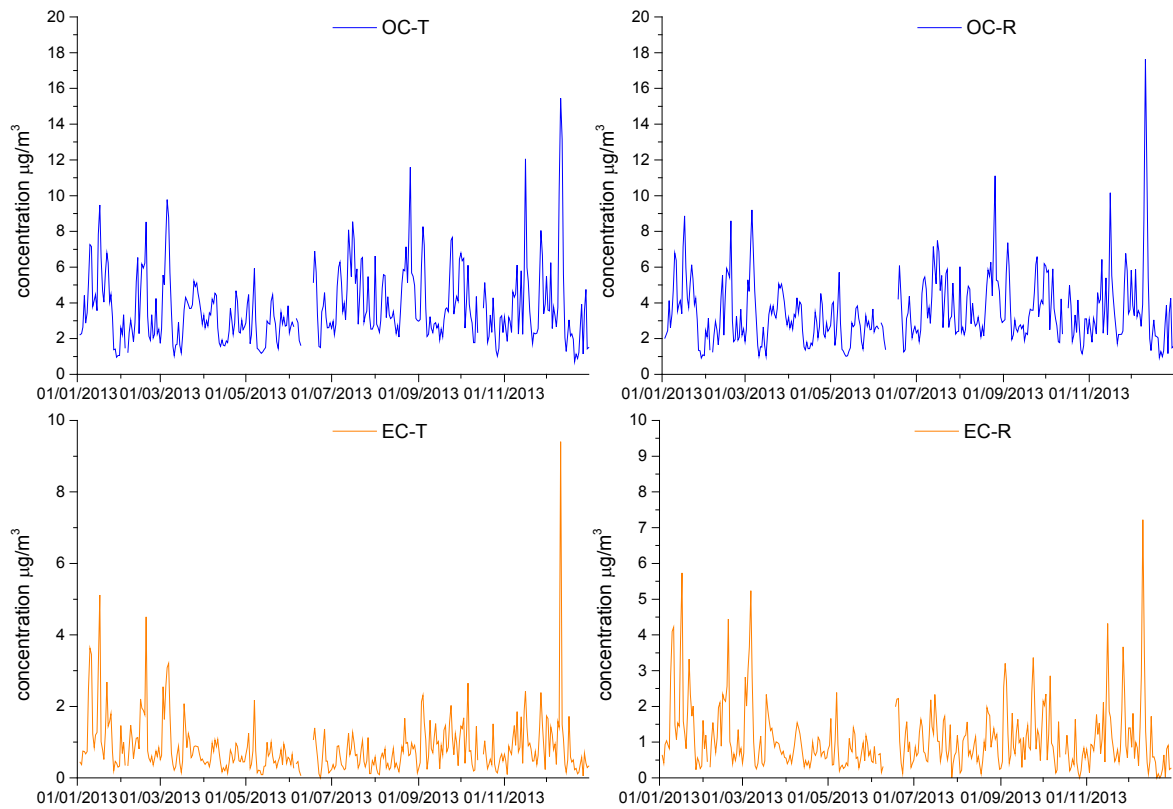


Figure 4-1 PM₁₀ OC and EC concentrations at Harwell during 2013

North Kensington



Marylebone Road

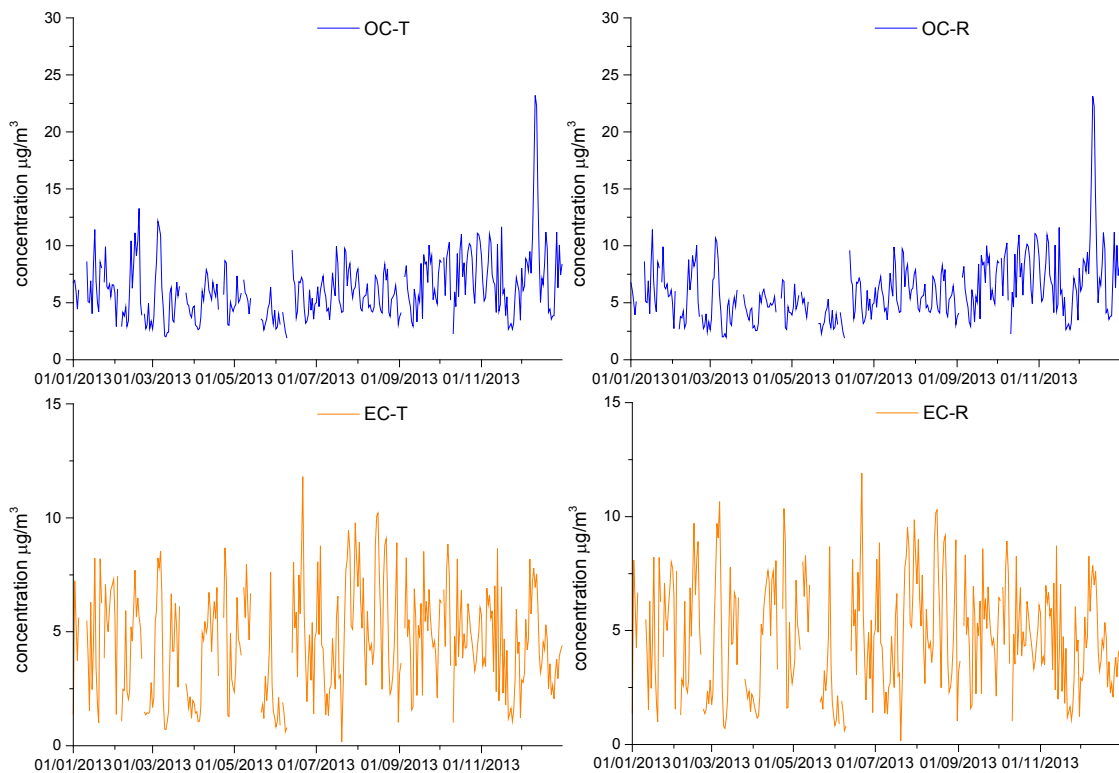


Figure 4-2 PM₁₀ OC and EC concentrations at North Kensington and Marylebone Road during 2013

Total Carbon

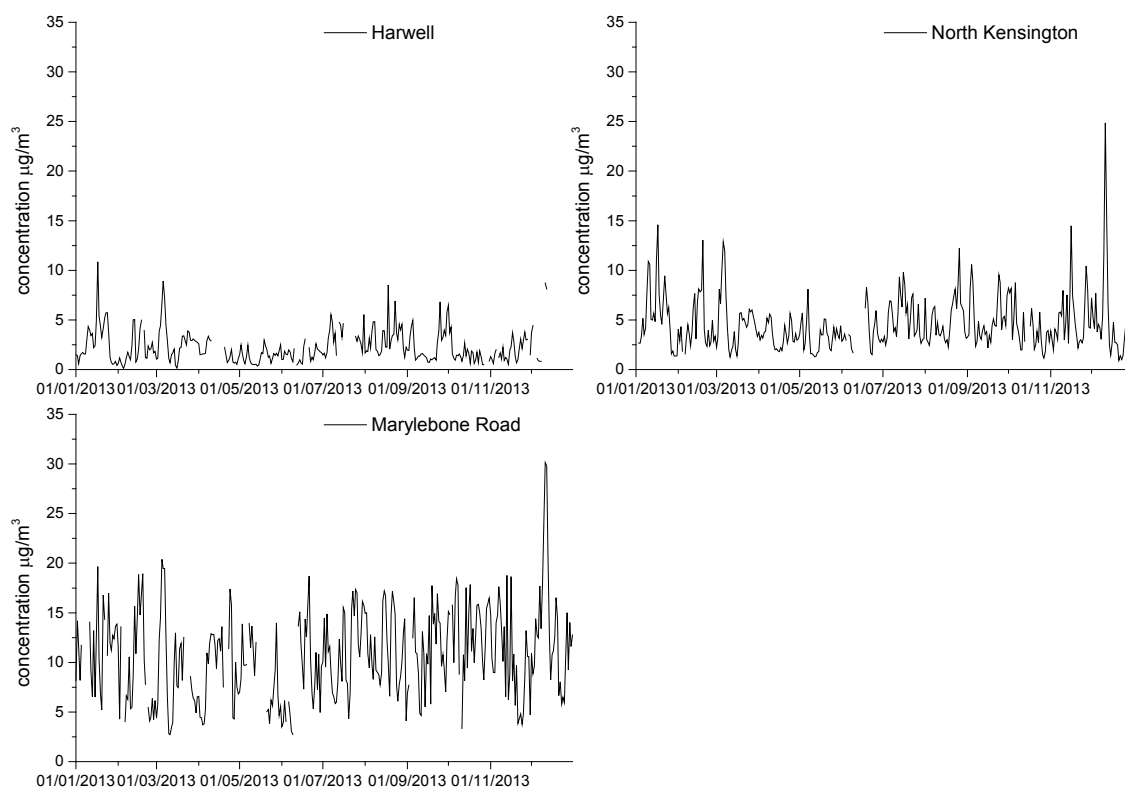


Figure 4-3 PM₁₀ TC concentrations at Harwell, North Kensington and Marylebone Road during 2013

4.1.1 Comparison between Elemental Carbon (PM₁₀) and Black Carbon (PM_{2.5})

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 45-55%. This is generally 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].

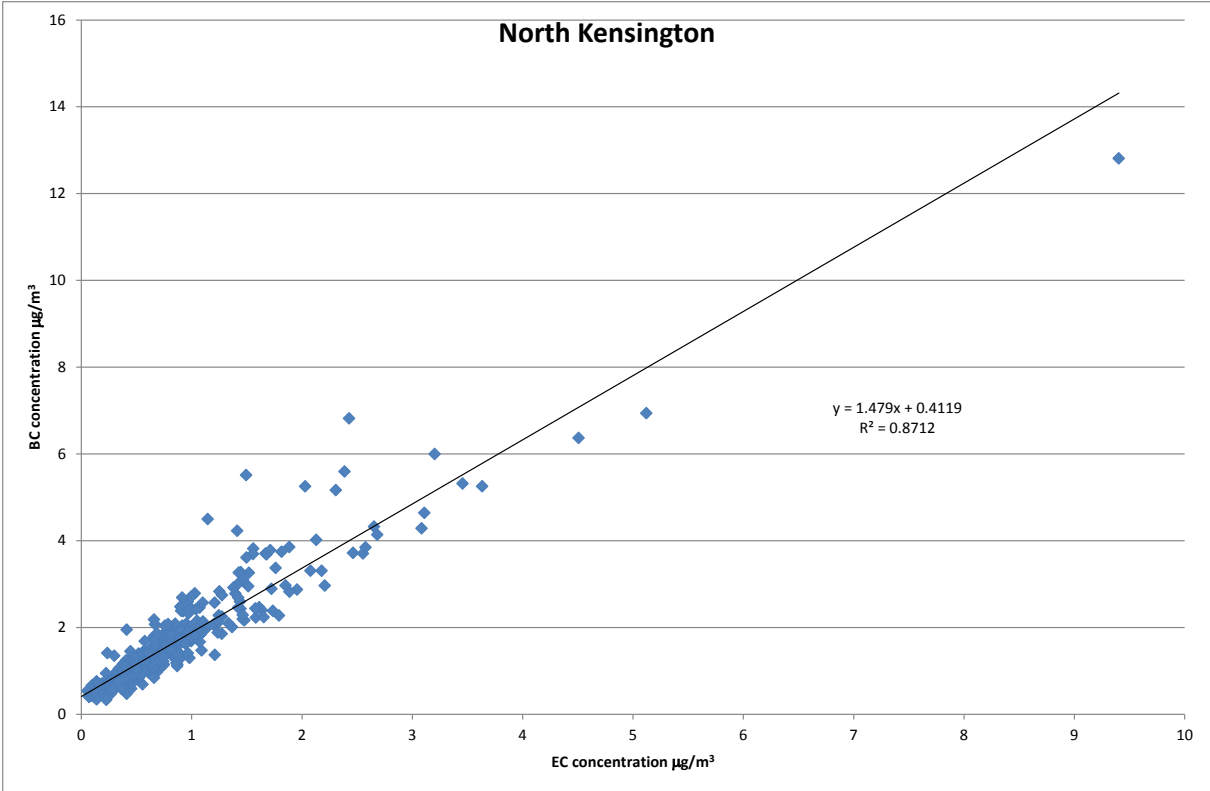


Figure 4-4 Comparison between PM_{2.5} BC and PM₁₀ EC (T) at North Kensington in 2013

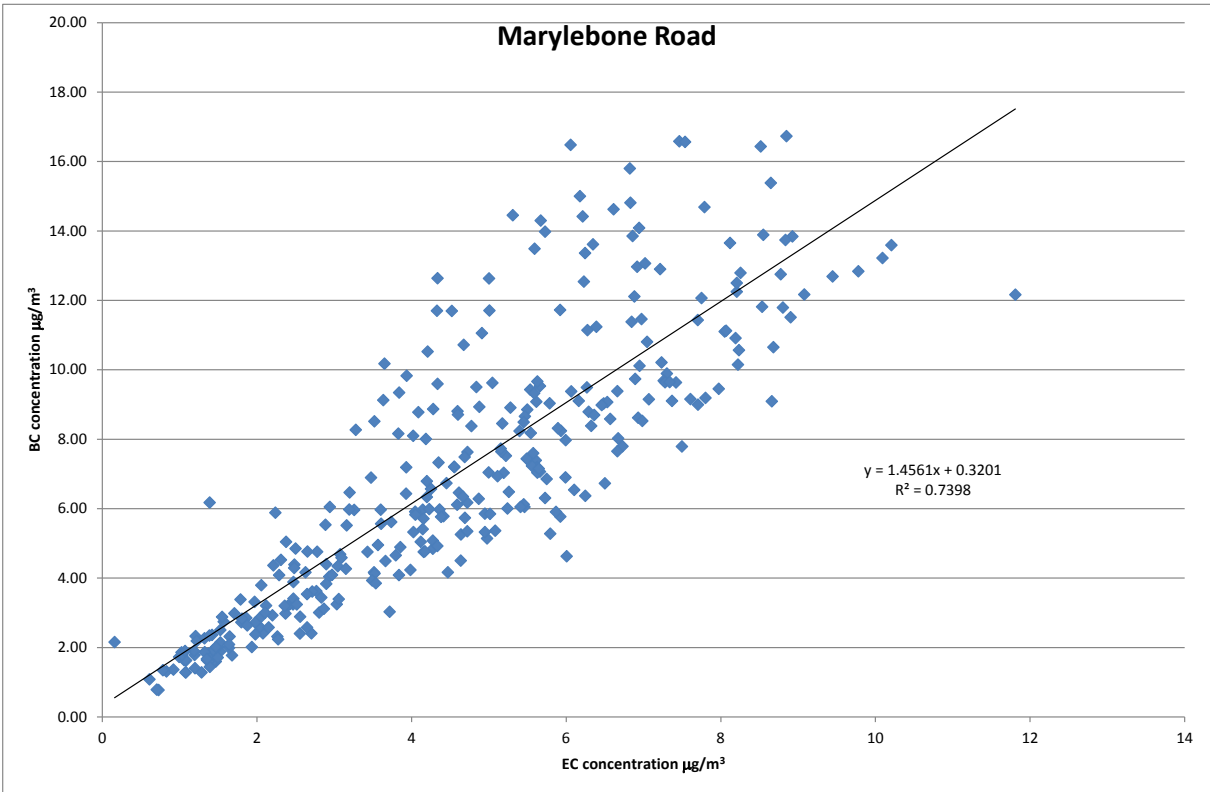


Figure 4-5 Comparison between PM_{2.5} BC and PM₁₀ EC (T) at Marylebone Road in 2013

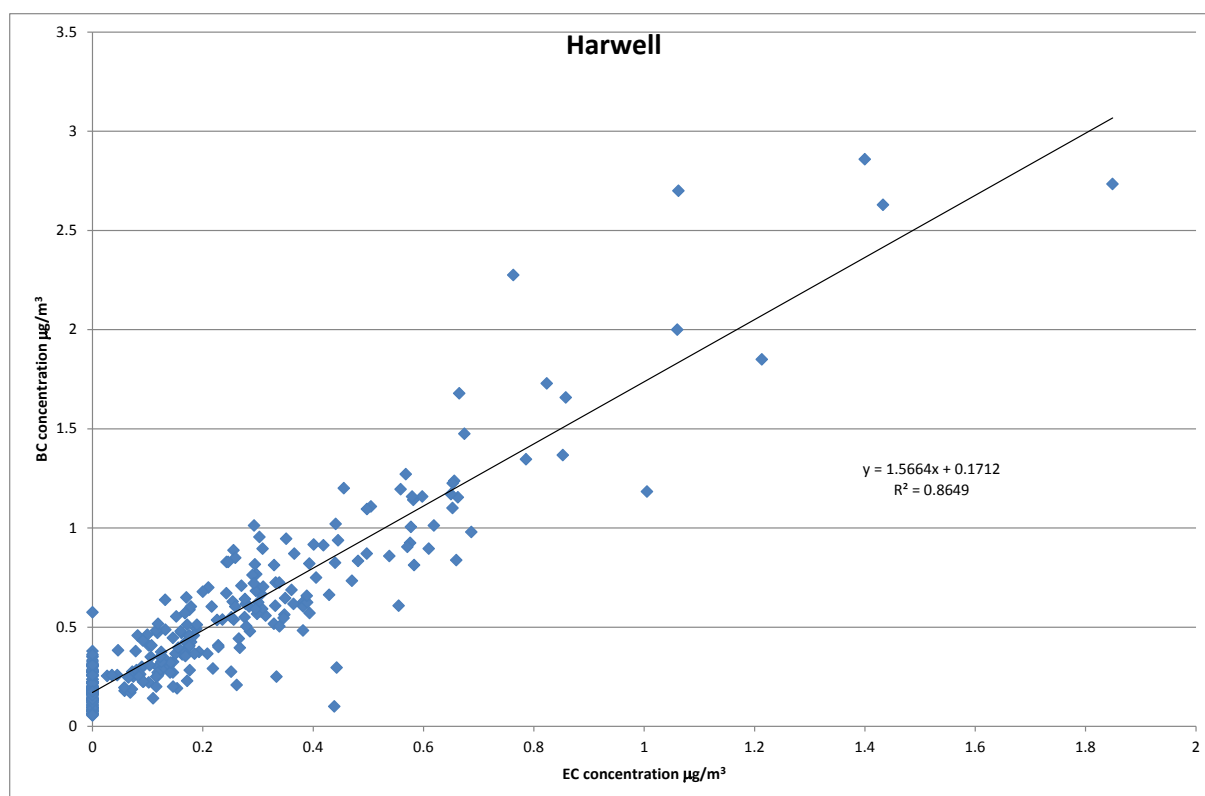


Figure 4-6 Comparison between PM_{2.5} BC and PM₁₀ EC (T) at Harwell in 2013

It can be seen that there is a good linear relationship between the Elemental Carbon and Black Carbon concentrations measured at the North Kensington and Harwell sites, while at Marylebone Road there is more scatter. The relationship between Black Carbon and Elemental Carbon has been quite variable year on year. This variability is shown in Table 4-2.

Table 4-2 Relationships between Black Carbon and Elemental Carbon over the period 2009 – 2013

Year	Harwell		North Kensington		Marylebone Road	
	Relationship	R ²	Relationship	R ²	Relationship	R ²
2009	N/A	N/A	0.97x + 0.33	0.858	1.20x + 0.56	0.776
2010	0.89x + 0.20	0.555	1.16x + 0.03	0.734	1.26x + 0.40	0.946
2011	1.42x + 0.16	0.844	1.16x + 0.14	0.810	1.36x + 0.95	0.924
2012	1.69x + 0.11	0.908	1.32x + 0.30	0.906	1.33x + 0.70	0.898
2013	1.57x + 0.17	0.865	1.48x + 0.41	0.871	1.46x + 0.32	0.740

Note: There is not enough BC data collected at Harwell to form a reliable relationship in 2009 as the aethalometer was only installed in November 2009.

It can be seen that the slopes, i.e. the amounts of Black Carbon relative to Elemental Carbon, have generally increased year on year at all sites, with the effect being larger at North Kensington and Harwell, where the slopes have increased from about 1 to about 1.5, than at Marylebone Road, where the slopes have increased from about 1.2 to 1.46.

There are three possible general explanations for this. (1) The method used for Black Carbon measurement has changed such that reported concentrations are now relatively higher than they used to be; (2) the method used for Elemental Carbon measurement has changed such that reported concentrations are now relatively lower than they used to be; and (3) the nature of the soot-like pollution has changed in a way that causes larger differences between the methods. As the methods have all been under the control of NPL over this period, and no significant changes to them have been

made, the first two explanations seem less likely than the third. These observations merit further investigation.

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 2013 was 88% for Harwell and 90% for Auchencorth Moss.

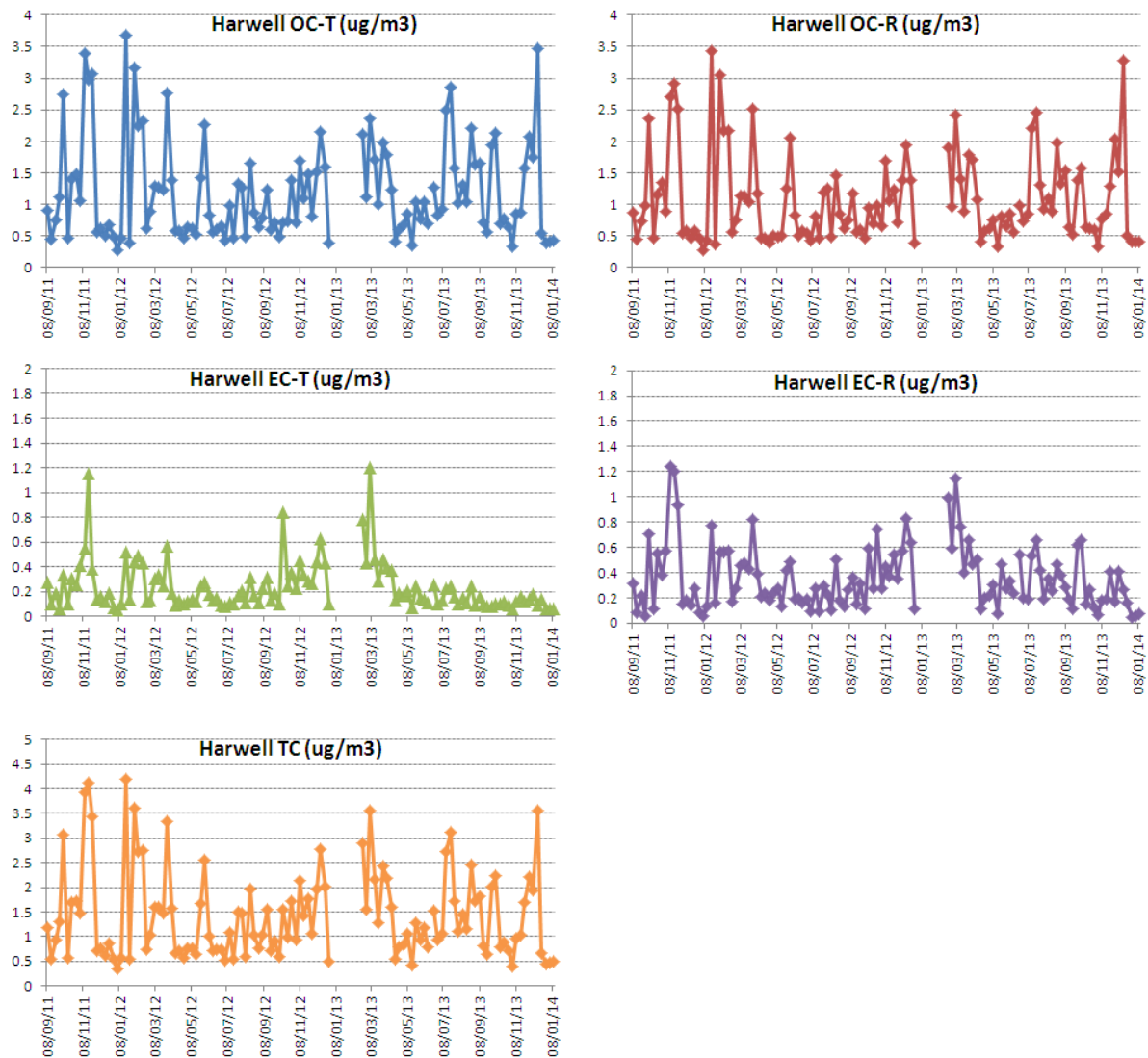


Figure 4-7 Time series of OC, EC and TC in the PM_{2.5} fraction at Harwell since the installation of the sampler (weekly samples).

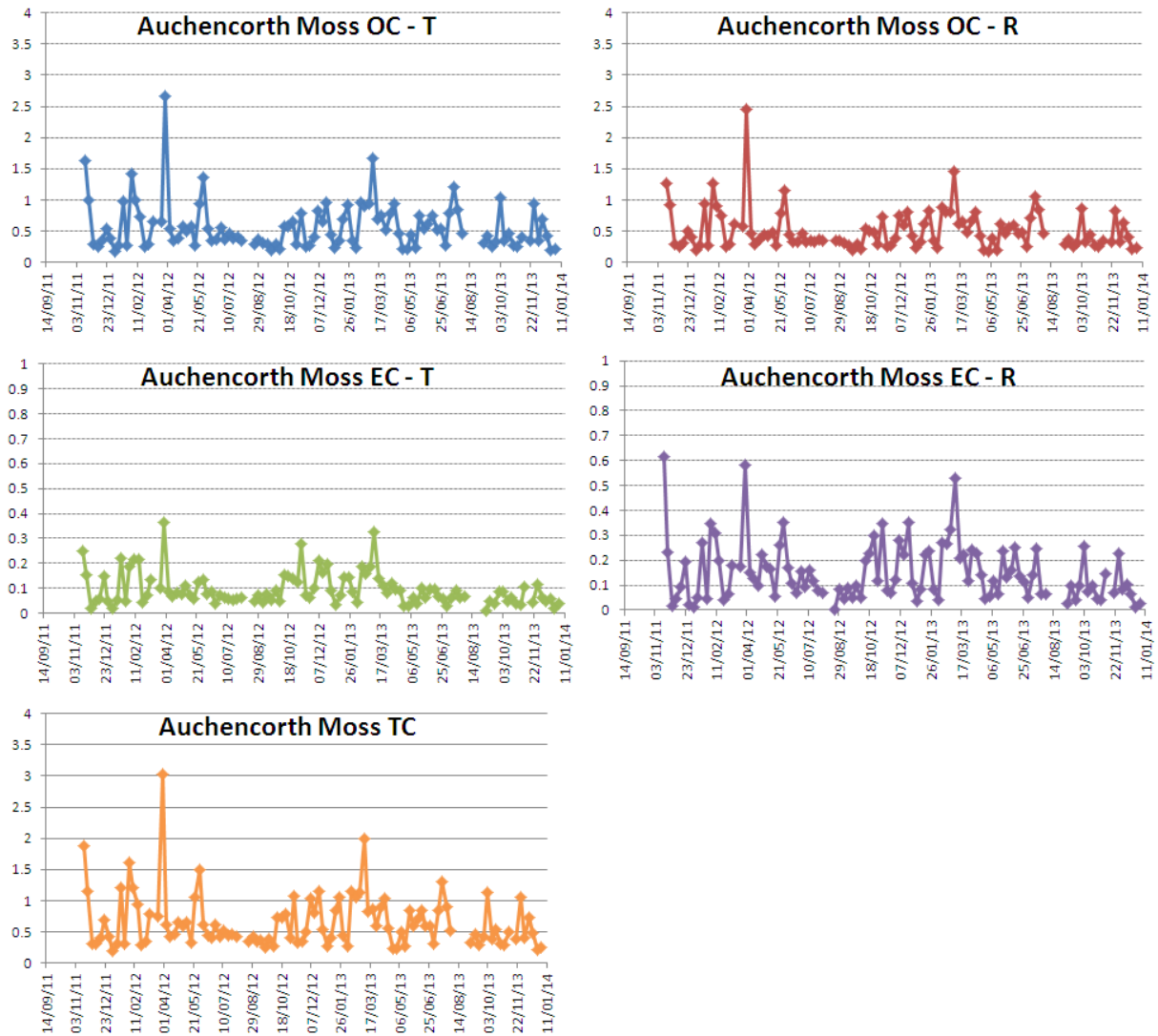


Figure 4-8 Time series of OC, EC and TC in the PM_{2.5} fraction at Auchencorth Moss since the installation of the sampler (weekly samples).

The PM_{2.5} carbon concentrations at Harwell were compared with weekly averages from the PM₁₀ filters from the Partisol (Figure 4-9). The correlation between the two measurements is good, with PM_{2.5} total carbon being on average about 60% of the PM₁₀ total carbon, with most of the difference being in the OC. This may be partly due to losses of semi-volatile OC during the longer (weekly) sampling period of the PM_{2.5} fraction rather than coarse OC.

Being a rural site, daily PM₁₀ EC concentrations can often be recorded as zero, whereas the larger weekly amounts are not, and this explains why the (low) weekly PM_{2.5} EC concentrations are often greater than those for PM₁₀.

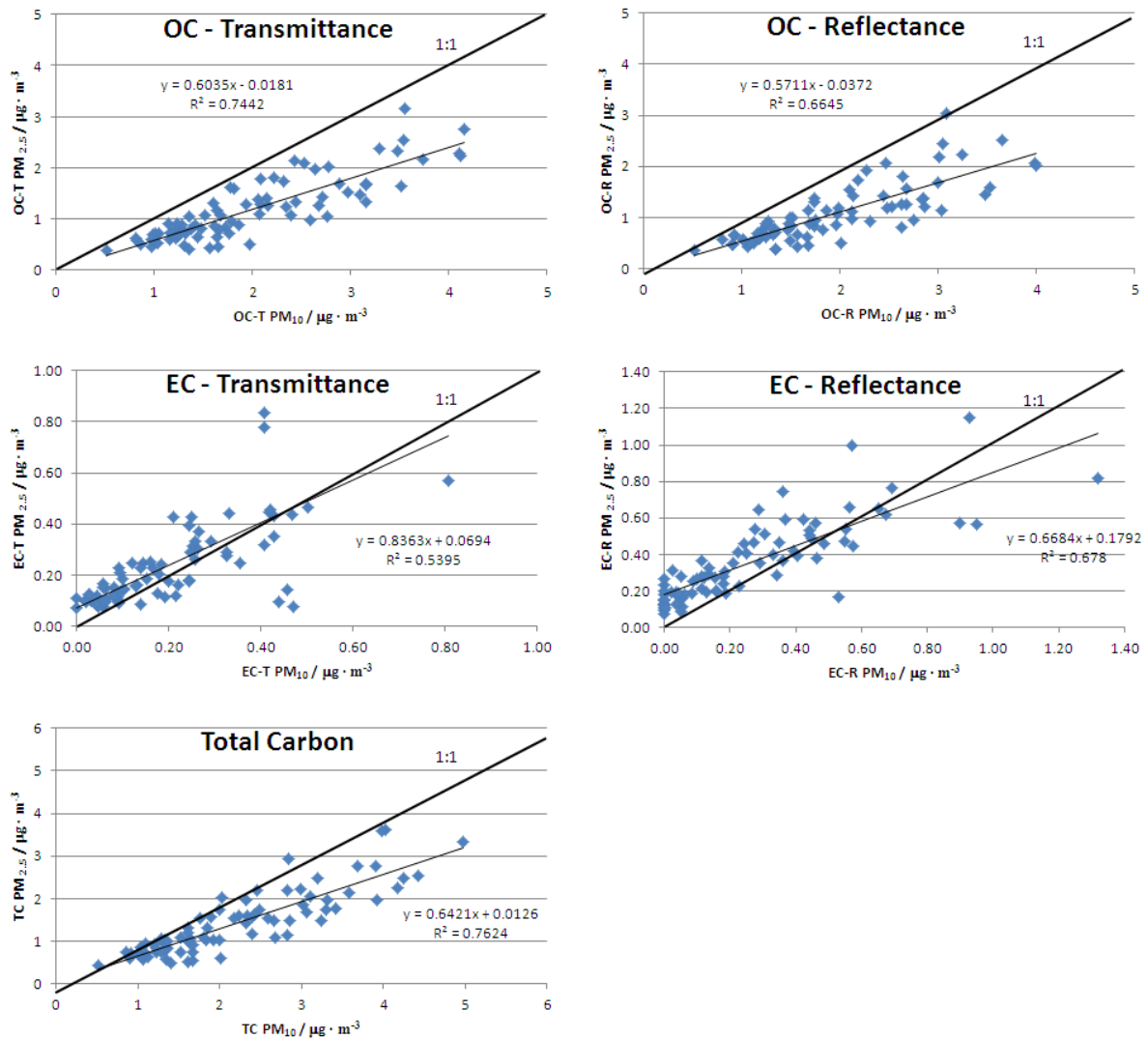


Figure 4-9 Comparison between PM₁₀ OC/EC weekly averages and PM_{2.5} OC/EC at Harwell

4.3 AUTOMATIC PM₁₀ ANION AND PM₁₀ CATION 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 PM₁₀ 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 PM₁₀. At Harwell a MARGA instrument was already operative under a different Network.

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

Table 4-3 Monthly data capture for URG analyser at North Kensington in 2013

	Chloride	Nitrate	Sulphate	Sodium	Ammonium	Potassium	Magnesium	Calcium
January	9%	9%	9%	9%	9%	9%	9%	9%
February	89%	89%	89%	89%	88%	89%	89%	89%
March	42%	42%	42%	42%	42%	42%	40%	42%
April	63%	63%	63%	63%	63%	63%	63%	63%
May	0%	0%	0%	0%	0%	0%	0%	0%
June	60%	66%	56%	68%	68%	68%	68%	68%
July	68%	68%	67%	68%	68%	68%	67%	68%
August	82%	82%	82%	82%	82%	82%	82%	82%
September	70%	70%	70%	82%	82%	82%	82%	82%
October	93%	94%	94%	94%	94%	94%	94%	94%
November	68%	73%	73%	53%	53%	53%	52%	53%
December	87%	87%	87%	87%	87%	87%	87%	87%
Average	61%	62%	61%	61%	61%	61%	61%	61%

Table 4-4 Monthly data capture for URG analyser at Marylebone Road in 2013

	Chloride	Nitrate	Sulphate	Sodium	Ammonium	Potassium	Magnesium	Calcium
January	0%	0%	0%	0%	0%	0%	0%	0%
February	30%	30%	30%	30%	30%	30%	30%	30%
March	70%	70%	70%	70%	70%	70%	68%	70%
April	63%	63%	63%	63%	63%	63%	63%	63%
May	23%	23%	23%	23%	23%	23%	23%	23%
June	61%	61%	61%	60%	60%	60%	59%	60%
July	21%	21%	21%	0%	0%	0%	0%	0%
August	0%	0%	0%	0%	0%	0%	0%	0%
September	0%	0%	0%	0%	0%	0%	0%	0%
October	0%	0%	0%	0%	0%	0%	0%	0%
November	0%	0%	0%	0%	0%	0%	0%	0%
December	0%	0%	0%	0%	0%	0%	0%	0%
Average	22%	22%	22%	20%	20%	20%	20%	20%

In January, problems with the procurement of consumables led to 0% data capture at Marylebone Road and 9% at North Kensington.

A contamination in the cation system and then a major break down in July within the anion system, caused loss of data for most of the year at Marylebone Road. The fault was then repaired at the beginning of January 2014 by Thermo Fisher Scientific.

In November 2012 a few changes were made to the analysers to improve the quality of the chromatography, and therefore of the data. 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.

Following the changes of the IC set-up, a few filters used for the PM₁₀ daily ECOC measurements at North Kensington in 2013 were analysed by Ion Chromatography as well at NPL and the results were compared with the daily averages from the URG instrument's measurements. Figure 4-10 shows the scatter plots for some of the ions. The comparison is overall good and better than the comparison initially performed in 2011, when a concentrator column was used instead of a sample loop [7].

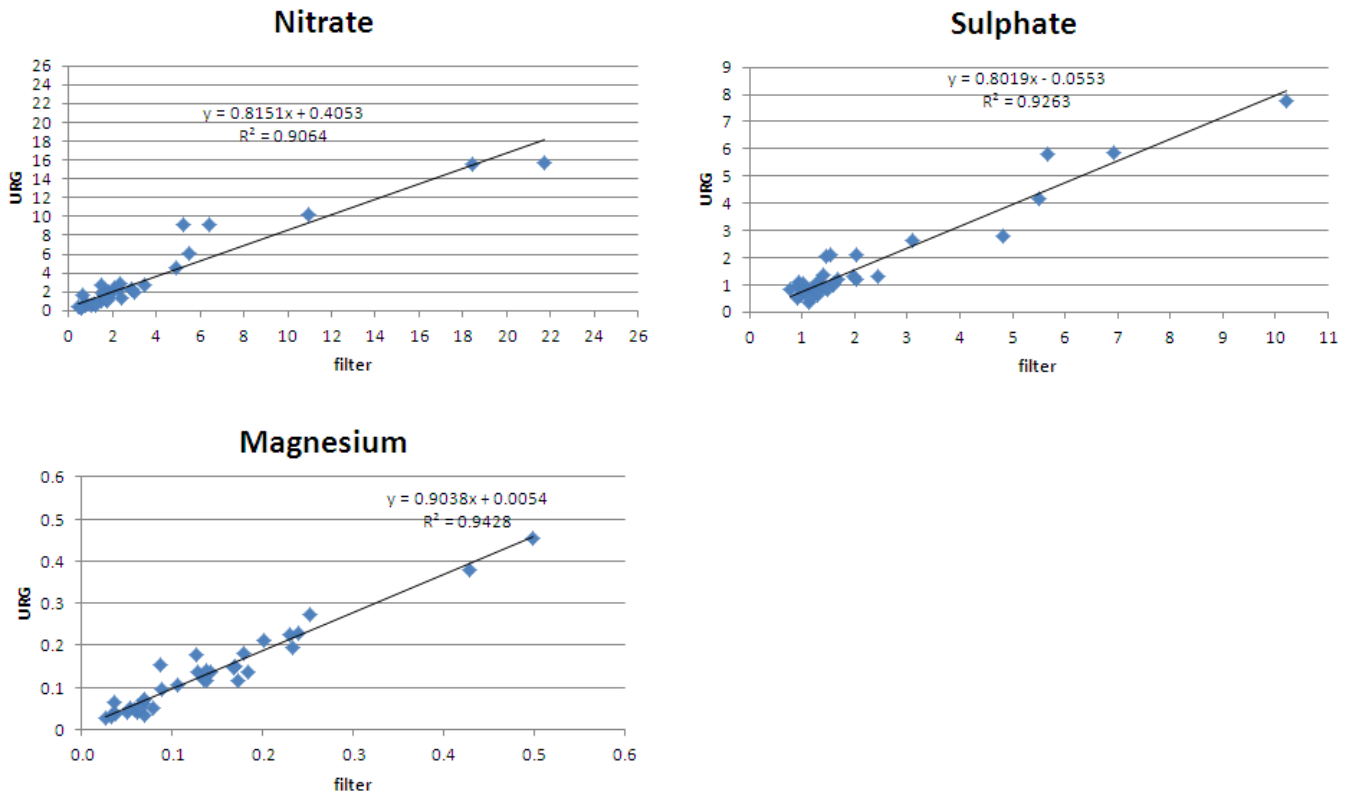


Figure 4-10 Scatter plots between filter-method and URG instrument for PM₁₀ nitrate, sulphate and magnesium measurements (North Kensington – 2013)

In the time series shown in Figure 4-11 and 4-12, some of the PM pollution episodes that occurred in 2013 can be identified.

Marylebone Road

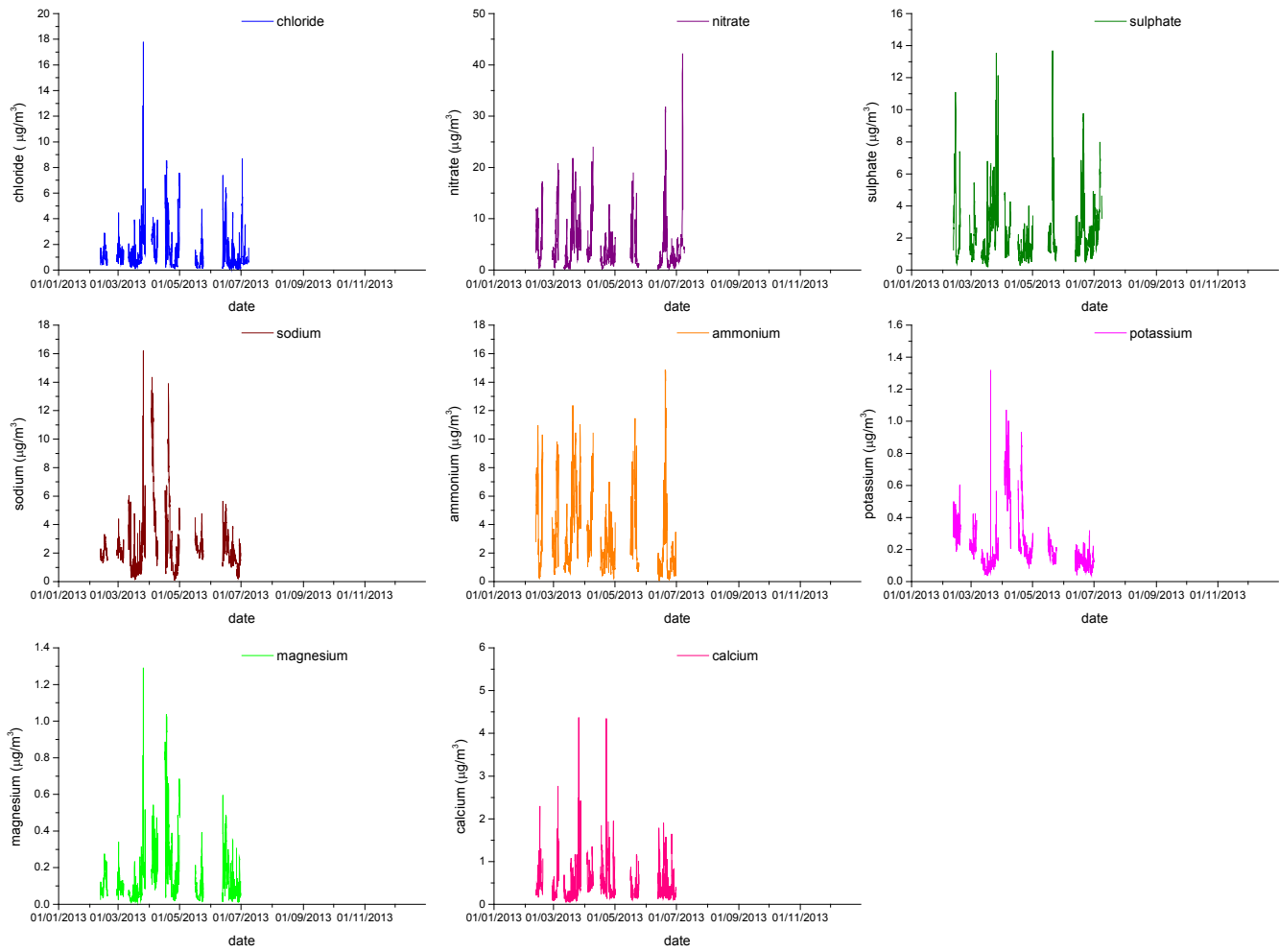


Figure 4-11 Time series for ion concentrations at Marylebone Road in 2013

North Kensington

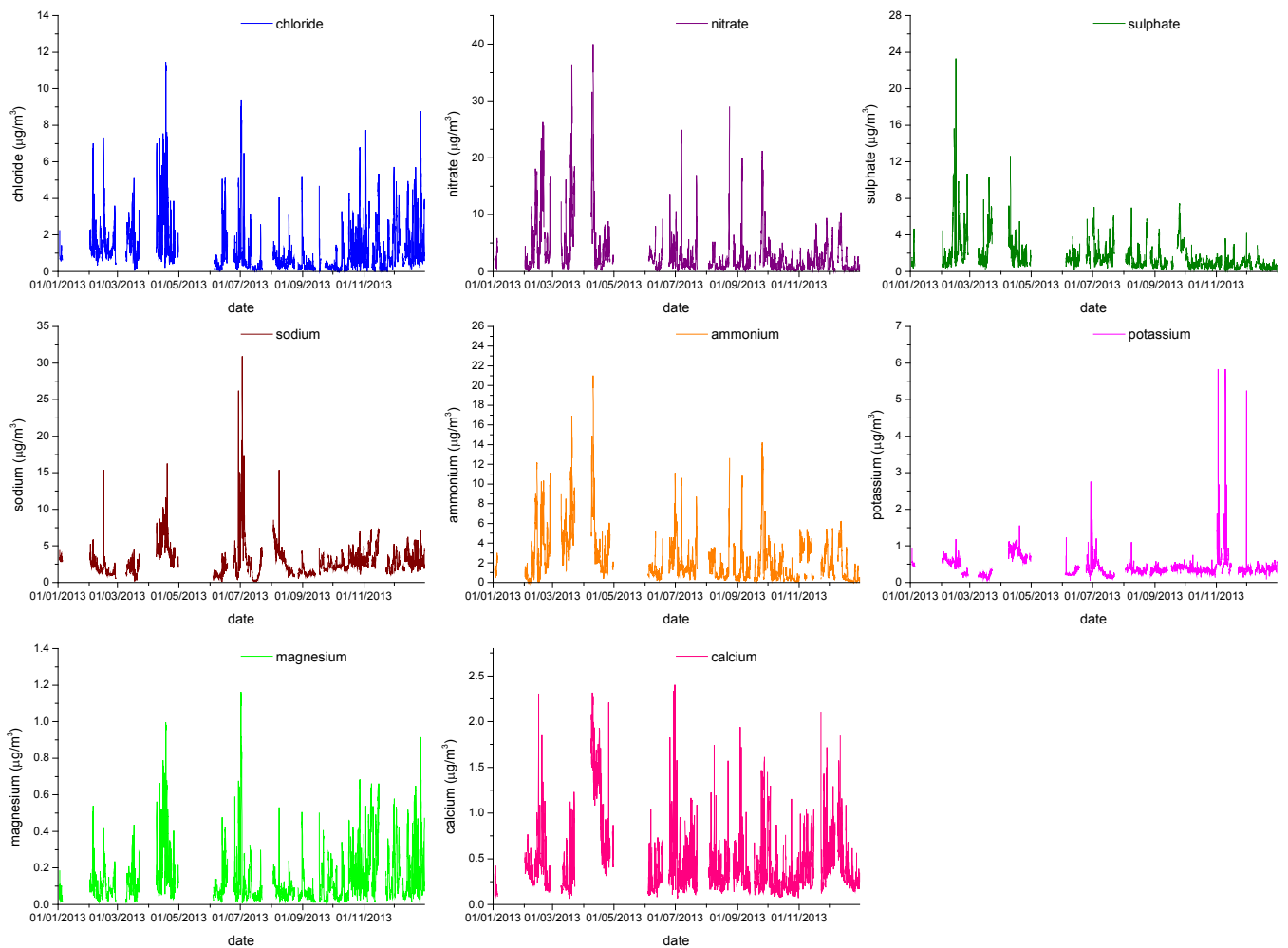


Figure 4-12 Time series for ion concentrations at North Kensington in 2013

‘Moderate’ PM_{10} and $PM_{2.5}$ concentrations were recorded in South-east England in mid-February, early and late March and early April. Pollution episodes in late winter and spring times are quite common and are normally caused by polluted air coming from the continent mixed with local emission, which lead to an increase of NO_3^- , SO_4^{2-} and NH_4^{2-} concentrations.

A PM episode occurred in summer (late August) which was due to an influx of pollution from the continent combined with warm and sunny conditions. This resulted in photochemical activity driving a pollution episode.

Higher concentrations appear in the Na^+ , Cl^- , K^+ and Mg^{2+} trends at the end June/beginning of July. Figure 4-13 shows a zoom of the trends during these days and a correlation between the four ions’ concentrations can be seen. These species are known to be the main components of sea-salt [8]. A back trajectory was carried out showing that the air masses during that period of time were coming primarily westerly from the northern Atlantic Ocean (see Figure 4-14).

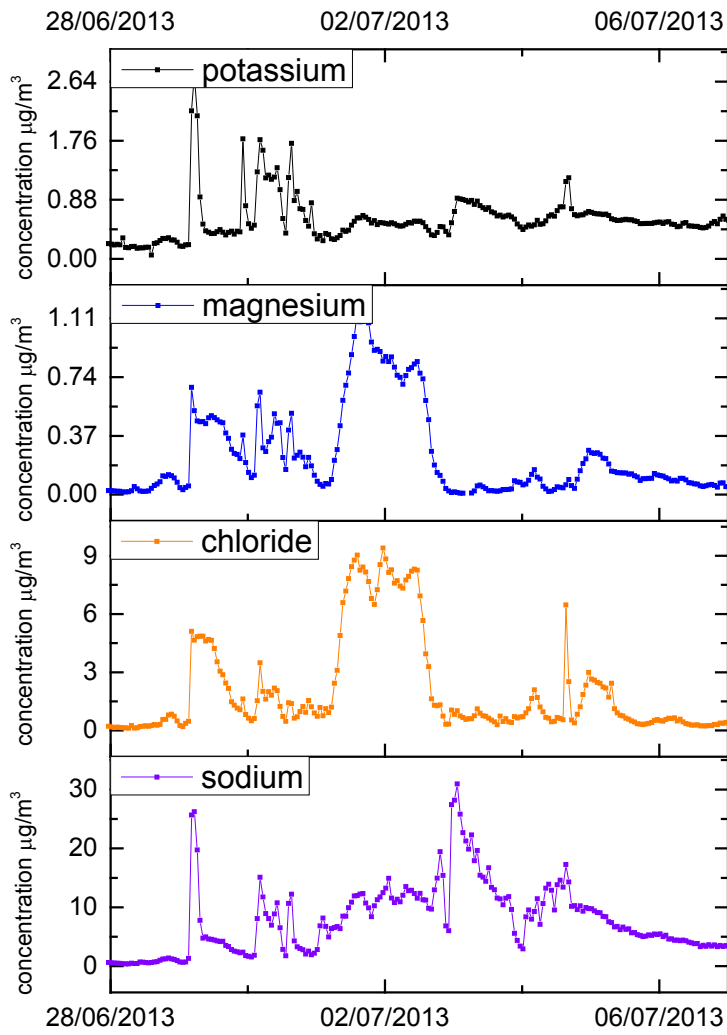


Figure 4-13 Potassium, magnesium, chloride and sodium concentration between 28th June and 7th July 2013 at North Kensington

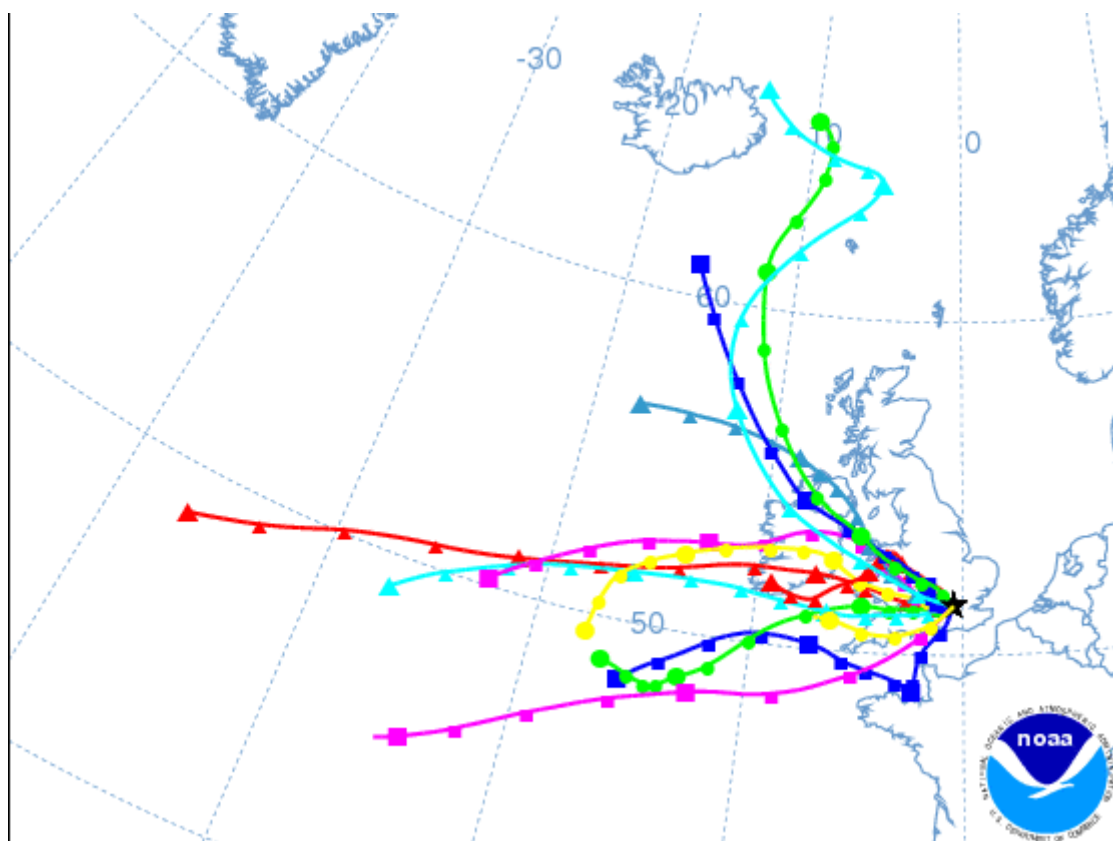


Figure 4-14 24-hour back trajectories ending in London for 96 hours from 4th July.

There is a good correlation between Mg^+ and Cl^- concentrations at North Kensington during the whole year ($R=0.91$), which leads to think that sea-salt could be the main source for these species, but less good between Na^+ and Cl^- concentrations ($R=0.57$). The Na^+ concentrations from URG instruments tend to be generally higher than expected and the reason for this behaviour is being investigated.

An interesting significant increase of K^+ concentrations were observed at North Kensington during the evenings and the nights of the two weekends at the beginning of November (1st, 2nd, 3rd November and 8th, 9th, 10th November), with the main peaks occurring on the two Saturdays, 2nd and 9th November (see Figure 4-15). These are believed to be caused by the fireworks in occasion of bonfire night. K^+ is one of the major components of fireworks [9 and therein cited literature]: 74% of black powder consists of KNO_3 , although no increase of NO_3^- concentrations could be found in this case. This is in agreement with previous work carried out on the contribution of fireworks to airborne particle concentrations [8,10].

An isolated K^+ peak was also observed on the night of 30th November. This corresponds to a slight increase in SO_4^{2-} concentrations as well. The reason for this increase is not yet clear.

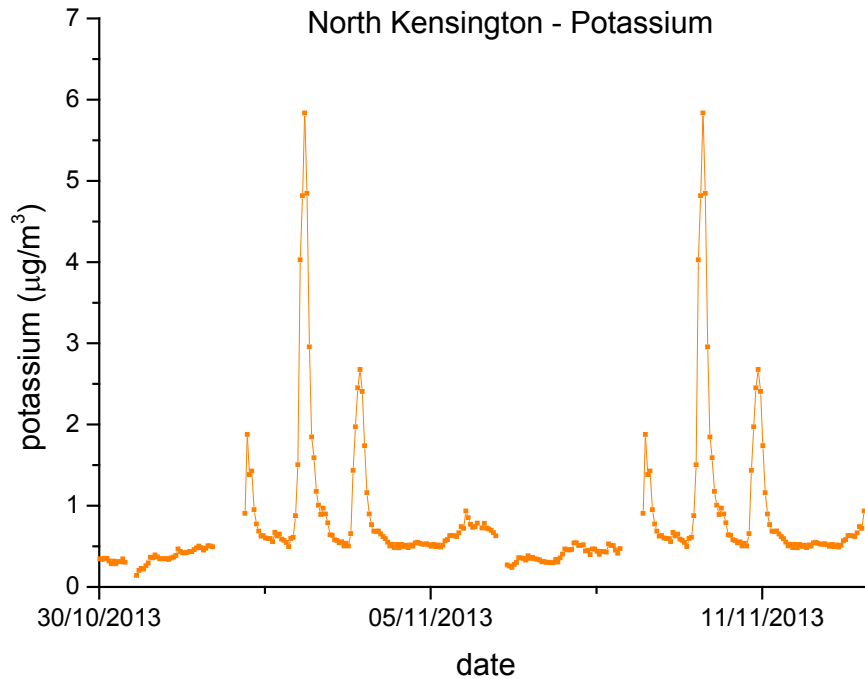


Figure 4-15 K^+ concentrations during the first half of November 2013 at North Kensington. The peaks are due to fireworks during the weekends in occasion of Bonfire night.

4.4 PARTICLE NUMBER AND SIZE DISTRIBUTIONS

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 2013 are shown in Figure 4-16. The plots have been shown on the same scale.

The reasons for the main data gaps were:

- **Harwell:** The laser of the CPC failed in December 2012 and no replacement is available from the manufacturer anymore. In May 2013 a loaned CPC was installed as replacement after being calibrated at NPL.
- **Birmingham:** The instrument was removed at the end of January for calibration at NPL and reinstalled at the beginning of March. On 23rd September the laser failed and not spare CPC was available as a replacement.
- **North Kensington:** The instrument was removed from site on 6th February for calibration and reinstalled on 21st February.
- **Marylebone Road:** The instrument was removed from site on 4th February for calibration at NPL and reinstalled on 22nd February. The instrument suffered from unstable flow in several occasions during the year which required new pump replacements and extra calibrations at NPL.

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 4-5 Monthly data capture for CPC instruments in 2013. 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. Note: ^ data capture calculated over the time the instrument was operational.

Month	Birmingham	Harwell	North Kensington	Marylebone Road
January	90%	-	94%	65%
February	50%	-	39%	72%
March	100%	-	81%	16%
April	97%	-	97%	94%
May	97%	100%^	99%	94%
June	97%	94%	82%	96%
July	100%	100%	100%	13%
August	100%	100%	99%	59%
September	100%^	97%	97%	31%
October	-	100%	100%	26%
November	-	97%	96%	59%
December	-	100%	100%	100%
Average	92%	98%	93%	60%

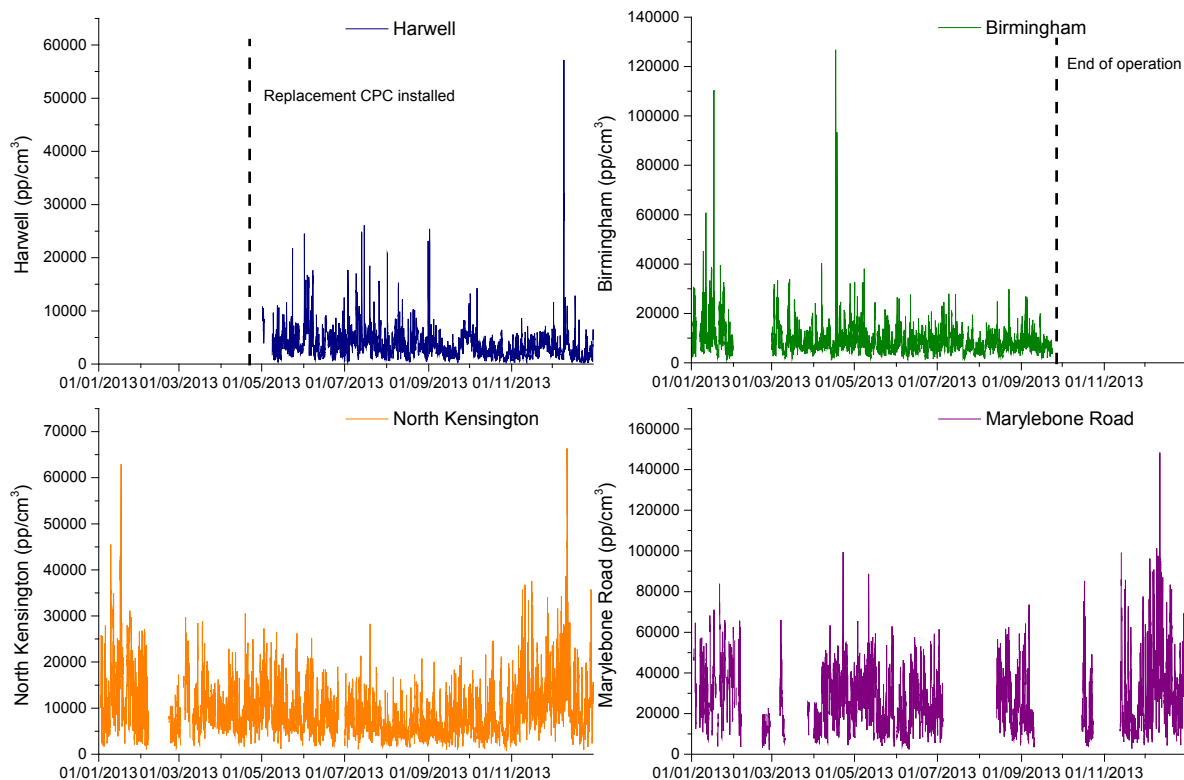


Figure 4-16 Time series of number concentrations during 2013 at the Network sites

High concentrations were recorded at Birmingham and North Kensington between 16th January and 18th January. This was due to a pollution episode caused by low winds and cold temperature that led to poor pollution dispersion. Pollution episodes of this kind at Marylebone Road are normally more

difficult to detect as particle concentrations are mainly driven by very local primary sources, specifically traffic.

High concentrations were also registered on 17th April and 18th April at the Birmingham site. Hourly PM₁₀ concentrations measured within the AURN Network showed concentrations up to 386 µg/m³ during those days at the same site.

The pollution episode on 11th and 12th December, described in Section 4.1, is also visible in the number concentrations at all the three operational 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.

4.4.2 Particle size number distributions

The SMPS instruments generate size spectra between 16 nm and 605 nm. Table 4-6 shows the monthly data captures.

The reasons for the main data gaps were:

- **Harwell:** The instrument was removed for service and calibration on 20th February and reinstalled on site on 12th March.
- **North Kensington:** Instrument removed for calibration at NPL on 16th February and was reinstalled on site on 5th March.
- **Marylebone Road:** Because of a possible leak in the system which introduced cabin air in the instrument, the January and February data had to be removed. The instrument was calibrated at NPL and reinstalled on site on 6th March.

Table 4-6 Monthly data captures for SMPS instruments during 2013. 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	100%	100%	0%
February	100%	100%	50%
March	53%	73%	81%
April	70%	93%	97%
May	67%	97%	87%
June	97%	95%	91%
July	100%	100%	72%
August	100%	92%	67%
September	100%	99%	96%
October	100%	99%	90%
November	100%	89%	98%
December	99%	81%	93%
Average	90%	93%	77%

The production of data from SMPS instruments is a complicated process, summarised schematically in Figure 4-17. Many stages of data processing are carried out by proprietary manufacturer's software to convert the raw data (number count versus Differential Mobility Analyser voltage) into the final data (number concentration versus particle size). While the size axis can be reliably calibrated using certified spheres, the number concentration axis, and hence both the scale and shape of the size distribution, is much less amenable to direct evaluation. Extra checks were performed again this year, as described in Section 4.4.3.

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 4-18. 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 [11].

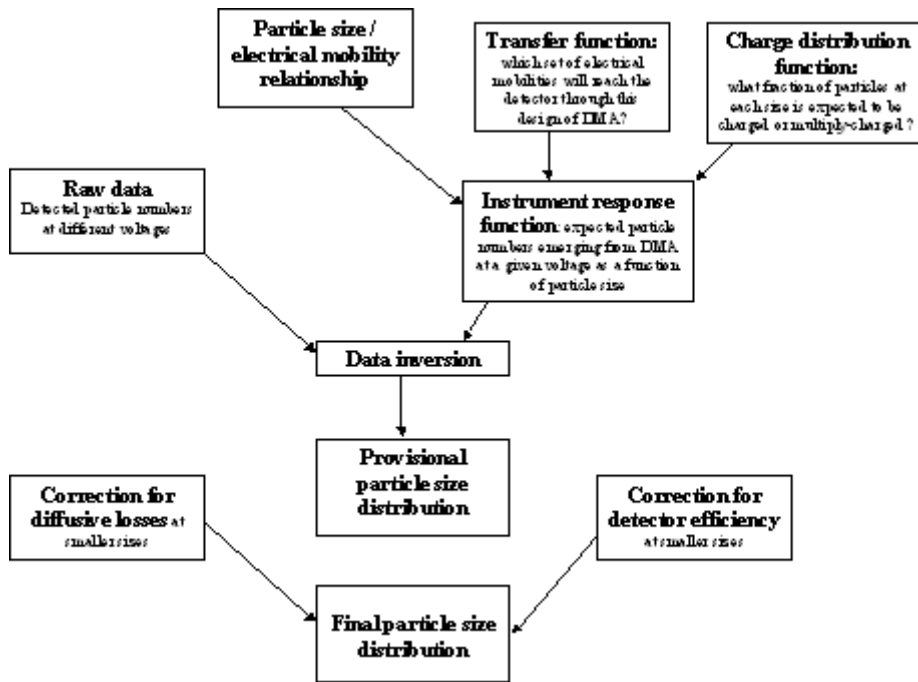


Figure 4-17 Schematic of the internal data processing of SMPS instrument in the Network

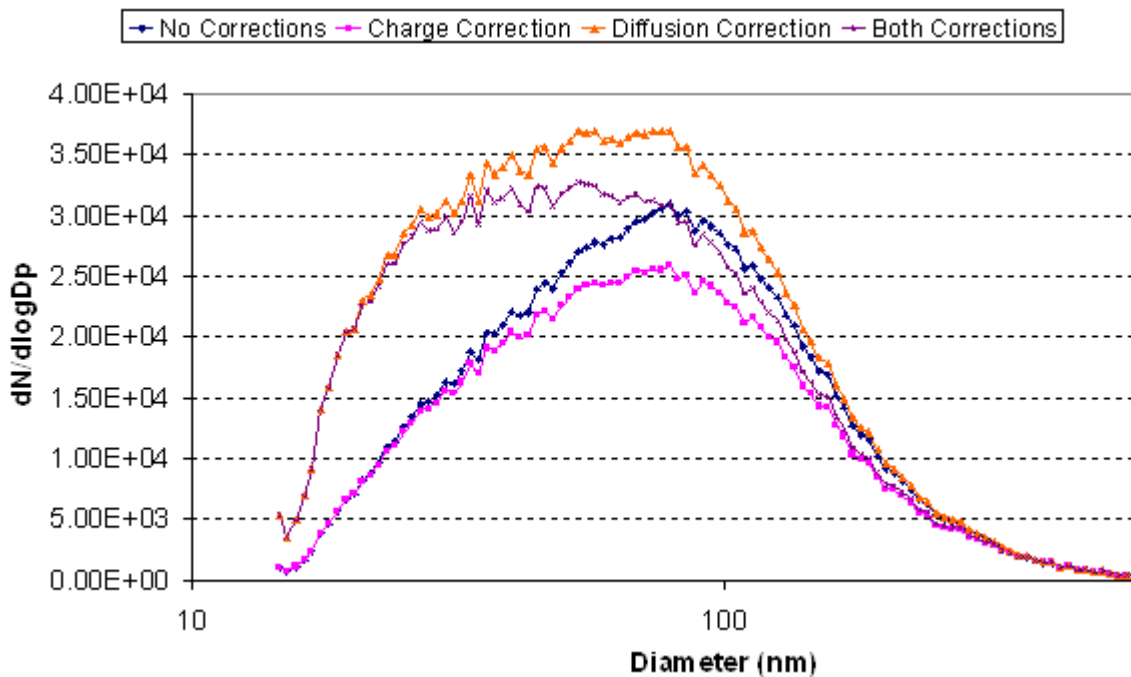


Figure 4-18 Effect of the multiple charge, the diffusion loss and their combined correction in the SMPS size spectrum.

The counts in each particle size bin measured during 2013 are presented as monthly averages in the left-hand panels of Figure 4-19 and as an annual average in the right-panel.

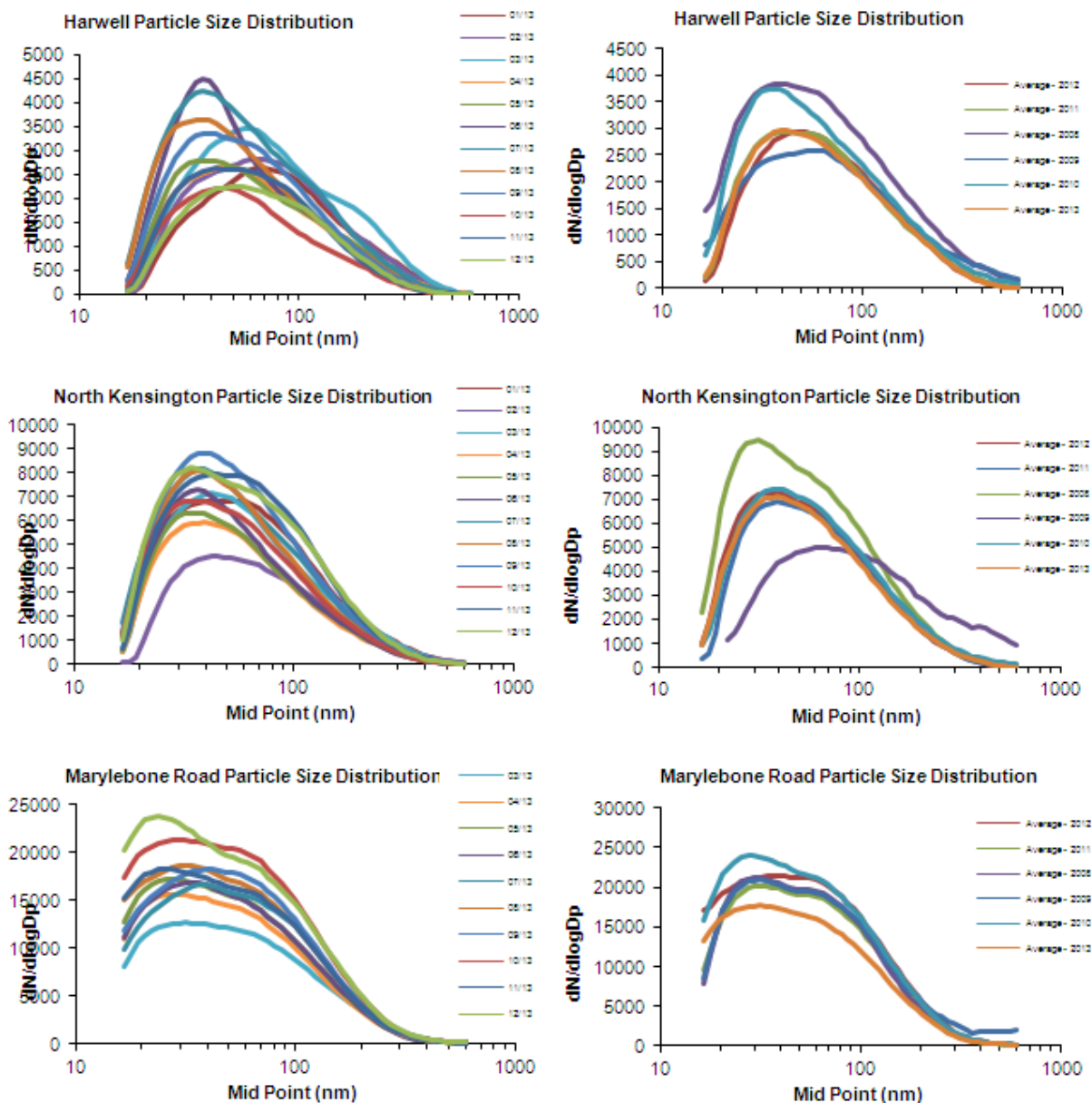


Figure 4-19 Monthly averaged particle size distributions at the Network sites during 2013 [left-hand panels] and comparison of the 2008, 2009, 2010, 2011, 2012 and 2013 annual-averaged size distributions [right-hand panels].

As observed in previous years, the size distributions at Harwell during the warmer months (May to September) 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 are likely to occur during warm days with high solar radiation when clean cool arctic or polar maritime air masses arrive in the UK [12,13].

4.4.3 SMPS checks and Intercomparison

To assess the performance of the network SMPSs, a series of experiments were carried out in the Airborne Nanoparticles lab at NPL (17 March 2014). The Marylebone (Mar), Harwell (Har) and North

Kensington (NK) SMPSs were tested in parallel, under controlled lab conditions. Certified latex spheres were used as calibration aerosols.

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 4-20. All three network SMPS units 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.

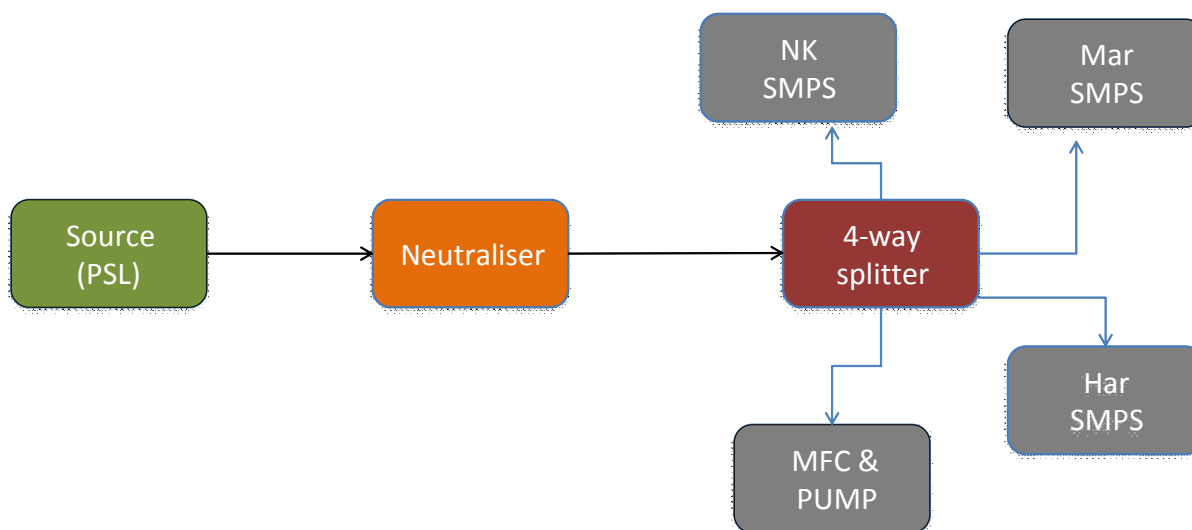


Figure 4-20 Schematic showing the parallel sampling of the three SMPS when connected to a flow splitter (with a Mass Flow Controller and pump to balance the flow) and fed with a single particle source (PSL), conditioned with a single neutraliser.

Results and Discussion

In Table 4-7 the PSL results for the three SMPS instruments are summarised and compared with the nominal diameters of the feeding polystyrene beads. In general, there is very good agreement amongst the three 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.

Conclusions

An intercomparison of three network SMPS units (Marylebone, Harwell and North Kensington) was performed under controlled lab conditions. The experiments with standard PSL aerosols showed that the three SMPSs can accurately and comparably measure size across the required nanoparticle range.

Table 4-7 Comparison of SMPS measured distributions with polystyrene latex (PSL) nominal values.

		PSL			
		59	92	125	203
		± 2	± 3	± 3	± 5
Site		nm	nm	nm	nm
Mar	Geometric mean	63.8	90.3	124.8	199.2
	Geometric st. dev.	1.08	1.08	1.06	1.06
Har	Geometric mean	63.7	90.2	123.9	198.2
	Geometric st. dev.	1.10	1.08	1.06	1.07
NKen	Geometric mean	65.0	91.8	126.5	202.2
	Geometric st. dev.	1.09	1.09	1.06	1.06
Mean					
2014		64.2	90.8	125.1	199.9
Mean					
2013		63.0	88.3	126.5	209.0

4.5 ANNUAL TRENDS

In this section, annual trends are reported for those species long-term measurements are available for.

4.5.1 Carbon measurements

Figure 4-21 shows the annual trends for OC/EC/TC measurements.

There is a general decrease of carbon concentrations at Marylebone Road and of EC concentrations at North Kensington. This decrease has been observed also in the Black Carbon long-term trend for Marylebone Road [3].

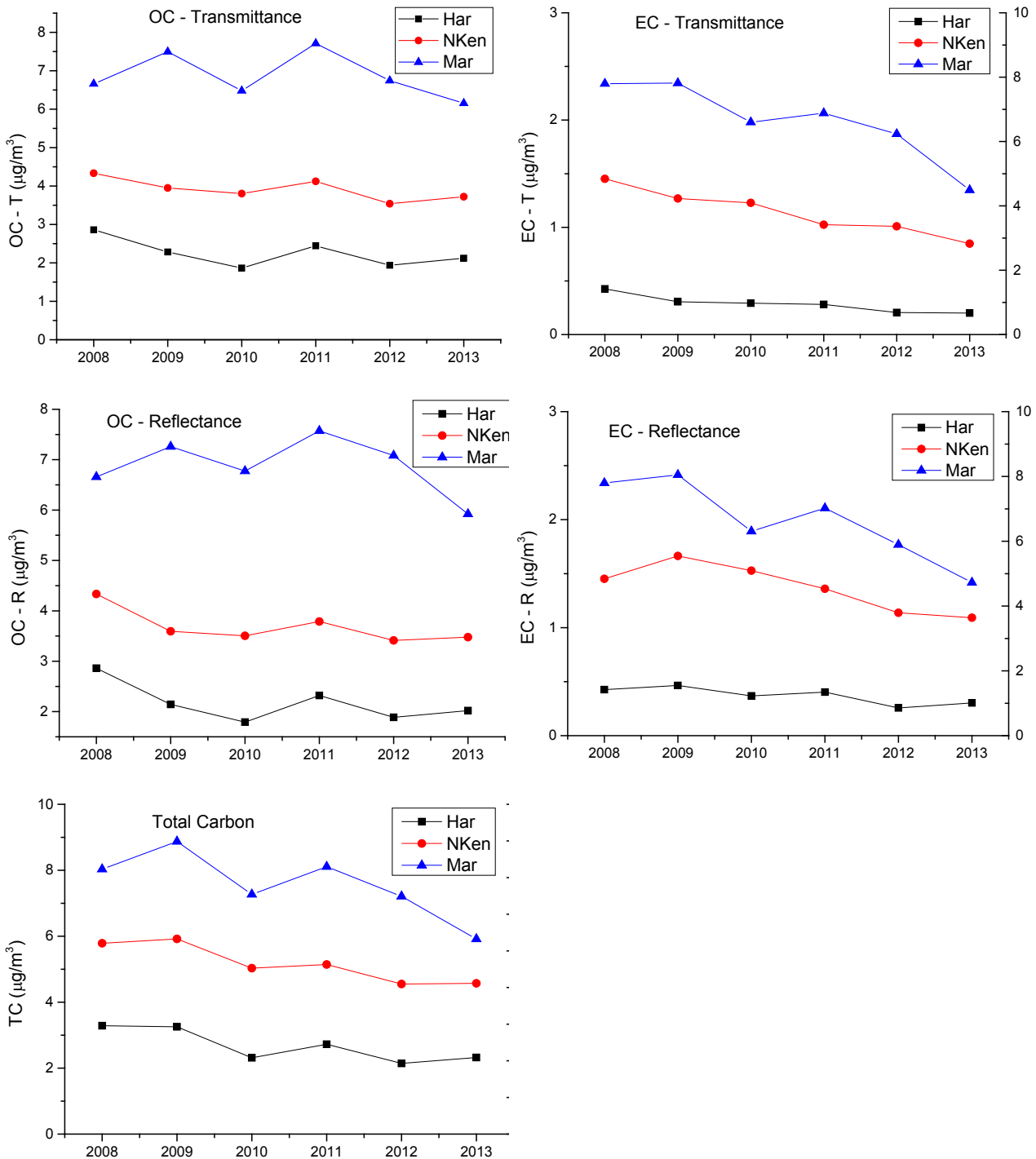


Figure 4-21 Annual trends for OC/EC/TC measurements. EC and TC values for Marylebone Road are shown on a secondary axis

Figure 4-22 shows long-term trend for the anion species. Before 2011, the anion concentrations were derived by using the manual method. The trend was clear and the three sites followed each other quite well. After the installation of the automatic instruments, some discontinuity can be observed.

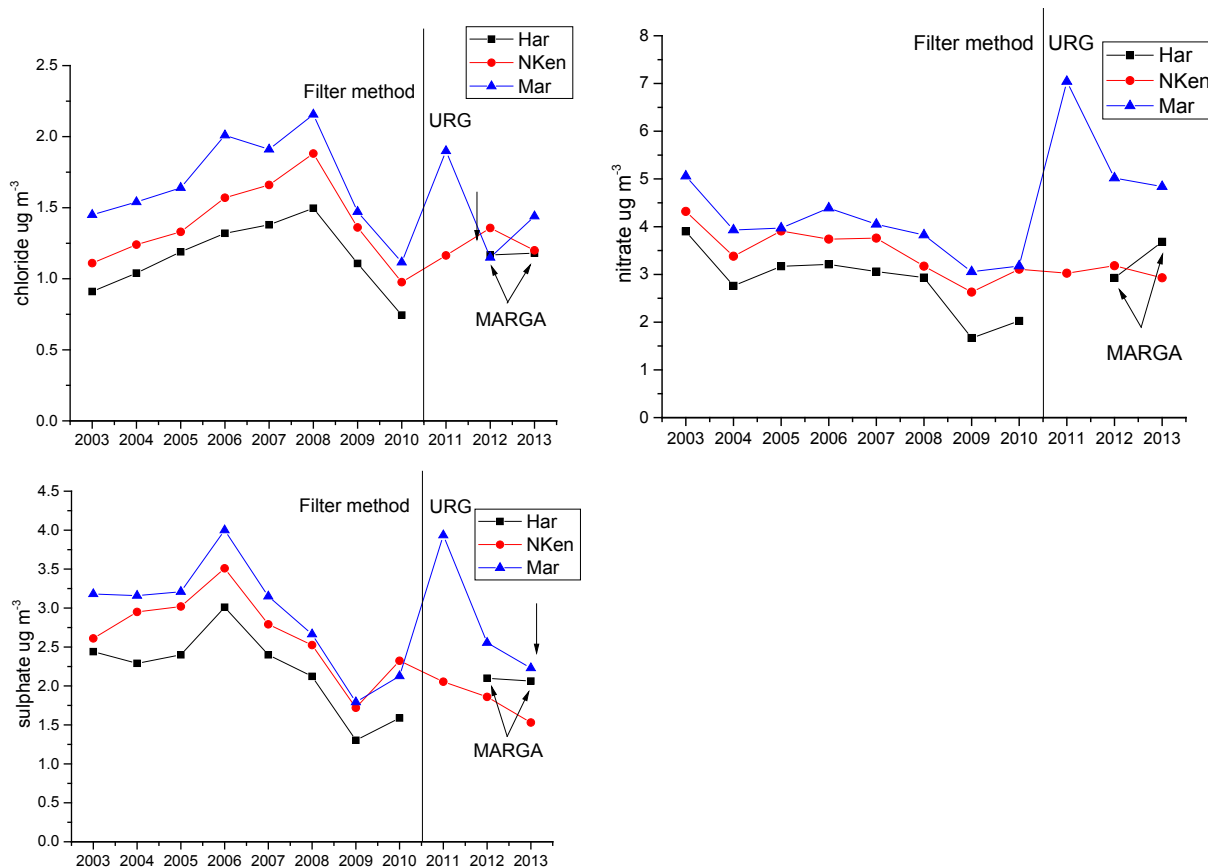


Figure 4-22 Anion long-term annual trends. Note: data capture for Marylebone Road in 2013 is only 22%. The 2012 and 2013 data for Harwell have been derived from the MARGA measurements.

Figure 4-23 shows long-term annual trends for CPC measurements at all sites. Long-term monthly trends are shown in Figure 4-24. The particle number concentrations have continued to slowly decrease 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.

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 % [14].

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 NO_x 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 [14].

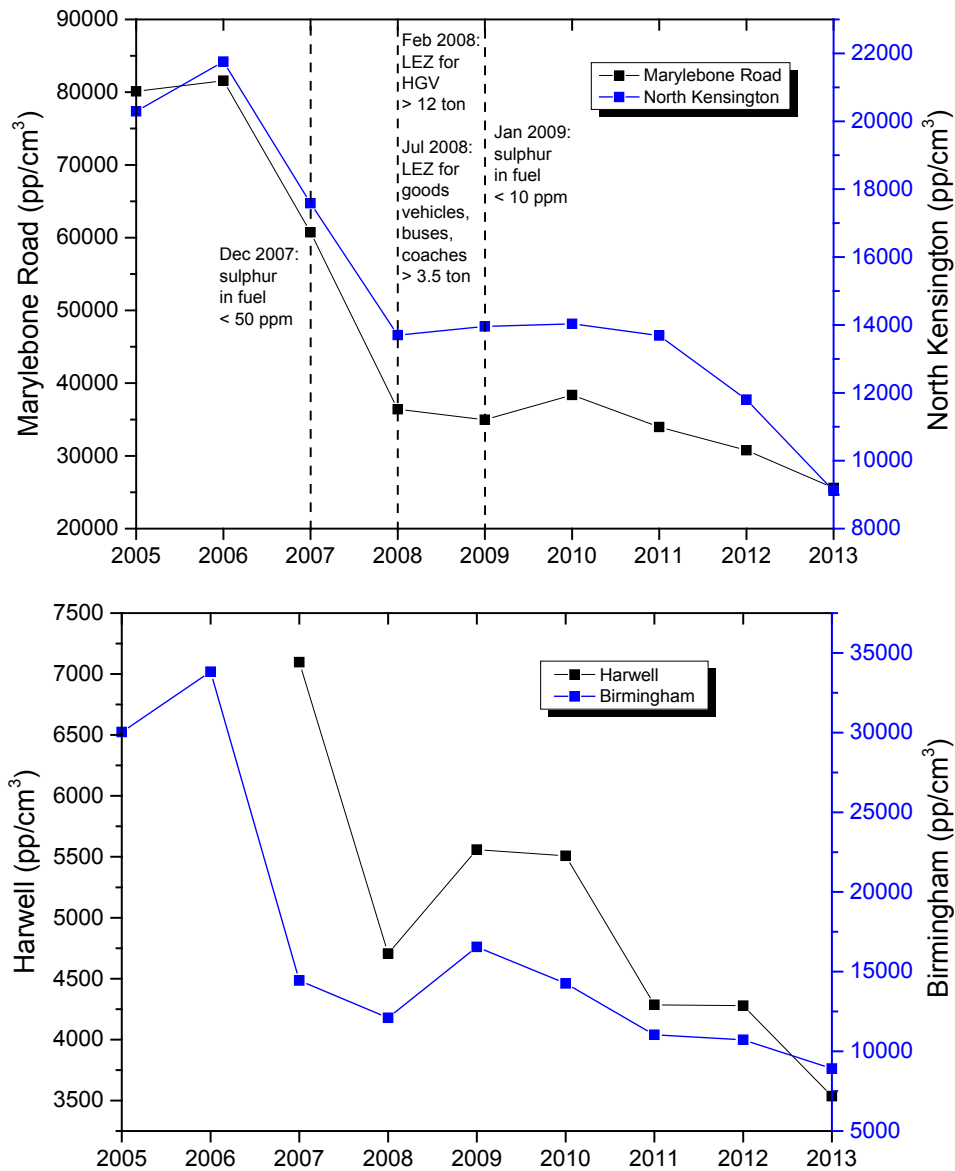


Figure 4-23 CPC long-term annual trends at all sites

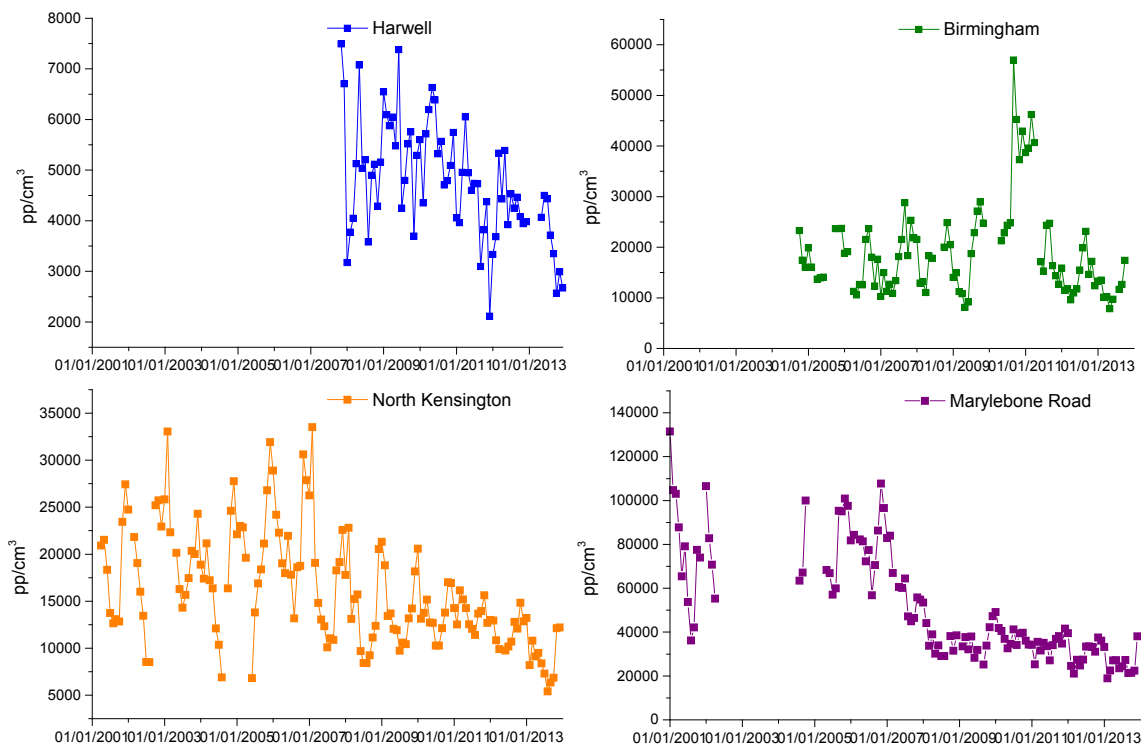


Figure 4-24 CPC long-term monthly trends at all Network sites

4.6 DIURNAL, WEEKLY AND MONTHLY PROFILES

Diurnal, weekly and monthly profiles have been plotted for the major water soluble ions and for particle number concentrations using the Openair tools [18,19,20].

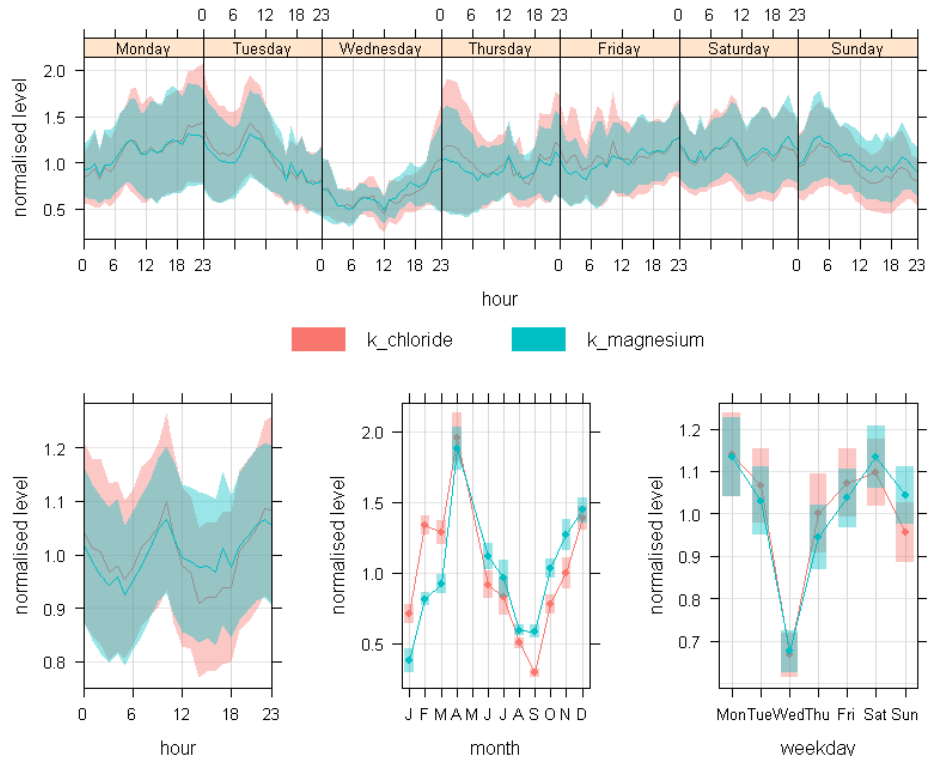
4.6.1 Profiles for anion and cation species

Figure 4-25 shows the profiles for Cl^- and Mg^+ concentrations at North Kensington and Marylebone Road. As mentioned in Section 4.3, there is a very good correlation between these two species, suggesting they derive from the same source, identifiable with sea salt.

The good correlation between SO_4^{2-} , NO_3^- and NH_4^+ in Figure 4-26 indicates the existence of both $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 . The lowest concentrations of NO_3^- and NH_4^+ in the afternoon are attributed to the dissociation of NH_4NO_3 at higher temperatures during the day. On the other hand, the broad peak of SO_4^{2-} in daytime is explained by the photochemical production with stronger solar radiation.

Ca^{2+} profiles at both sites show values characteristic of traffic contribution, possibly re-suspension of crustal material from road surfaces (see Figure 4-27).

North Kensington



Marylebone Road

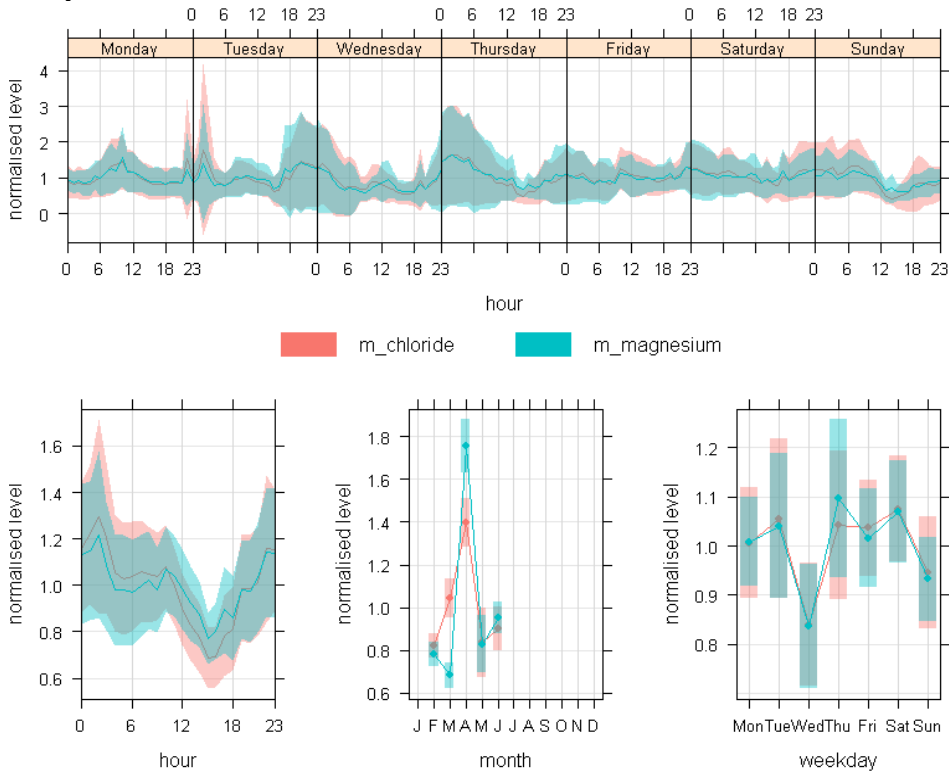
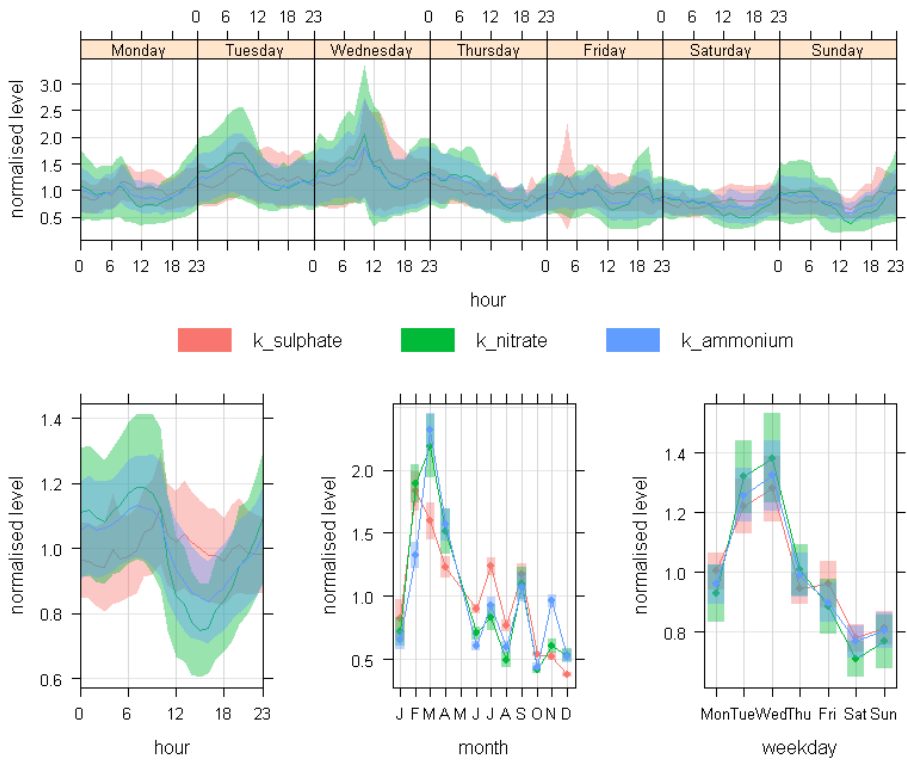


Figure 4-25 Diurnal, weekly and monthly profiles for Cl⁻ and Mg⁺ concentrations during 2013 at North Kensington (top) and Marylebone Road (bottom).

North Kensington



Marylebone Road

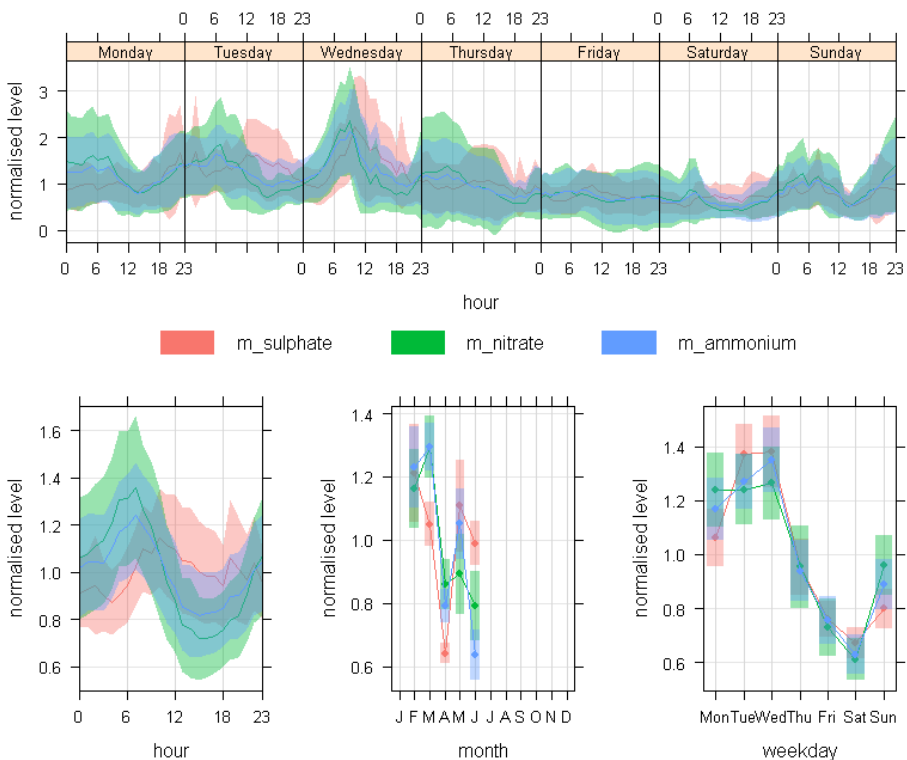
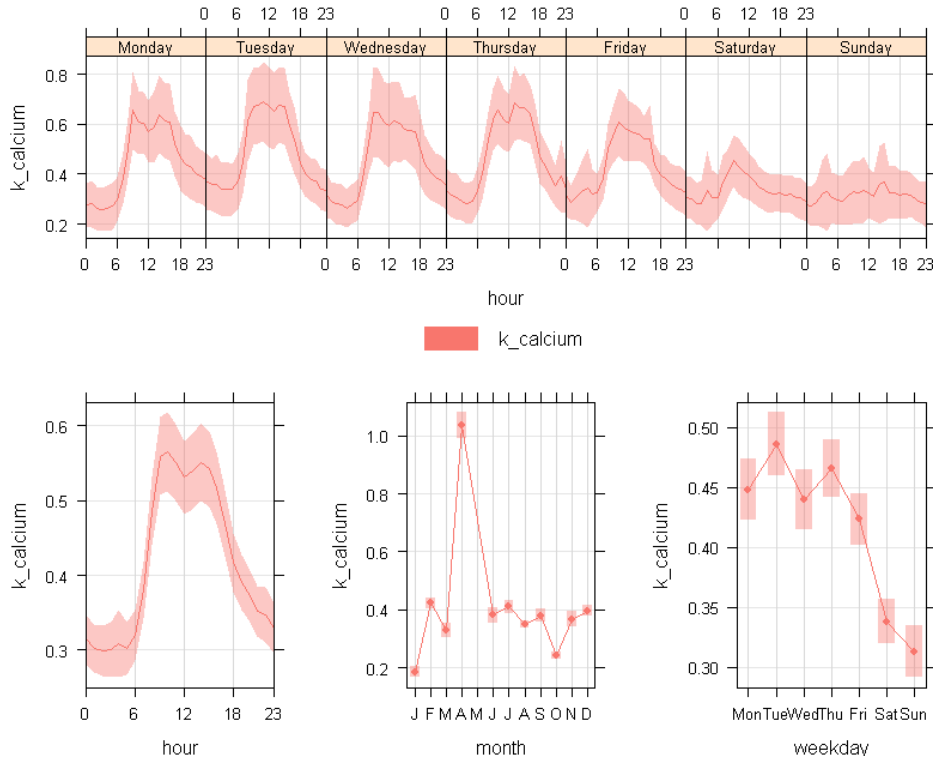


Figure 4-26 Diurnal, weekly and monthly profiles for NO_3^- , SO_4^{2-} and NH_4^+ during 2013 at North Kensington (top) and Marylebone Road (bottom).

North Kensington



Marylebone Road

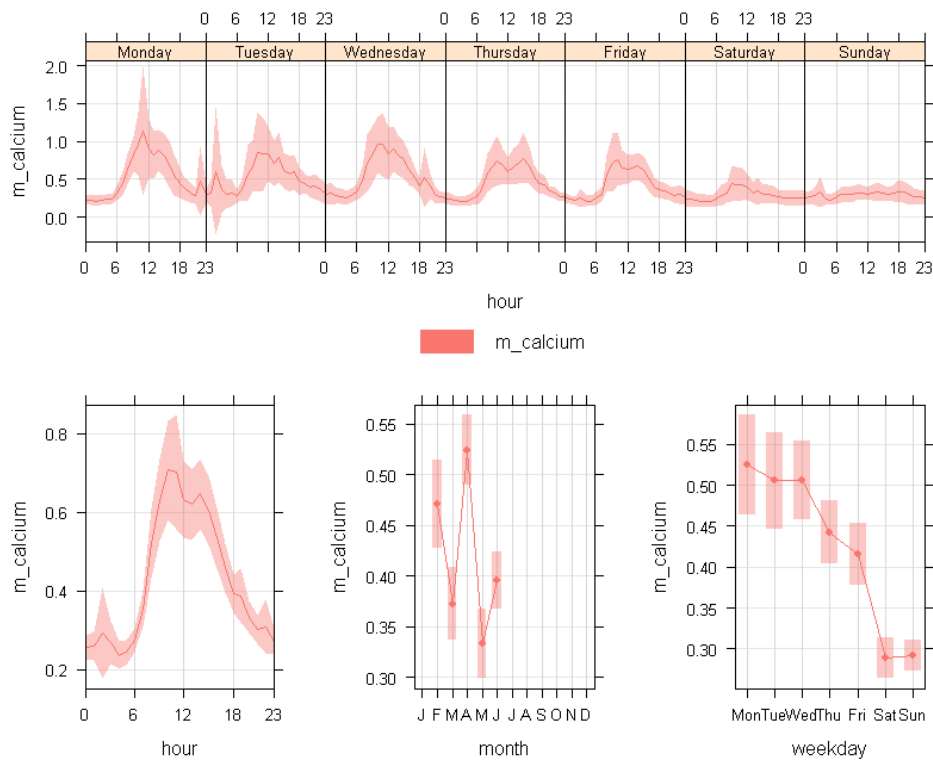


Figure 4-27 Diurnal, weekly and monthly profiles for Ca^{2+} during 2013 at North Kensington (top) and Marylebone Road (bottom).

4.6.2 Profiles for number concentrations

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 (photochemistry activities). 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 4.4.2.

At urban and urban background sites, the trends show a strong correlation with anthropogenic sources, with lower concentrations during the weekend, reflecting the traffic profile. 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.

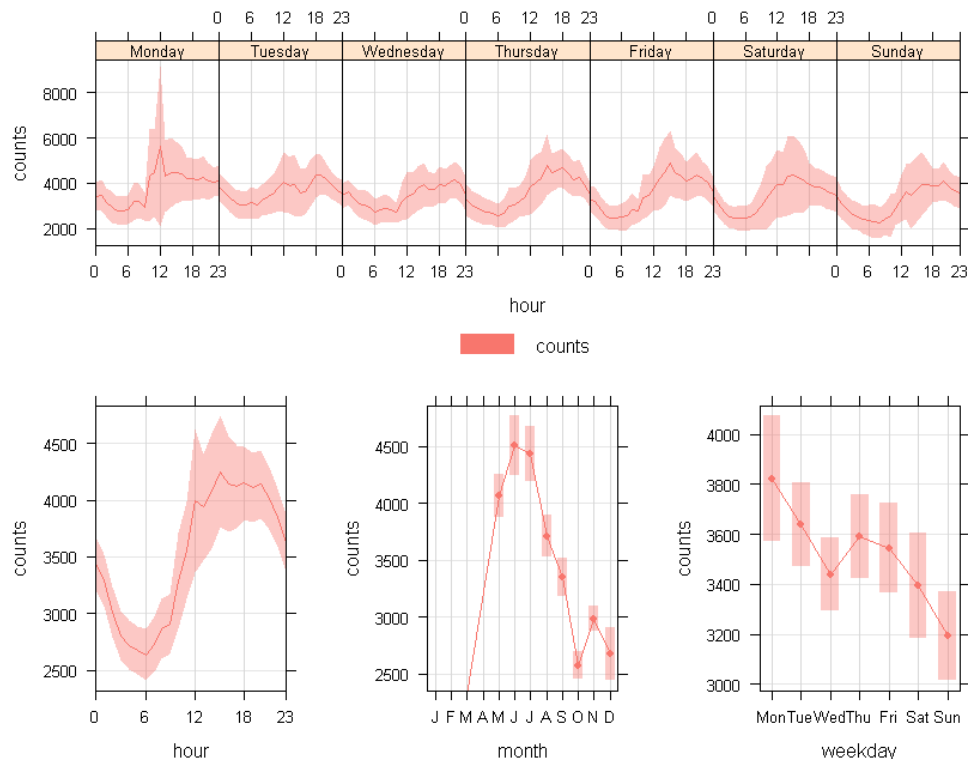


Figure 4-28 Diurnal, weekly and monthly profiles for number concentrations at Harwell in 2013

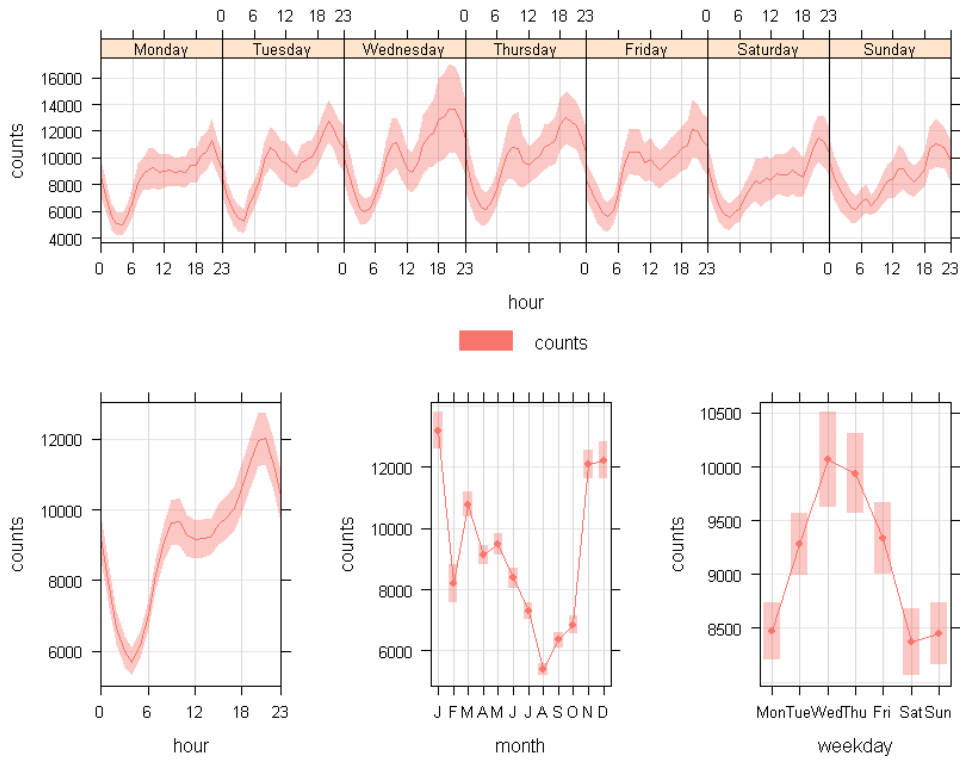


Figure 4-29 Diurnal, weekly and monthly profiles for number concentrations at North Kensington in 2013

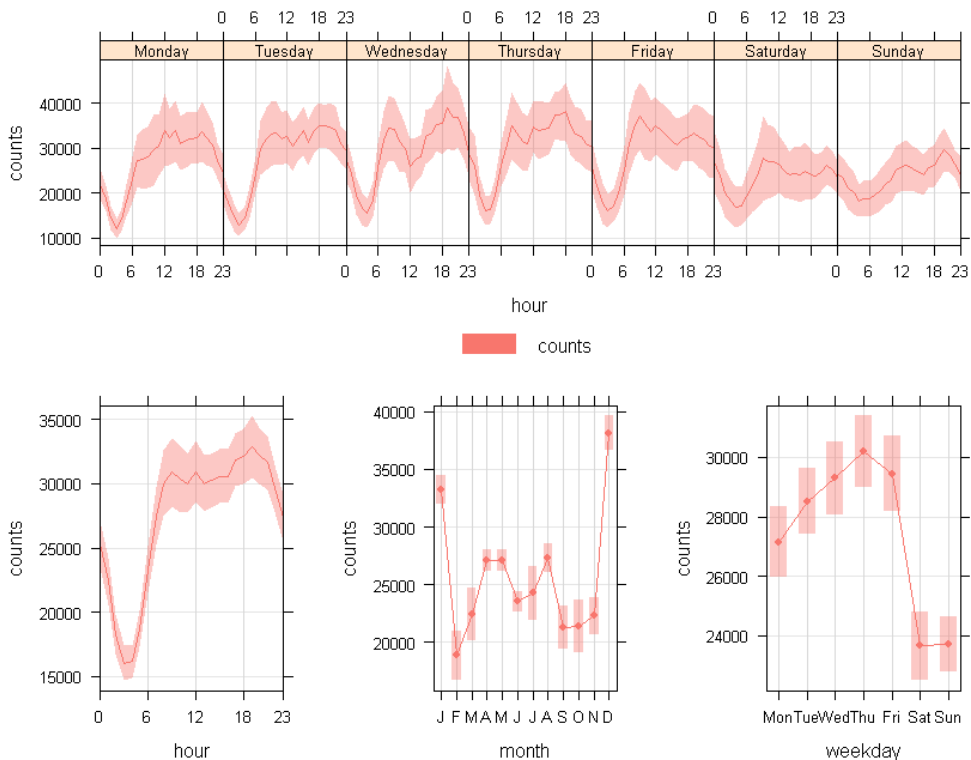


Figure 4-30 Diurnal, weekly and monthly profiles for number concentrations at Marylebone Road in 2013

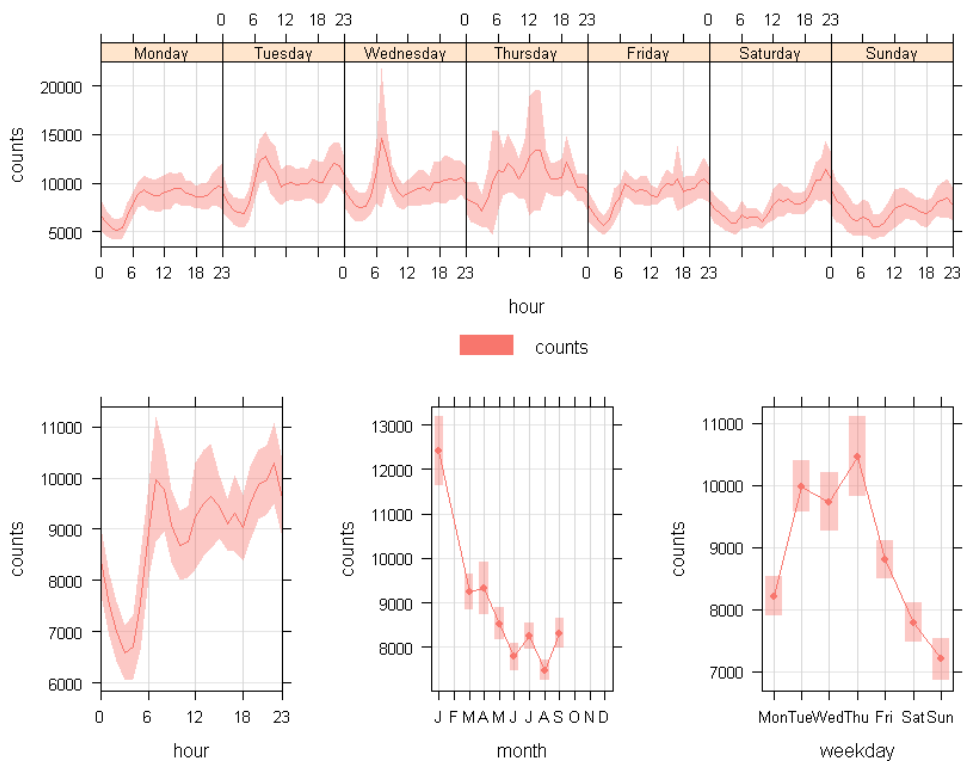


Figure 4-31 Diurnal, weekly and monthly profiles for number concentrations at Birmingham in 2013

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 at 20.55, 205.4 and 421.8 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 20.55 nm and 421.8 nm size bins follow opposite trends, probably depending on day/night chemistry and the height of the mixing layer.

At North Kensington, Figure 4-33, the 205.4 and 421.8 nm size bin trends show the typical rush hours in the morning and evening, along with domestic heating. Particles with 20.55 nm diameter seem to have different sources but are possibly connected to domestic heating in the evenings, mainly gas.

At Marylebone Road, Figure 4-34 in contrast, the trends for the different sizes are strongly correlated, demonstrating 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.

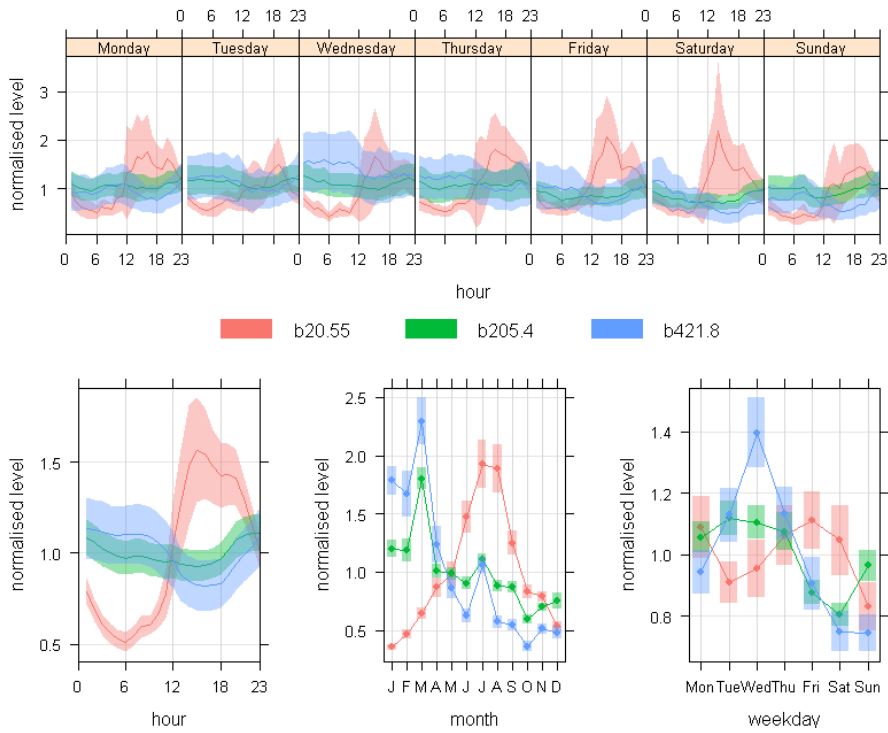


Figure 4-32 Diurnal, weekly and monthly profiles for 3 SMPS size bins at Harwell in 2013

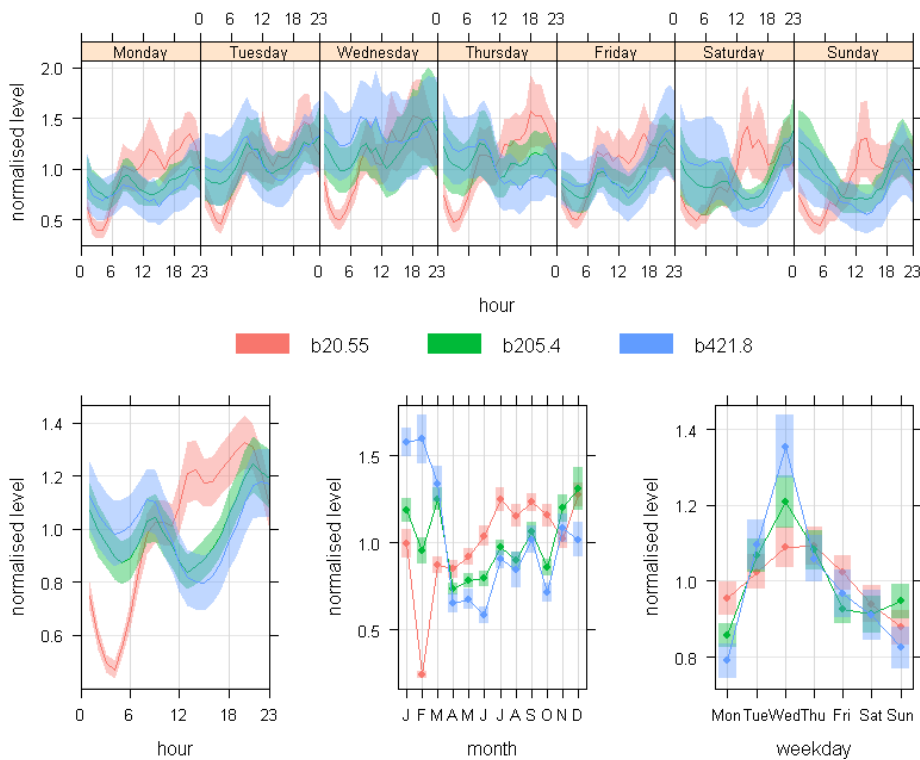


Figure 4-33 Diurnal, weekly and monthly profiles for 3 SMPS size bins at North Kensington in 2013

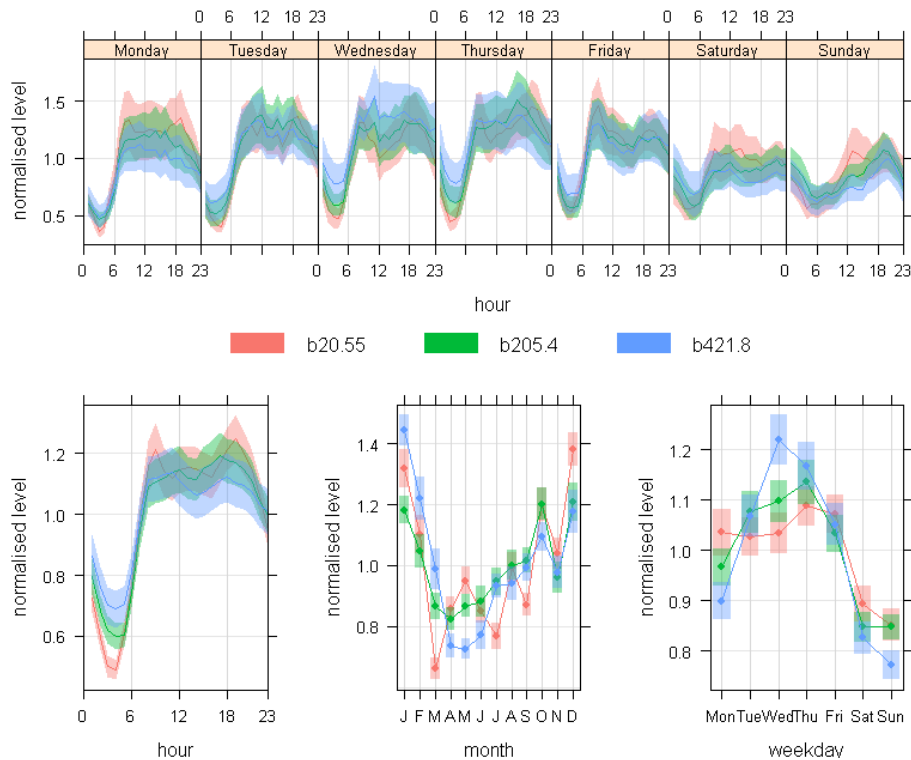


Figure 4-34 Diurnal, weekly and monthly profiles for 3 SMPS size bins at Marylebone Road in 2013

4.7 METEOROLOGICAL DATA

Although not a formal part of this measurements programme, meteorological data have been collated from the measurements made at Rochester as part of the Defra monitoring networks. Monthly data captures for the meteorological masts during 2013 are displayed in Table 4-8. Wind roses are shown in Annex 1.

Table 4-8 Monthly data capture for meteorological instruments in 2013 at Rochester

January 2013	93%
February 2013	100%
March 2013	100%
April 2013	97%
May 2013	97%
June 2013	100%
July 2013	97%
August 2013	99.9%
September 2013	100.0%
October 2013	100.0%
November 2013	100.0%
December 2013	100.0%
Average	99%

5 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.

5.1 UPDATE ON RELATED UK ACTIVITIES

5.1.1 London specific measures

The characterisation of the chemical composition of PM is of particular importance in London. Roadside locations in London were the only areas identified as likely to exceed the PM₁₀ 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 buses, coaches and lighter lorries were brought 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. HGVs, buses and coaches needed to meet Euro IV particulate matter standards 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.

5.1.2 Research Council Activities in London

ClearfLo is a large NERC-funded project involving 11 UK partners. The ambition is to provide integrated measurements of the meteorology, composition and particulate loading of London's urban atmosphere, made at street level and at elevated sites, complemented by modelling to improve predictive capability for air quality. Long-term measurements 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 through 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.

5.1.3 Defra and other National Monitoring activities

AURN measurements of PM₁₀ and PM_{2.5}

Any investigation of PM should ultimately be linked to the officially reported PM₁₀ and PM_{2.5} measurements from the AURN, which are based primarily on TEOM-FDMS instruments, with some gravimetric data using Partisol (1 m³/hr) and reference (2.3 m³/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 rural 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 PM₁₀ 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).

5.2 UPDATE ON EUROPEAN ACTIVITIES

5.2.1 EU Air Quality Directive 2008/50/EC

The EU Air Quality Review Process, aimed at the revision of the 2008 Directive on Ambient Air Quality and Cleaner Air for Europe, is underway, but the timescale for this is not clear. It appears that more attention is currently being given to a revision of the 2001 National Emissions Ceilings Directive, which was the main focus for the European Clean Air Policy Package issued for discussion in December 2013. The proposal is to expand the set of pollutants covered by ceilings to: (primary) PM, SO₂, NO_x, VOCs, NH₃ and CH₄.

5.2.2 CEN standards

2013 has seen considerable CEN activity in the areas covered by this Network.

CEN TC 264 WG 15 has completed the process of updating the gravimetric PM₁₀ standard EN 12341:1998, together with the gravimetric PM_{2.5} standard EN 14907:2005, to form a revised EN

12341. The revised EN 12341 designates one sampler design (at 2.3 m³/hr) as the reference, and attempts to clarify the status of other “established” samplers such as the Digitel (at 30 m³/hr) and the Partisol (at 1 m³/hr) by giving them special status (in Annex B of the standard). The proposed changes in the standard, for example limiting the relative humidity during filter conditioning to 45-50% rather than the present 45-55%, are expected to reduce variations rather than produce step changes to the data.

The working group has also produced a CEN Technical Specification CEN/TS 16450 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.

Both of these documents may change relatively soon in the light of validation work being carried out to check various specific parts of the documents.

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.

The most relevant aspect of this work is that the performance characteristics of “compliant” CPCs are to be set out in the TS. It is clear that manufacturers will need to modify their instruments before any compliant instruments are available. These performance characteristics were finalised in April 2014.

- 2) Standard methods for measuring particle number concentration over more limited size ranges, as used to form size distributions, ie SMPSs, with appropriate sampling, operating, QA/QC and calibration procedures. This document has only recently been started, but the 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 is currently underway in both areas. One significant issue to be explored during validation work is whether there are practical limits to the concentrations for EC (and OC) – in $\mu\text{g}\cdot\text{cm}^{-2}$ 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 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 $\text{PM}_{2.5}$ 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.

6 MAIN FINDINGS OF TOPIC REPORTS IN 2013

Two Topic Reports were produced during the year on the subjects of “Elemental and Organic Carbon” and on the “Analysis of the hourly measurements of chloride, nitrate, sulphate, sodium, ammonium, potassium, magnesium and calcium within PM_{10} particulate matter at roadside, urban background and rural sites”.

6.1 ELEMENTAL AND ORGANIC CARBON

The dependence of data collected during 2010–2 from roadside, urban background and rural sites on day of the week and month of the year, along with wind and temperature conditions was established and the secondary component of organic carbon (SOC) calculated assuming that primary organic carbon (POC) is associated with elemental carbon (EC).

Concentrations of SOC were almost identical at the roadside (London Marylebone Road: LMR) and urban background sites (London North Kensington: LNK) which is consistent with behaviour as a regional secondary pollutant, although the strong decline of concentration with wind speed at low wind speeds (Figure 6-1) may indicate some primary particulate from local discrete sources, or an influence of wind speed on the particle/vapour partitioning of semi-volatile components of secondary organic particles.

The wind speed dependence and a higher concentration of SOC at lower temperatures (Figure 6-2), may be a result of the presence of wood smoke or the semi-volatile nature of organic carbon particulate, while concentration increases at higher temperatures may be due to enhanced formation

due to photochemical processes during the warmer periods of the year. Similar dependencies of “UV particulate matter” from the co-located aethalometer network support this interpretation of the presence of wood smoke. It was concluded that non-traffic sources of organic carbon were to be dominant, comprising a strong secondary component, but with contributions of other primary sources such as wood smoke.

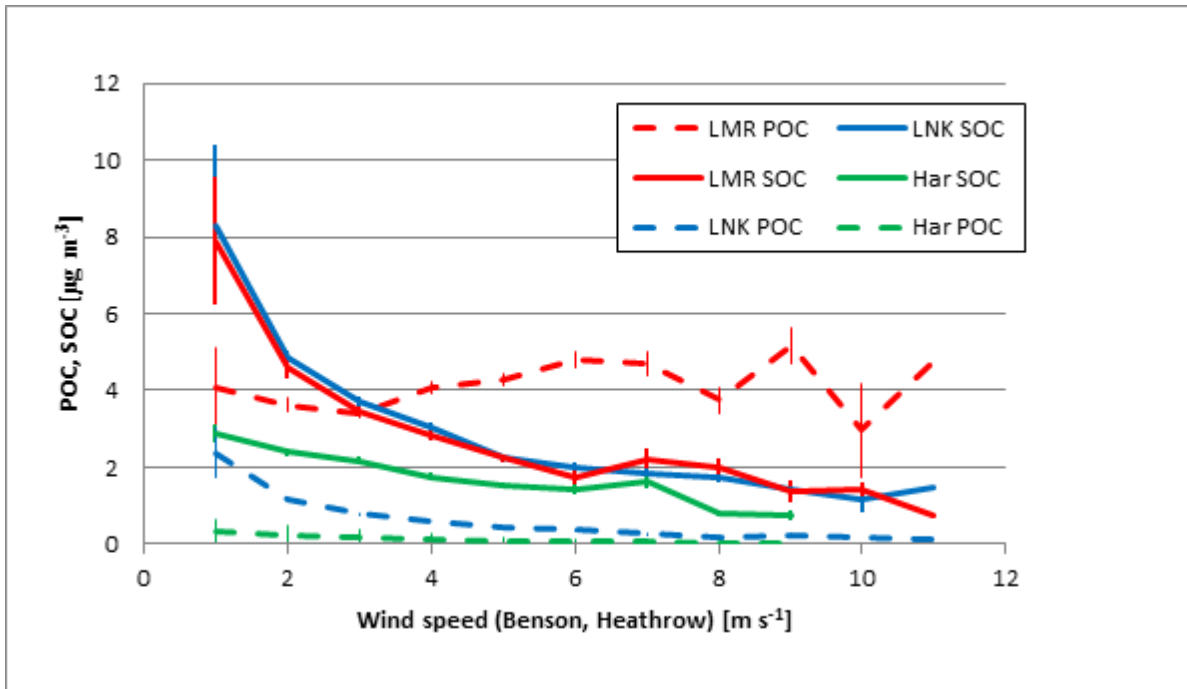


Figure 6-1: Primary (POC) and secondary organic carbon (SOC) concentrations versus wind speed measured at Benson (Harwell) and Heathrow (LNK, LMR)

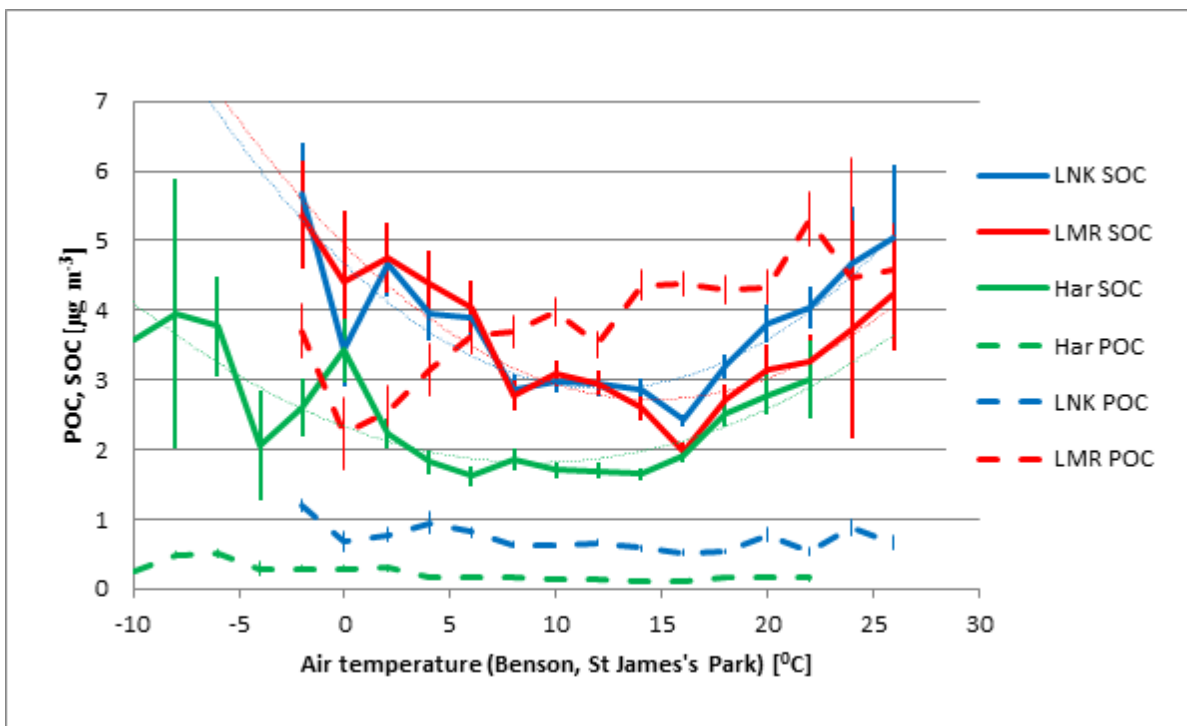


Figure 6-2: Primary (POC) and secondary organic carbon (SOC) concentrations versus air temperature measured at Benson (Harwell) and St James's Park (LNK, LMR)

6.2 ANALYSIS OF THE HOURLY MEASUREMENTS OF CHLORIDE, NITRATE, SULPHATE, SODIUM, AMMONIUM, MAGNESIUM, POTASSIUM AND CALCIUM WITHIN PM₁₀

Hourly chemical speciation data obtained during 2011 and 2012 from the URG-9000B particle analysers at London Marylebone Road and London North Kensington, and the MARGA analysers at Harwell and Auchencorth Moss were analysed, and while there are major gaps in the data set, day of the week and diurnal effects were examined along with the influence of meteorological conditions.

Diurnal profiles (Figure 6-3) of the concentrations of chloride (marine), nitrate (secondary combustion) and calcium (geological) particulate show a slight dip in chloride concentrations during the afternoon, probably due to increased dispersion, with a larger dip in the concentrations of nitrate at similar times of day, which is likely to be a result of the decomposition of the particulate due to higher temperatures. Calcium concentrations are higher at the London urban sites during the working day, while at the rural Harwell site (where the local surface geology is chalk) concentrations are generally much higher and increase during the afternoon and evening.

Chloride concentrations show (Figure 6-4) an increase with higher wind speeds compatible with increased emissions in higher wind speeds over the ocean, while nitrate concentrations fall with increasing wind speed, particularly at the urban sites where local sources of precursor gases are important. In the case of calcium, different concentration – wind speed relationships are evident between the sites, with concentrations increasing with wind speed at the roadside site Marylebone Road (LMR), while they decrease with wind speed at the rural (chalk influenced) site (Harwell). The behaviour at Marylebone Road is suggestive of resuspension of road dusts at higher wind speeds while the reduction of calcium concentrations with wind speed at Harwell suggests a primary emissions source in the easterly wind sector (Figure 6-5(c)).

Chloride concentrations tend to be higher during south westerly winds (Figure 6-5), particularly at Harwell and North Kensington (LNK), possibly in part due to winds from this direction being generally stronger. In contrast, nitrate concentrations are greater in north easterly - and at the urban sites (LNK and LMR) easterly – winds. Calcium concentrations are greatest at Harwell in easterly winds - the direction of most of the activity on the adjacent business park, while at the roadside site (LMR) there is a broad band of increased concentration in southerly winds – a result of particulate re-suspended from the roadway being transported to the sampling position on the south side of the street by recirculating air within the street canyon. There is no evidence of additional material in westerly winds from the direction of the nearby light controlled junction and pedestrian crossing which is seen in exhaust emissions measured at this location.

Examination (Figure 6-6) of a high concentration event in October 2012 when hourly urban PM₁₀ concentrations peaked at over 80 µg m⁻³ on 24 October showed high concentrations of nitrate at the three south east England sites, while chloride concentrations were low, and calcium concentrations did not show any prolonged period of high values, demonstrating that the event was a result of the build-up of secondary pollutants.

The availability of an increasing amount of hourly, chemically speciated, particulate concentration data allows for a better understanding of the process causing variation in the PM₁₀ concentrations.

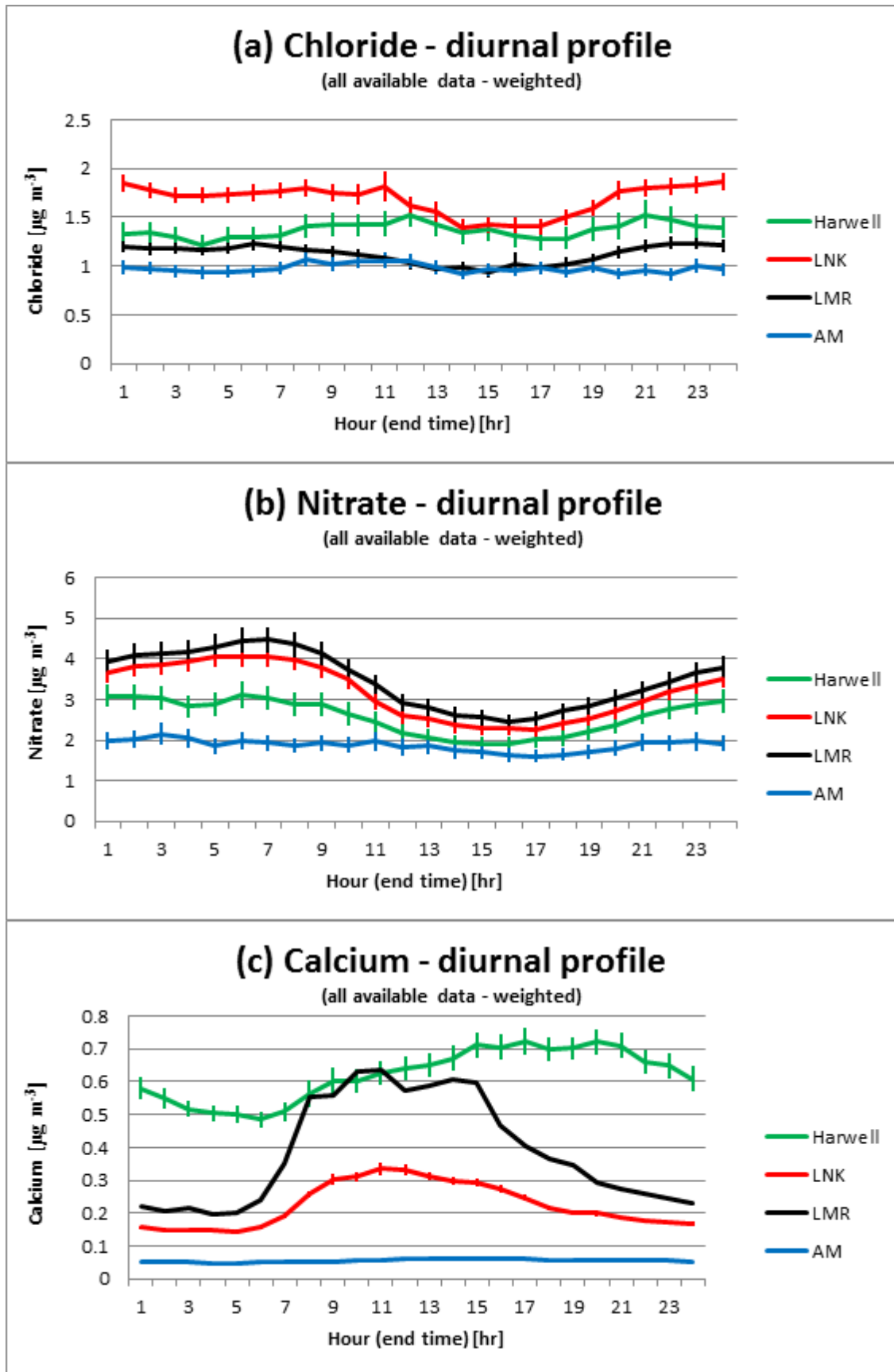


Figure 6-3: Weighted diurnal profiles of URG-9000B and MARGA analytes at Harwell (Harwell), North Kensington (LNK), Marylebone Road (LMR) and Auchencorth Moss (AM): (a) chloride; (b) nitrate; (c) calcium.

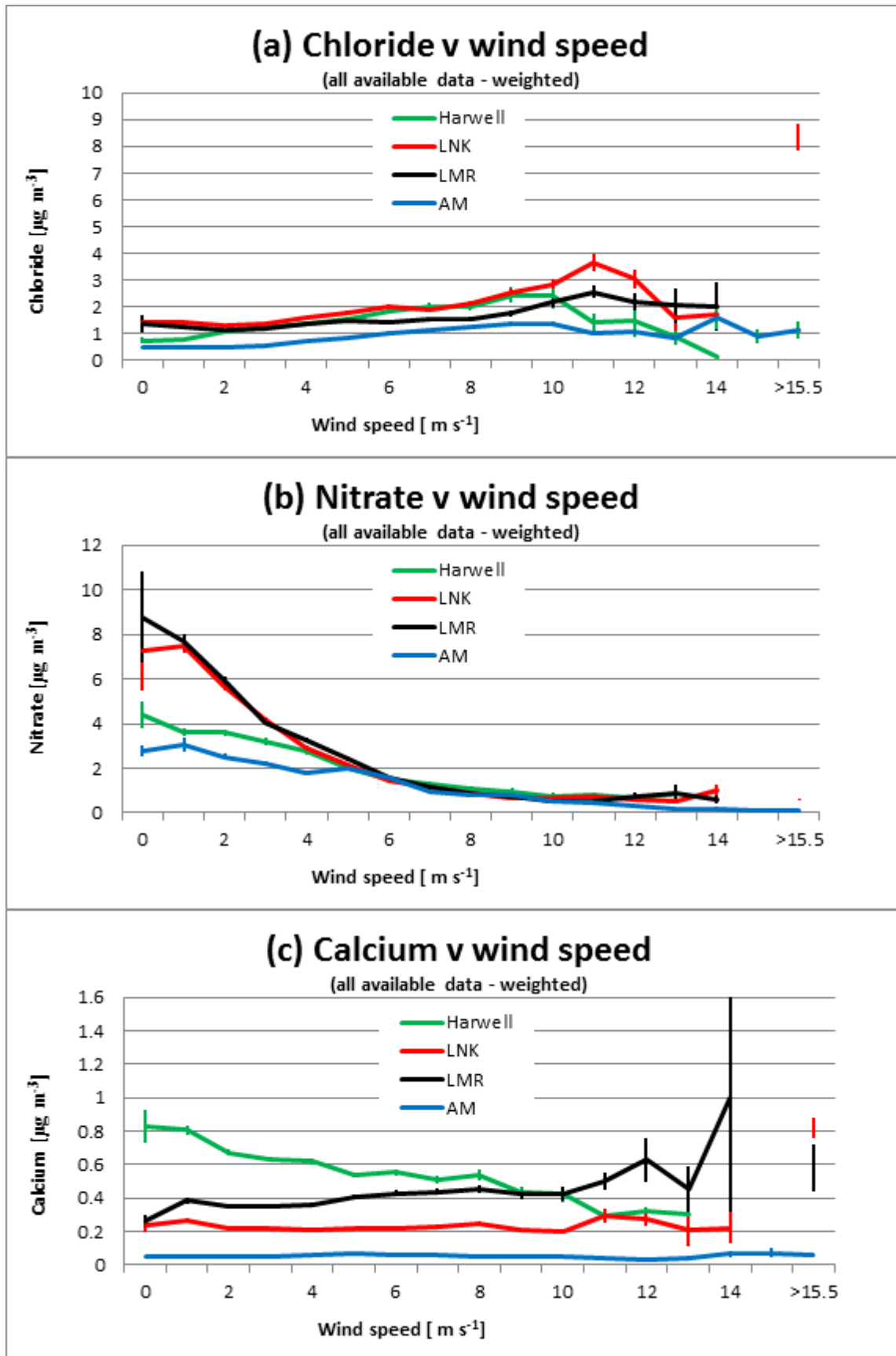


Figure 6-4: Weighted plots of URG-9000B and MARGA analytes versus wind speed at Harwell (Harwell), North Kensington (LNK), Marylebone Road (LMR) and Auchencorth Moss (AM): (a) chloride; (b) nitrate; (c) calcium.

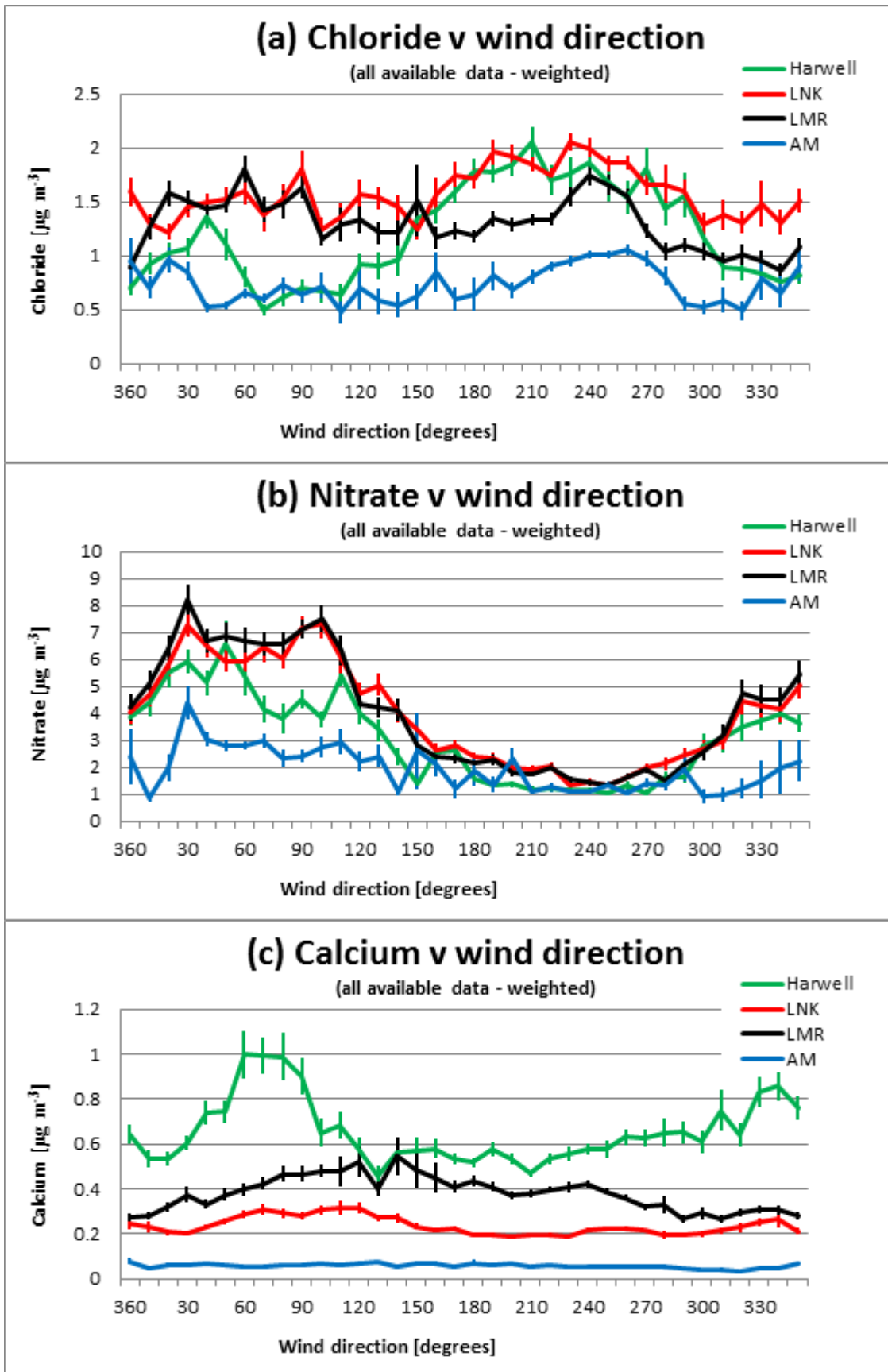


Figure 6-5: Weighted plots of URG-9000B and MARGA analytes versus wind direction at Harwell (Harwell), North Kensington (LNK), Marylebone Road (LMR) and Auchencorth Moss (AM): (a) chloride; (b) nitrate; (c) calcium.

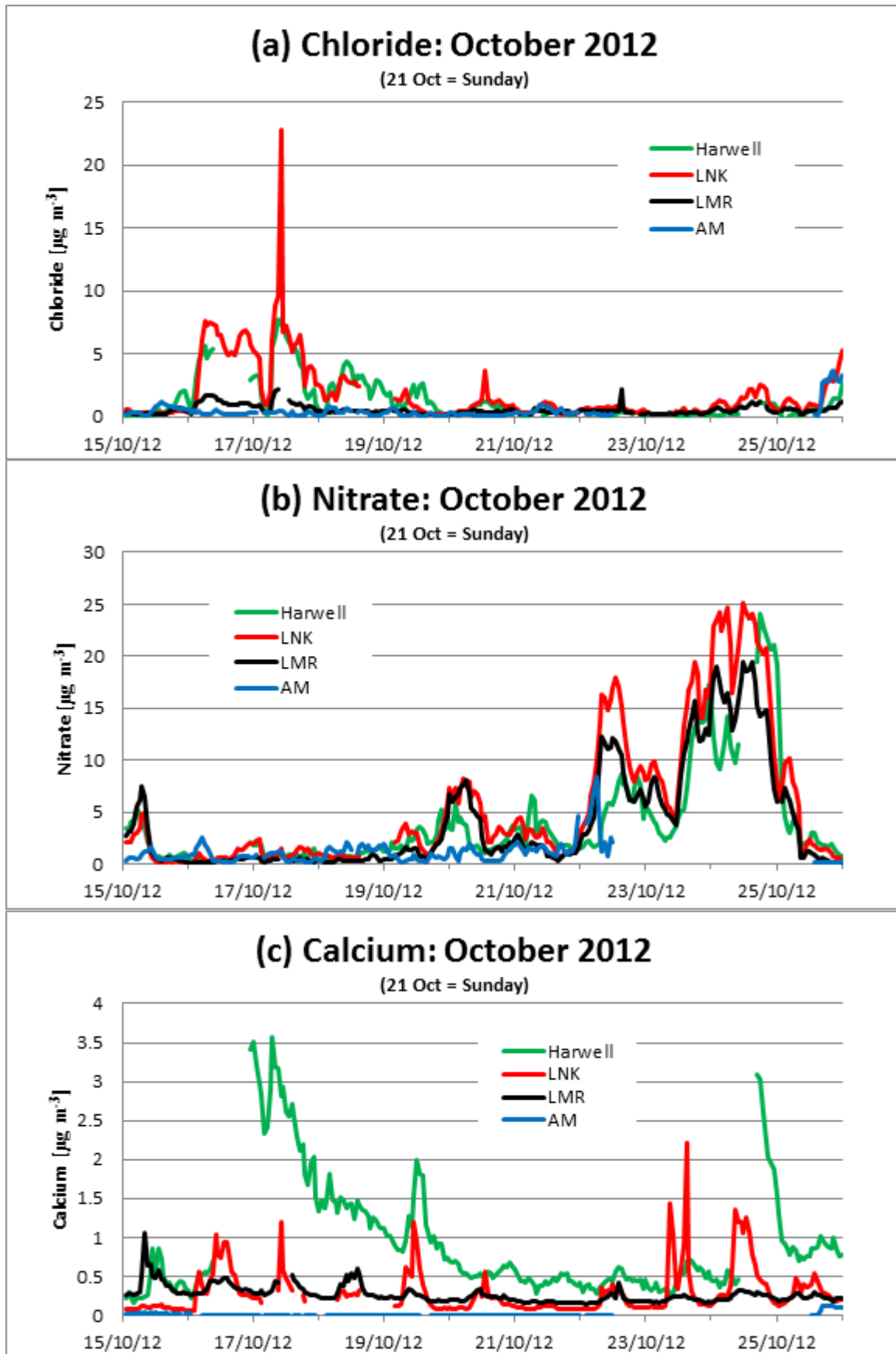


Figure 6-6: Concentrations of URG-9000B and MARGA analytes at Harwell (Har), North Kensington (LNK), Marylebone Road (LMR) and Auchencorth Moss (AM) during the period 15 to 25 October 2012: (a) chloride; (b) nitrate; (c) calcium.

7 CONCLUSIONS

The primary purpose of this report is to summarise both the operational history of the Network in 2013 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 2013. Possible sources could be identified, but further investigation is required.

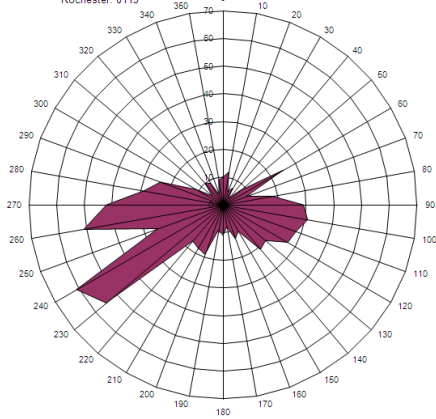
8 ACKNOWLEDGEMENTS

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

ANNEX 1. WIND ROSES AT ROCHESTER

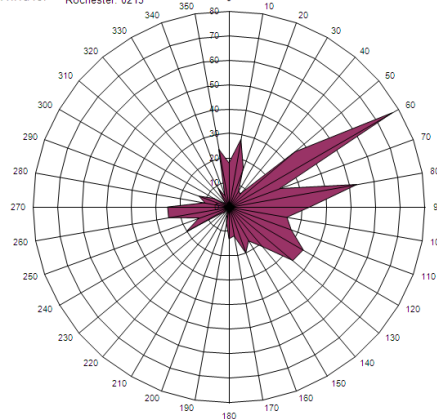
January 2013

Average Wind for Rochester: 0113 1.39m s⁻¹ at 254.82 Degrees



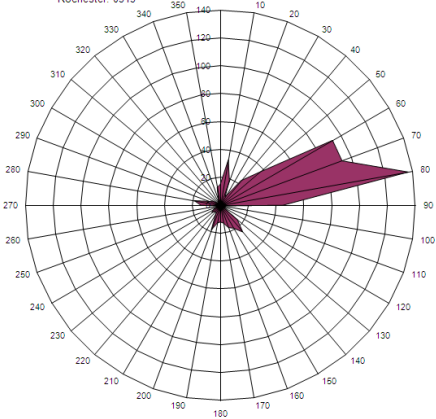
February 2013

Average Wind for Rochester: 0213 1.26m s⁻¹ at 177.39 Degrees



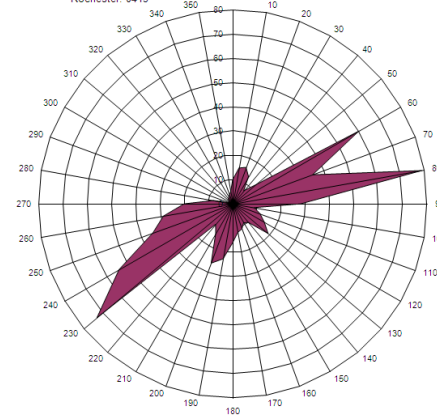
March 2013

Average Wind for Rochester: 0313 2.43m s⁻¹ at 67.17 Degrees



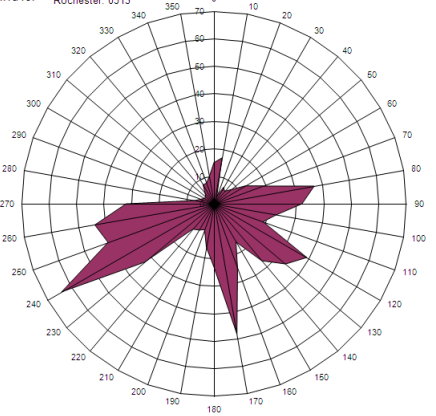
April 2013

Average Wind for Rochester: 0413 0.31m s⁻¹ at 250.64 Degrees



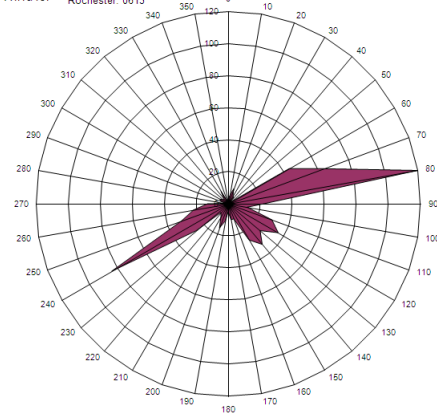
May 2013

Average Wind for Rochester: 0513 1.65m s⁻¹ at 101.39 Degrees



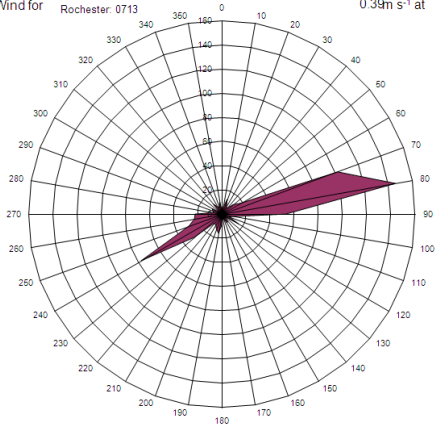
June 2013

Average Wind for Rochester: 0613 0.62m s⁻¹ at 103.78 Degrees



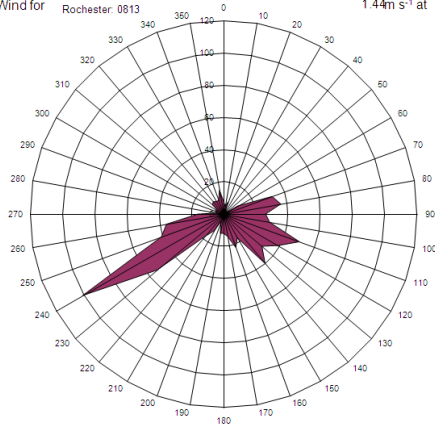
July 2013

Average Wind for Rochester: 0713 0.39m s⁻¹ at 296.86 Degrees



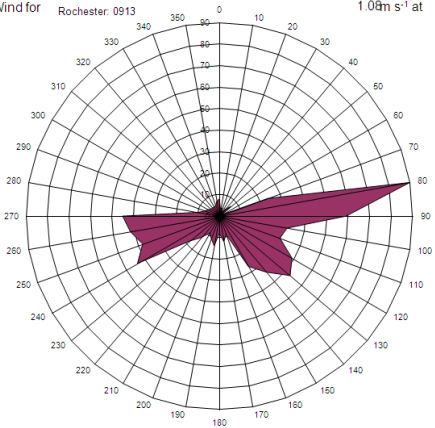
August 2013

Average Wind for Rochester: 0813 1.44m s⁻¹ at 90.97 Degrees



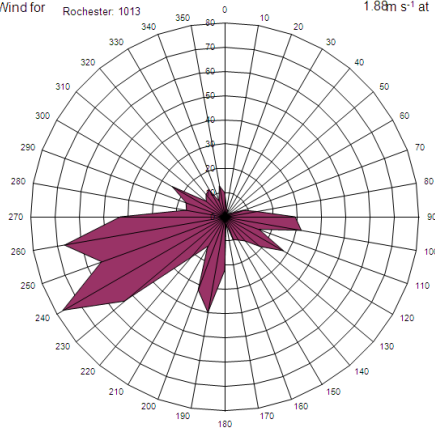
September 2013

Average Wind for Rochester: 0913 1.09m s⁻¹ at 111.24 Degrees



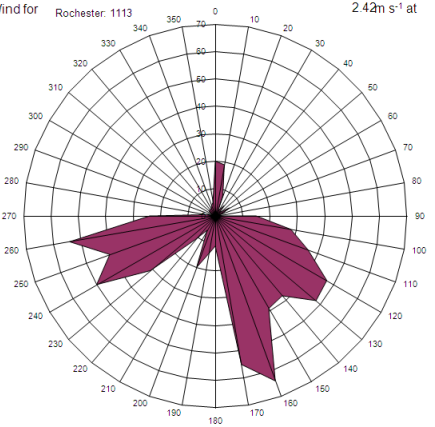
October 2013

Average Wind for Rochester: 1013 1.89m s⁻¹ at 249.93 Degrees



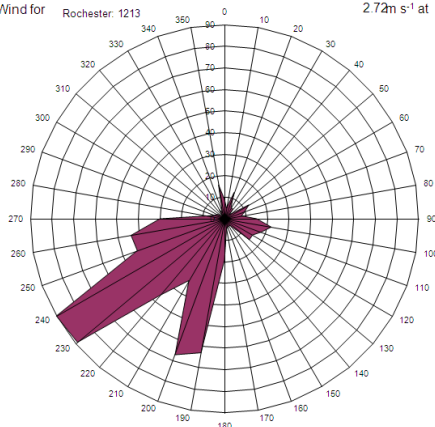
November 2013

Average Wind for Rochester: 1113 2.42m s⁻¹ at 119.40 Degrees



December 2013

Average Wind for Rochester: 1213 2.72m s⁻¹ at 233.23 Degrees



ANNEX2. 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 PM₁₀ 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.

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