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# Airborne Particulate Concentrations and Numbers in the United Kingdom (phase 3)
# Annual report 2014

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Annual report 2014

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Approved on behalf of NPLML by Martyn Sené, Operations Director

## 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 2014 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 2014.
- Data capture per instrument per month.
- Comparison of 2014 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 report published in 2014.

The Network operated four 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.

Total number concentrations (CPC) were measured at Harwell, North Kensington and Marylebone Road. The 2014 data were compared with data from recent years. Following the large drop in concentration seen over the period 2006-2008, the London sites showed a further drop over the period 2011-2013 coinciding with the introduction of phases III and IV of LEZ (Low Emission Zones). A similar behaviour can be seen in the EC concentrations at Marylebone Road. 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 also measured at Harwell, North Kensington and Marylebone Road. The drops observed in the CPC concentrations are not observed in the SMPS concentrations, probably because most of the particles produced by combustion processes are outside the size range covered by the SMPS instruments.

A series of experiments were carried out at NPL to check the performance of the three Network SMPS instruments. The experiments with standard PSL aerosols showed that the three SMPSs can accurately and comparably measure size across the required nanoparticle range. The results for broad size distributions generally showed good agreement at the ±5% level for each size bin, ±10% is considered good in other comparisons.

One topic report was published as part of this contract in 2014 on measurements of cooking organic aerosols.

The Network data is available electronically via the Defra UK-Air website http://uk-air.defra.gov.uk/.

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# 1 INTRODUCTION

The UK Airborne Particulate Concentrations and Numbers Network (AQ0604) operates four 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 2014 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 used by the University of Birmingham to gain further understanding of particulate matter, its sources, composition and possible control options. One topic report was published in 2014 and a description of its main findings is given in Section 6.

# 2 NETWORK OPERATION

## 2.1 OVERVIEW

The operation of the Network in 2014 was structured in the same way as the previous year with the exception being that the CPC in Birmingham was no longer operating. King's College London (KCL) has continued its role as the Central Management and Control Unit (CMCU). It has carried out activities including routine collection of data from site, initial data validation and instrument fault finding, routine liaison with the Local Site Operators (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

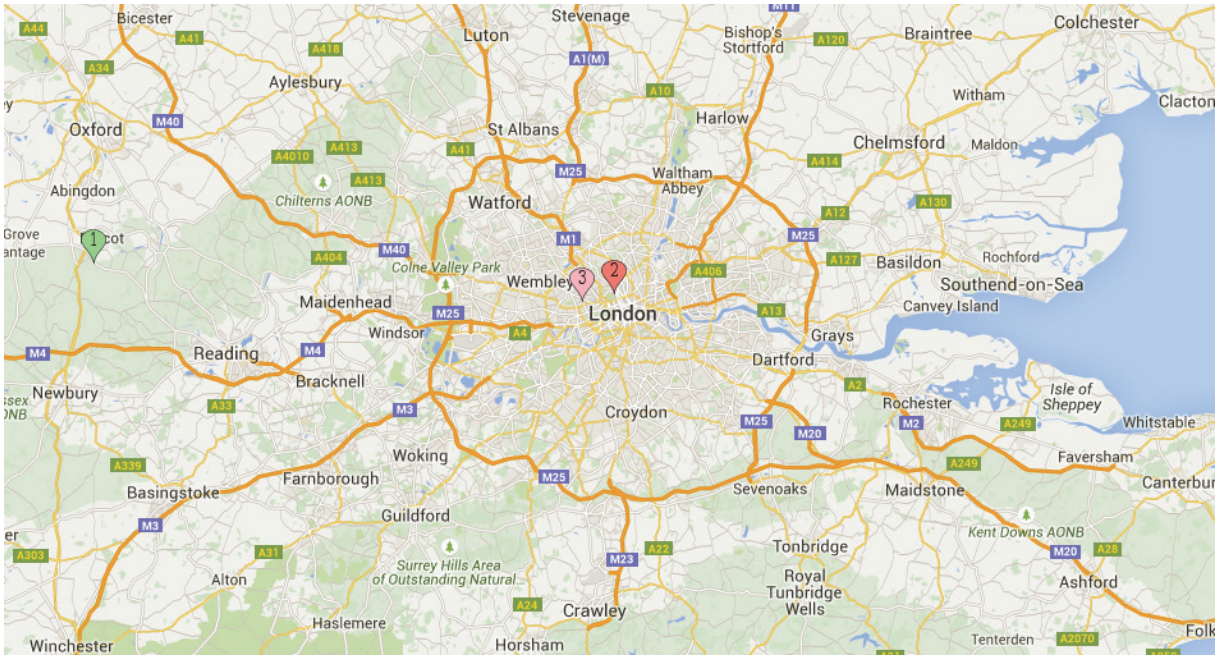
The measurement programme during 2014 is shown in Table 2-1. Wind speed and direction are reported for the Rochester site.

**Table 2-1 Network structure during 2014**

| 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 |
|---|---|---|---|---|---|---|
| **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 |

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.




1 Harwell
2 Marylebone Road
3 North Kensington
4 Auchencorth Moss

**Figure 2-1 Network sites**

## 2.3 INTRUMENTATION

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 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.

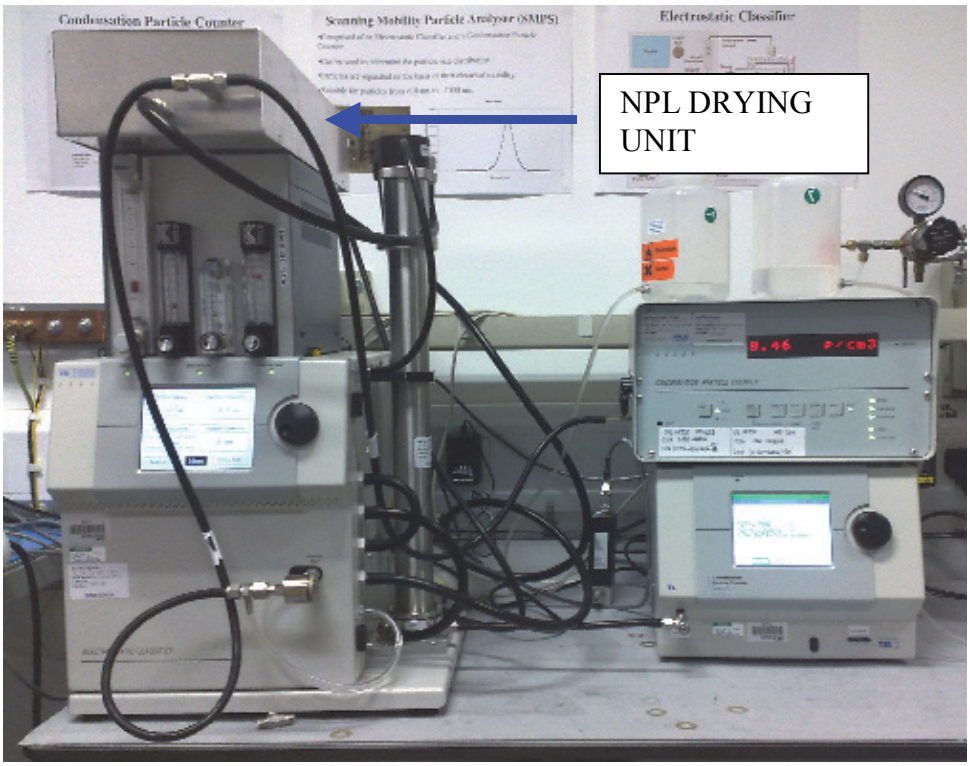



**Figure 2-2 Typical configuration of CPC, SMPS and NPL drying unit at the Network sites**

### 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 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.

(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, $\alpha$ [$m^{-1}$], 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 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 $BC_{corrected} = (1+k.ATN)\ BC_{uncorrected}$, 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 2014 Black Carbon Network report [3].

**Figure 2-5 Magee Scientific aethalometer**

### 2.3.5 URG – AIM 9000B ($PM_{10}$ anion and cation measurements)

The URG – AIM (Ambient Ion Monitor) 9000-B (Figure 2-6) provides time-resolved direct measurements of anion particulate ($Cl^-$, $NO_3^-$ and $SO_4^{2-}$) and cation particulate ($Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$).

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 $PM_{10}$ 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 Monitor**

# 3 DATA QUALITY

## 3.1 QA/QC PROCEDURES

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

- Continued training of and regular communication with Local Site Operators (LSOs).
- The KCL Duty Officer is available to advise LSOs 365 days per year.
- Scheduled instrument services and calibrations.
- An annual audit of all sites and instruments conducted by NPL.
- Calibration data produced at audit by the Equipment Support Unit (ESU) and regular calibrations carried out automatically or by the LSOs are all used to produce an appropriate scaling factor to apply to the data.
- Field blank filters have been analysed to evaluate the contamination due to the transport of the filters to the sites and back to the laboratory.
- Routine maintenance is carried out on all instruments according to manufacturers' instructions.

- The ESU is contracted to respond to breakdowns within 48 hours.
- Data collection is automated by the MONNET system at KCL.
- Automatic and manual data validation is followed by rigorous ratification procedures.

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.

### 3.2 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 ($PM_{10}$)

#### 4.1.1 OC/EC/TC time trends

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, 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.

The annual data capture for the Partisol 2025 instruments in 2014 were 94%, 96% and 96% respectively at Harwell, North Kensington and Marylebone Road. The time trends of OC, EC and TC (Total Carbon – the sum of OC and EC) are displayed in Figure 4-1, Figure 4-2 and Figure 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.

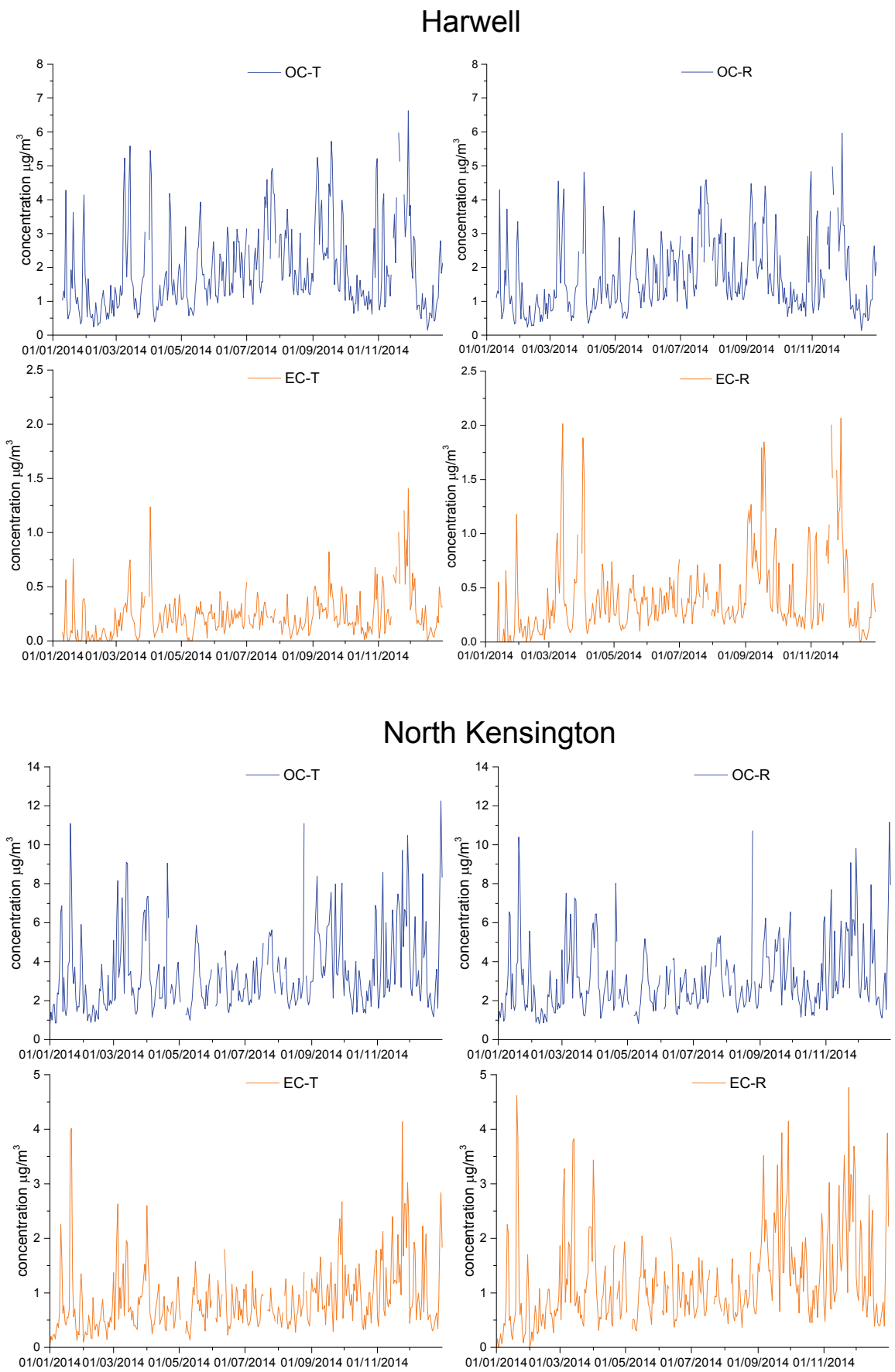



**Figure 4-1 $PM_{10}$ OC and EC concentrations at Harwell (top) and North Kensington (bottom) during 2014**

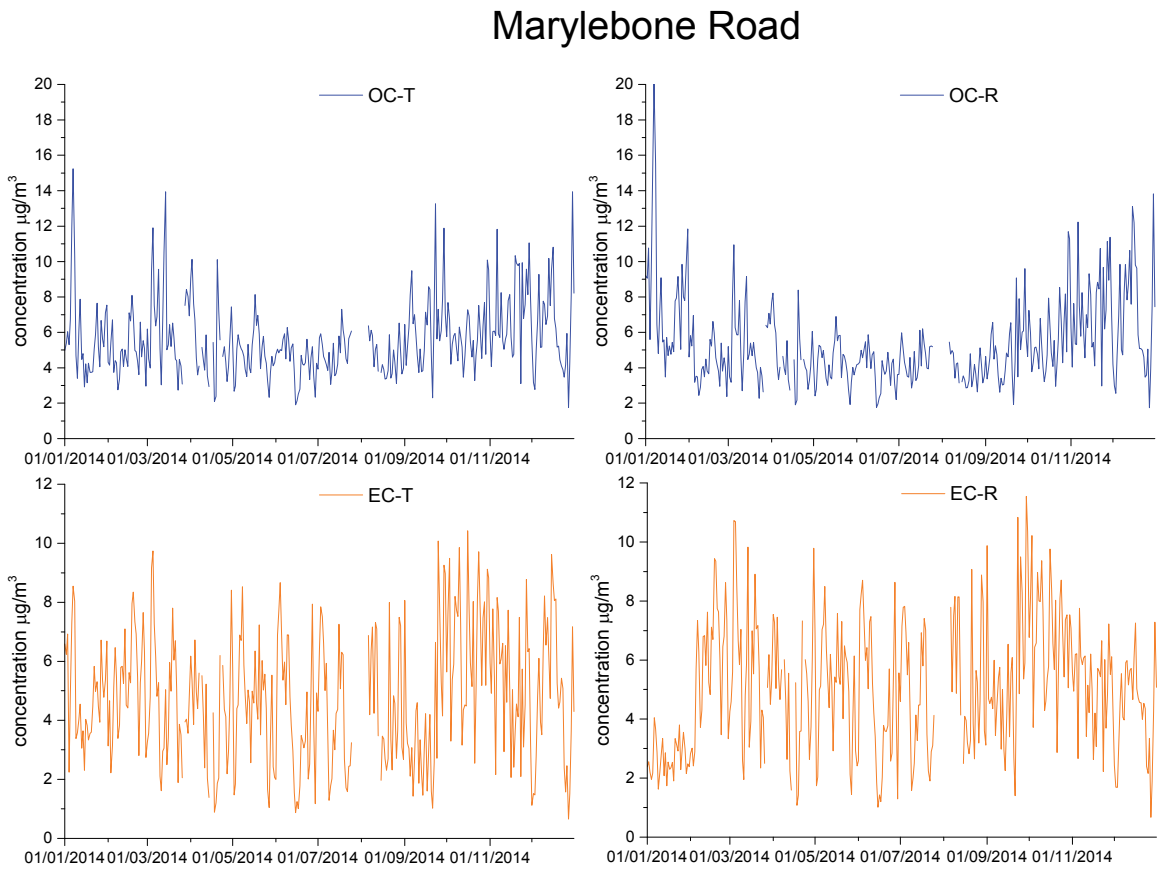



**Figure 4-2 $PM_{10}$ OC and EC concentrations at Marylebone Road during 2014**

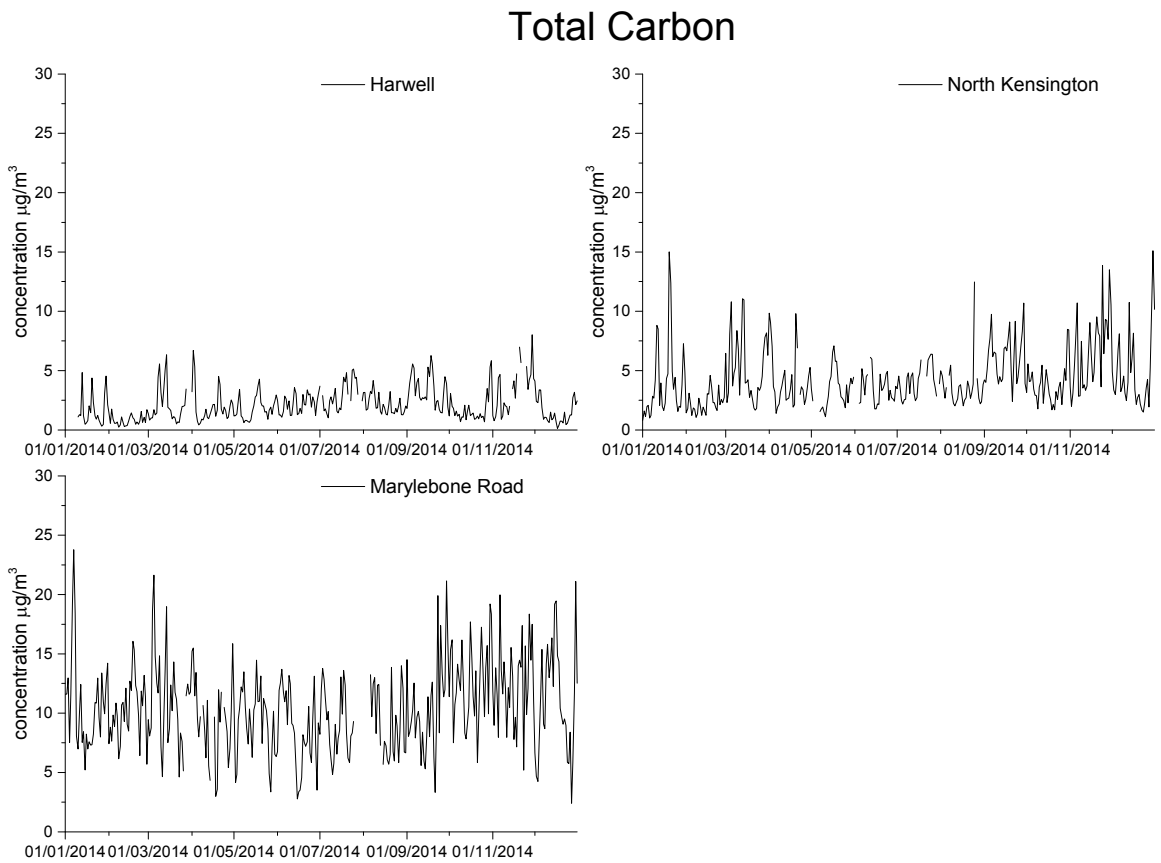



**Figure 4-3 $PM_{10}$ TC concentrations at Harwell, North Kensington and Marylebone Road during 2014**

### 4.1.2 Comparison with 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 Figure 4-4. The regression is calculated according to the Reduced Major Axis (RMA) method [4].

It can be seen that there is a generally good linear relationship between the Elemental Carbon and Black Carbon concentrations ($R^2 > 0.8$ at all sites), but with a variable ratio. The relationship between Black Carbon and Elemental Carbon has been quite variable year on year. This variability is shown in Table 4-1.

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

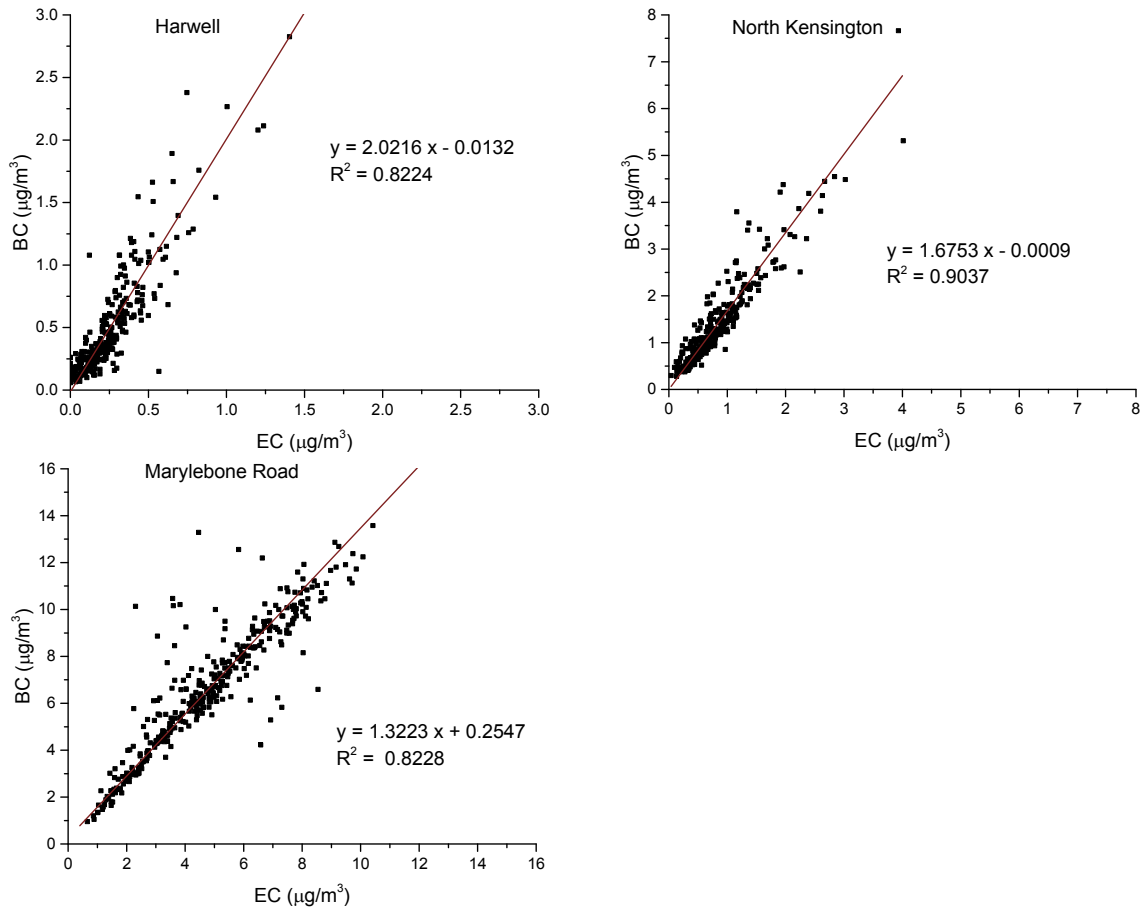



**Figure 4-4 Comparison between $PM_{2.5}$ BC and $PM_{10}$ EC (TOT) at the 3 sites in 2014**

It can be seen from Table 4-1 that the ratios of measured Black Carbon to Elemental Carbon have generally increased year on year at Harwell and North Kensington. 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..

The Black Carbon method has not changed in any significant way over the years. The OCEC Sunset analyser was upgraded in early 2014 with a new optical system with a more powerful laser. This should have improved the determination of the OC/EC split point and improved the quality of the EC results. This seems to be apparent from the reduced scatter in the Marylebone Road data in 2014 compared to 2013, but the slope there did not change significantly, and this upgrade would not explain the increases in slope observed before the upgrade took place.

**Table 4-1 Relationships between Black Carbon and Elemental Carbon over the period 2009 – 2014**

| | Harwell | | North Kensington | | Marylebone Road | |
|---|---|---|---|---|---|---|
| **Year** | **Relationship** | **$R^2$** | **Relationship** | **$R^2$** | **Relationship** | **$R^2$** |
| 2009 | N/A | N/A | 1.05 x + 0.20 | 0.858 | 1.36 x - 0.69 | 0.776 |
| 2010 | 1.32 x + 0.06 | 0.555 | 1.37 x – 0.32 | 0.734 | 1.28 x + 0.56 | 0.946 |
| 2011 | 1.52 x + 0.18 | 0.844 | 1.26 x + 0.07 | 0.810 | 1.50 x - 0.35 | 0.924 |
| 2012 | 1.84 x + 0.06 | 0.908 | 1.42 x + 0.17 | 0.906 | 1.43 x + 0.005 | 0.898 |
| 2013 | 1.74 x + 0.17 | 0.865 | 1.59 x + 0.33 | 0.871 | 1.47 x + 0.39 | 0.679 |
| 2014 | 2.02 x - 0.01 | 0.802 | 1.68 x - 0.001 | 0.872 | 1.3 x + 0.25 | 0.819 |

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

## 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 [6], 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 2014 was 96% for Harwell and 100% for Auchencorth Moss. Figure 4-5 shows the time trends for these measurements since the installation of the samplers.

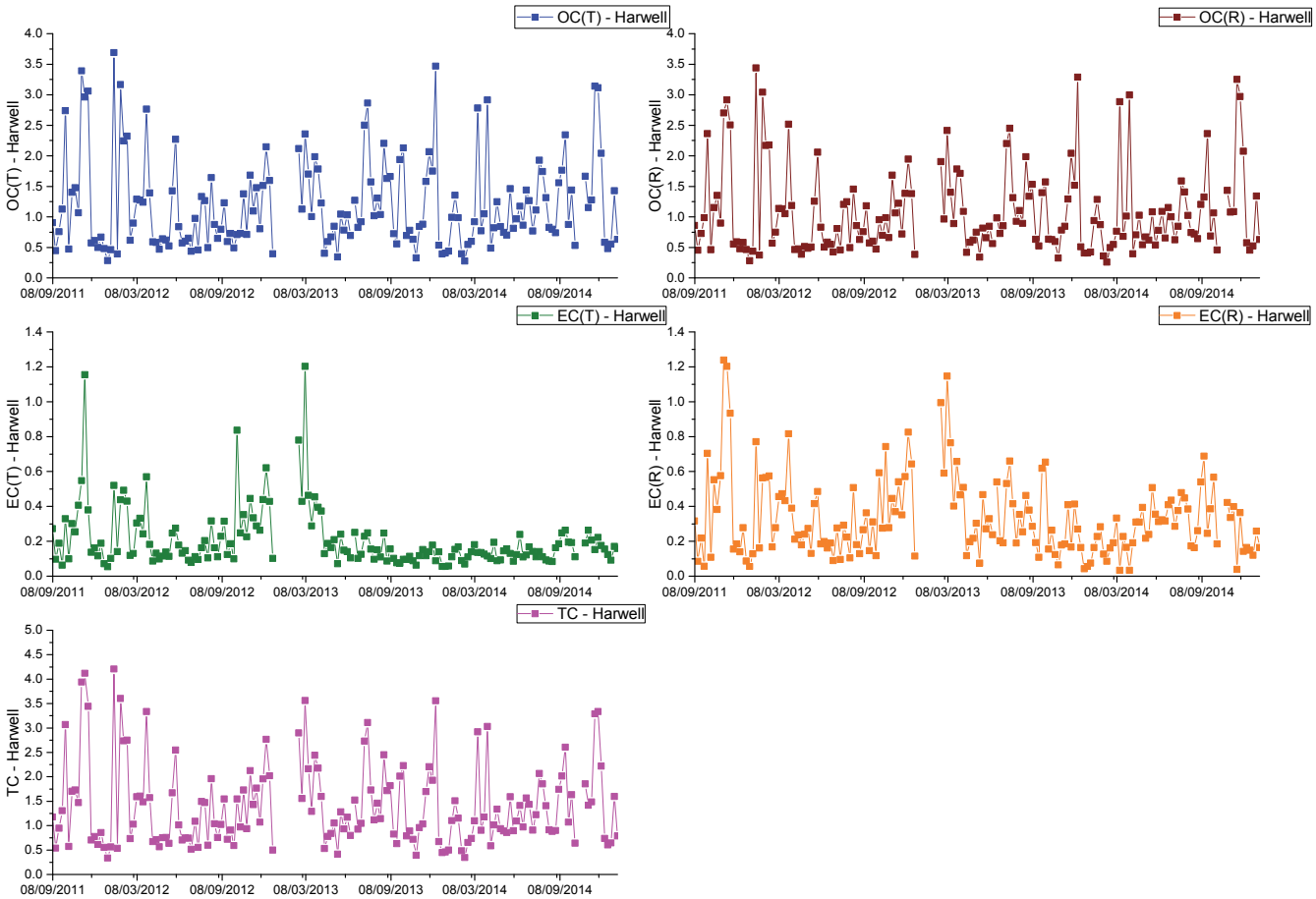



**Figure 4-5 Time series of OC, EC and TC in the $PM_{2.5}$ fraction at Harwell since the installation of the sampler (weekly samples) (µg/m$^3$)**

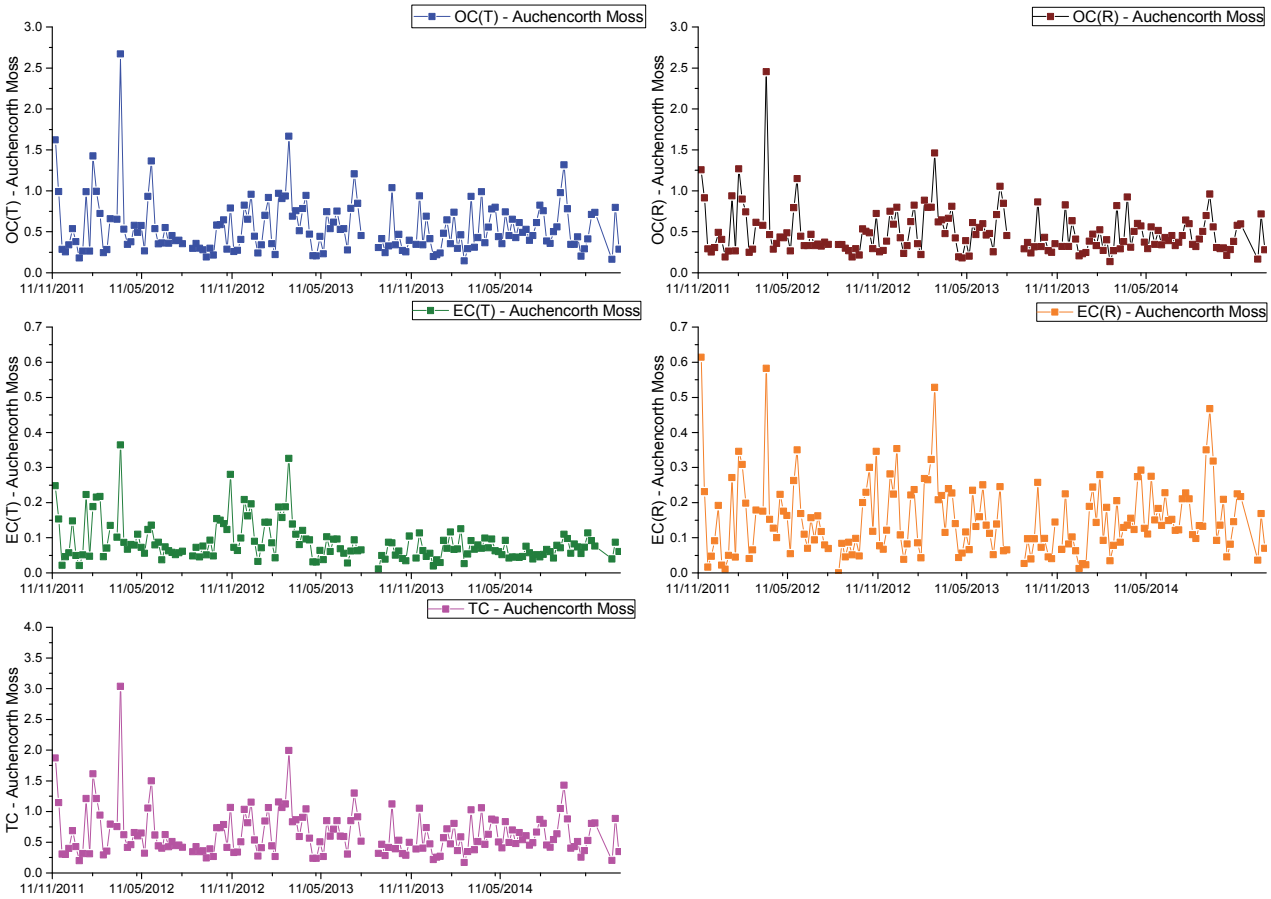



**Figure 4-6 Time series of OC, EC and TC in the $PM_{2.5}$ fraction at Auchencorth since the installation of the sampler (weekly samples) (µg/m$^3$)**

The $PM_{2.5}$ carbon concentrations at Harwell were compared with weekly averages from the $PM_{10}$ filters from the Partisol (Figure 4-7 ). The correlation between the two measurements is good, with $PM_{2.5}$ total carbon being on average about 65% of the $PM_{10}$ 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 $PM_{10}$ EC concentrations can often be recorded as zero (below the detection limit), 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 $PM_{10}$.

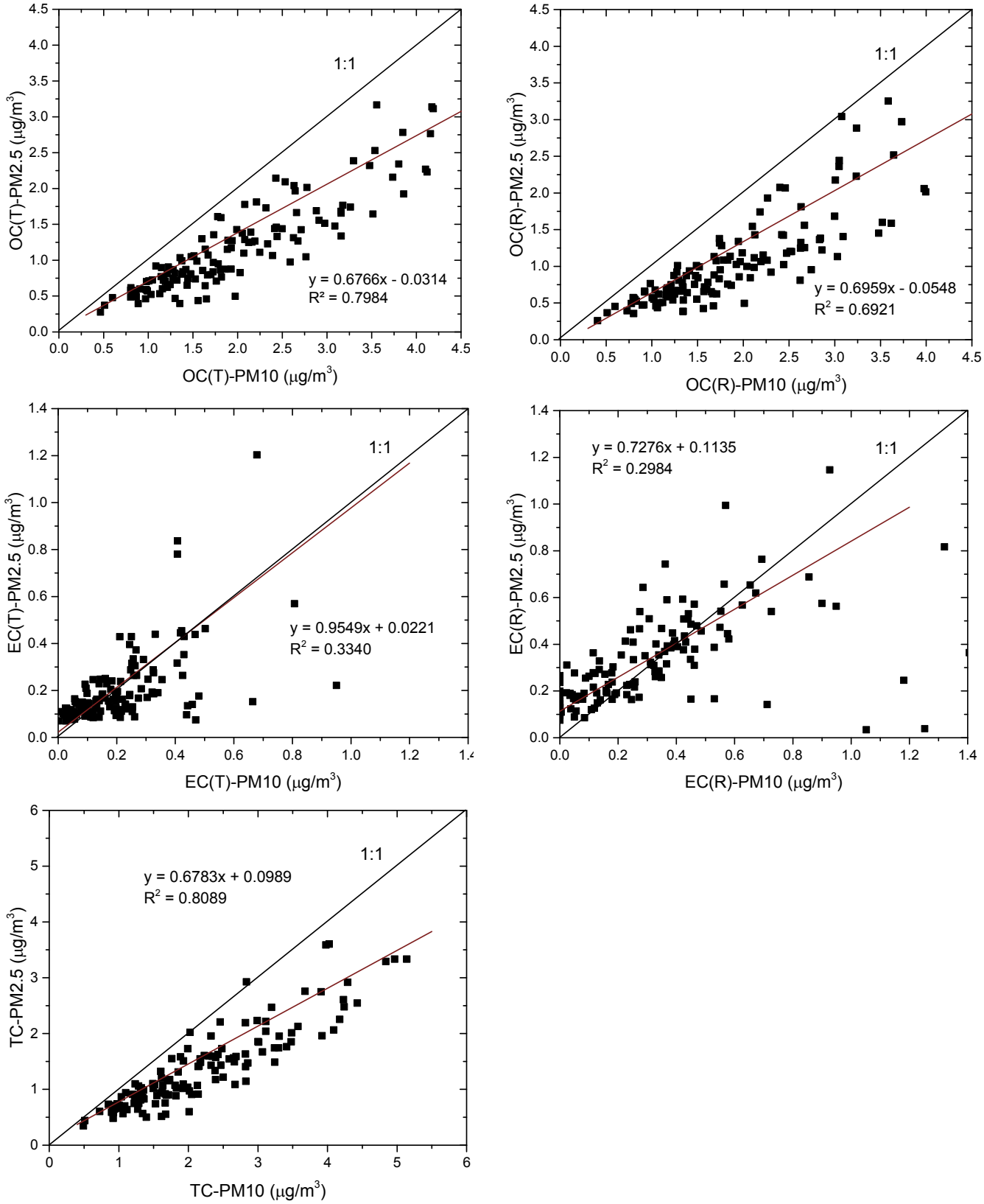



**Figure 4-7 Comparison between $PM_{10}$ OC/EC weekly averages and $PM_{2.5}$ OC/EC at Harwell**

## 4.3 AUTOMATIC $PM_{10}$ ANION AND 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 ($Cl^-$), nitrate ($NO_3^-$), sulphate ($SO_4^{2-}$), sodium ($Na^+$), ammonium ($NH_4^+$), potassium ($K^+$), magnesium ($Mg^{2+}$) and calcium ($Ca^{2+}$) 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 in operation, under a different Network.

The annual data capture was 41% for Marylebone Road and 78% for North Kensington.

The low data capture at Marylebone Road was due to serious issues in the anion chromatograph which required the system to be sent to Thermo Fisher for repair.

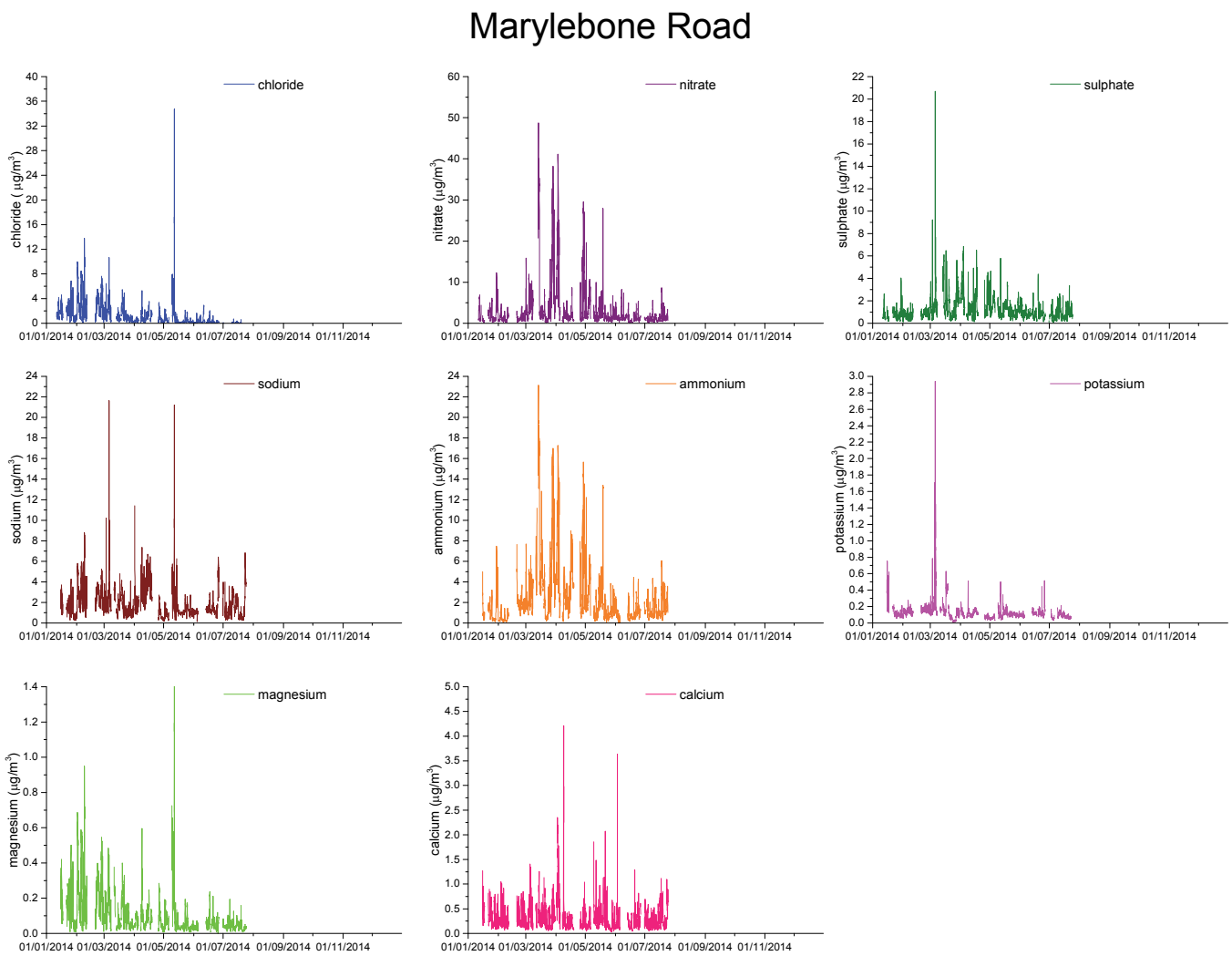



**Figure 4-8 Time series for ion concentrations at Marylebone Road in 2014**

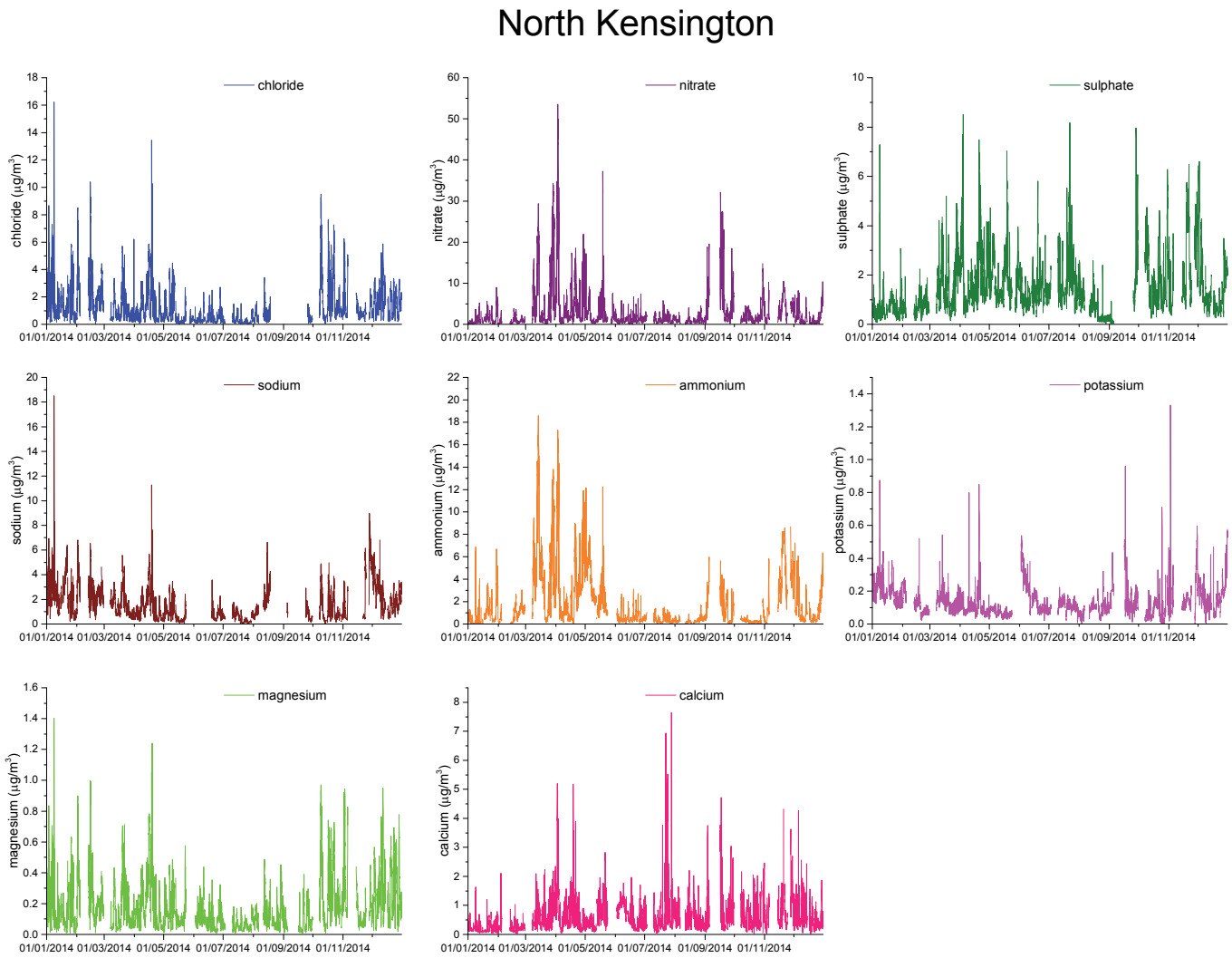



**Figure 4-9 Time series for ion concentrations at North Kensington in 2014**

## 4.4 PARTICLE NUMBERS AND SIZE DISTRIBUTIONS

Time series of hourly particle number concentrations (between about 7nm and several microns in diameter) measured at network sites during 2014 are shown in Figure 4-10. The plots have been shown on the same scale.

The reasons for the main data gaps were:

- **Harwell:** The instrument was removed for calibration at NPL on 4 February and re-installed on 18 February.
- **North Kensington:** The instrument was removed from site on 18 March for calibration and reinstalled on 15 May.
- **Marylebone Road:** The instrument suffered from unstable flow on several occasions during the year which required new pump replacements and extra calibrations at NPL. The CPC was eventually stripped down and the cause of the problem was identified as a clogged filter.

The average annual data captures for the CPC instruments during 2014 were 87%, 80% and 49% respectively for Harwell, North Kensington and Marylebone Road.

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.

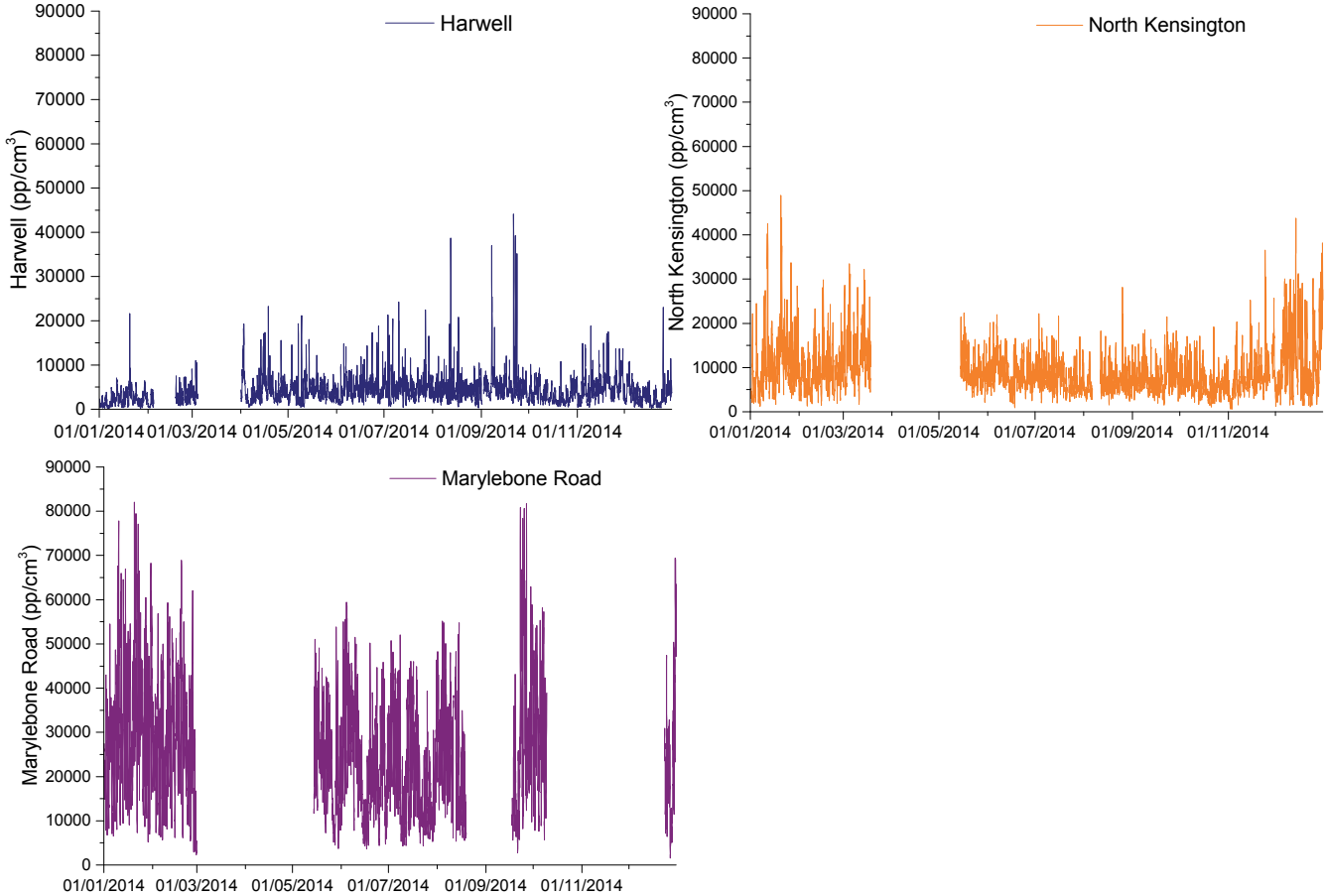



**Figure 4-10 Time series of number concentrations during 2014 at the Network sites**

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.

### 4.4.1 Particle size number distributions

The SMPS instruments generate size spectra between 16 nm and 605 nm.

The reasons for the main data gaps were:

- **Harwell:** The instrument was removed for service and calibration on 25 February and reinstalled on site in March, although communication problems with the PC did not let recording measurements until 1 April.

- **North Kensington:** Instrument removed for calibration at NPL on 19 February and was reinstalled on site on 18 March.

- **Marylebone Road:** Instrument removed for calibration at NPL on 19 February and was reinstalled on site on 18 March. The pump in the CPC failed in August and it was replaced at NPL. The CPC was re-installed on 2 September.

The annual data captures for the SMPS instruments during 2014 were 85%, 86% and 82% respectively for Harwell, North Kensington and Marylebone Road.

The production of data from SMPS instruments is a complicated process, summarised schematically in Figure 4-11. 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 4.4.2.

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 [7].

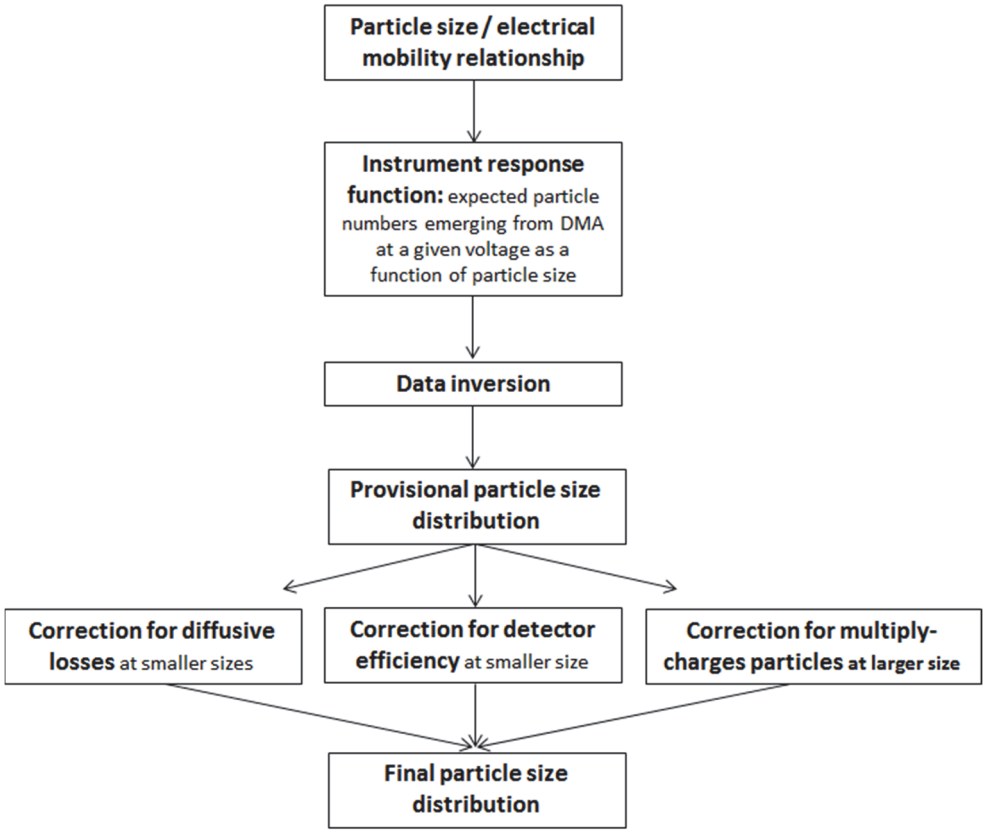



**Figure 4-11 Schematic of the internal data processing of SMPS instrument in the Network**

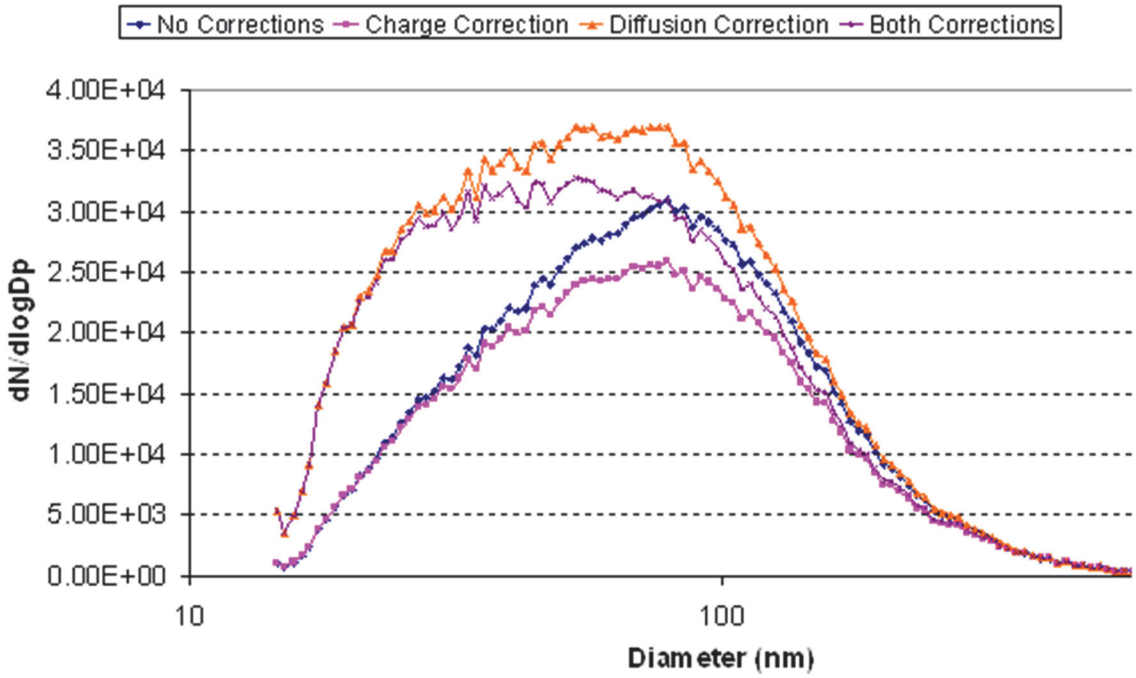



**Figure 4-12 Effect of the multiple charge, the diffusion loss and their combined correction in the SMPS size spectrum**

The counts in each particle size bin measured during 2014 are presented as monthly averages in the left-hand panels of Figure 4-13 and as an annual average in the right-panel.

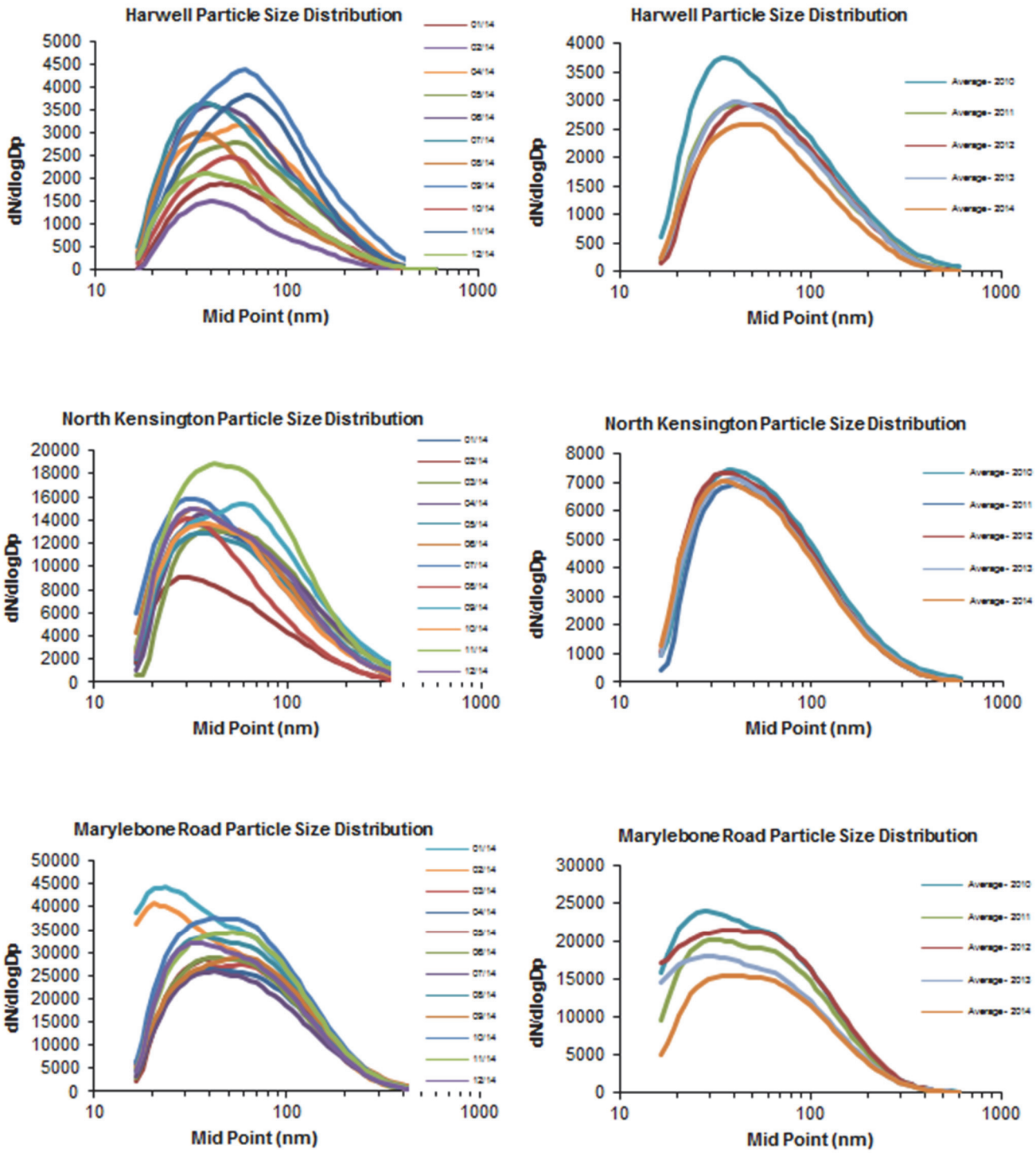



**Figure 4-13 Monthly averaged particle size distributions at the Network sites during 2014 [left-hand panels] and comparison of the 2008, 2009, 2010, 2011, 2012 and 2013 annual-averaged size distributions [right-hand panels]**

### 4.4.2 SMPS checks and inter-comparison

**Introduction**

To assess the performance of the network SMPSs, a series of experiments were carried out in the Airborne Nanoparticles lab at NPL (13 February 2015). The Marylebone (Mar), Harwell (Har) and North Kensington (NK) SMPSs were tested in parallel, along with an NPL-based SMPS, under controlled lab conditions. 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 radioactive source (neutraliser). An in-house neutraliser (TSI 3077A) was therefore shared with all SMPS units. The configuration used is shown in Figure 4-14. 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 41 ± 4 nm, 60 ± 4 nm, 92 ± 3 nm, 125 ± 3 nm and 203 ± 5 nm. A CAST soot generator was used to produce a broad size distribution centred around 55nm and a Bi-modal size distribution.

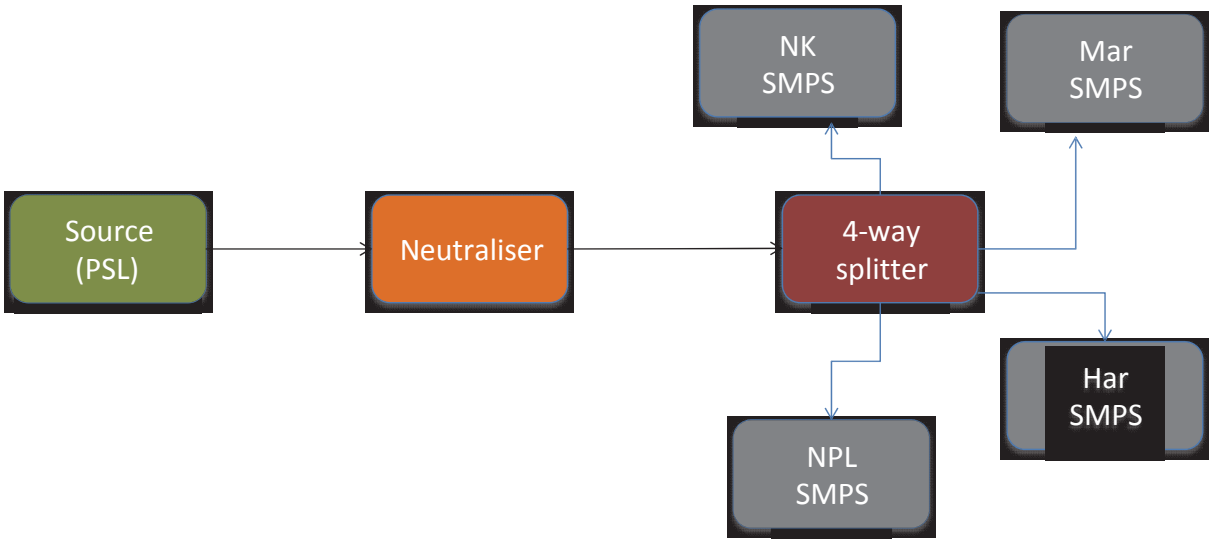



**Figure 4-14 Schematic showing the parallel sampling of the four SMPS when connected to a flow splitter and fed with a single particle source (PSL) or the broader size range of the CAST (soot), conditioned with a single neutraliser.**

**Results and Discussion**

In Table 4-2 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.

Figure 4-15 and Figure 4-15 show the size distributions recorded for a 55nm single modal CAST input and a Bi-modal CAST input respectively.

**Conclusions**

The experiments with standard PSL aerosols showed that the three SMPSs can accurately and comparably measure size across the required nanoparticle range. The results for broad size distributions generally showed good agreement at the ±5% level for each size bin; ±10% is considered good in other comparisons. The most notable anomaly was a difference of about 20% between the Harwell instrument and the others in the Bi-modal peak at around 200nm, which is hard to explain.

**Table 4-2 Comparison of SMPS measured distributions with polystyrene latex (PSL) nominal values**

| | | PSL | | | | |
|---|---|---|---|---|---|---|
| | | **41** ± 4 nm | **60** ± 4 nm | **92** ± 3 nm | **125** ± 3 nm | **203** ± 5 nm |
| **Site** | | | | | | |
| **Mar** | Geometric mean | **41.5** | **64.0** | **89.9** | **124.4** | **198.7** |
| | Geometric st. dev. | 1.11 | 1.08 | 1.07 | 1.05 | 1.05 |
| **Har** | Geometric mean | **41.5** | **63.3** | **89.6** | **124.0** | **198.1** |
| | Geometric st. dev. | 1.11 | 1.09 | 1.07 | 1.06 | 1.06 |
| **NK** | Geometric mean | **42.9** | **65.0** | **91.0** | **125.9** | **201.3** |
| | Geometric st. dev. | 1.11 | 1.07 | 1.07 | 1.06 | 1.06 |
| **Mean 2014** | | **42.0** | **64.1** | **90.2** | **124.8** | **199.4** |
| Mean 2013 | | N/A | 64.2 | 90.8 | 125.1 | 199.9 |

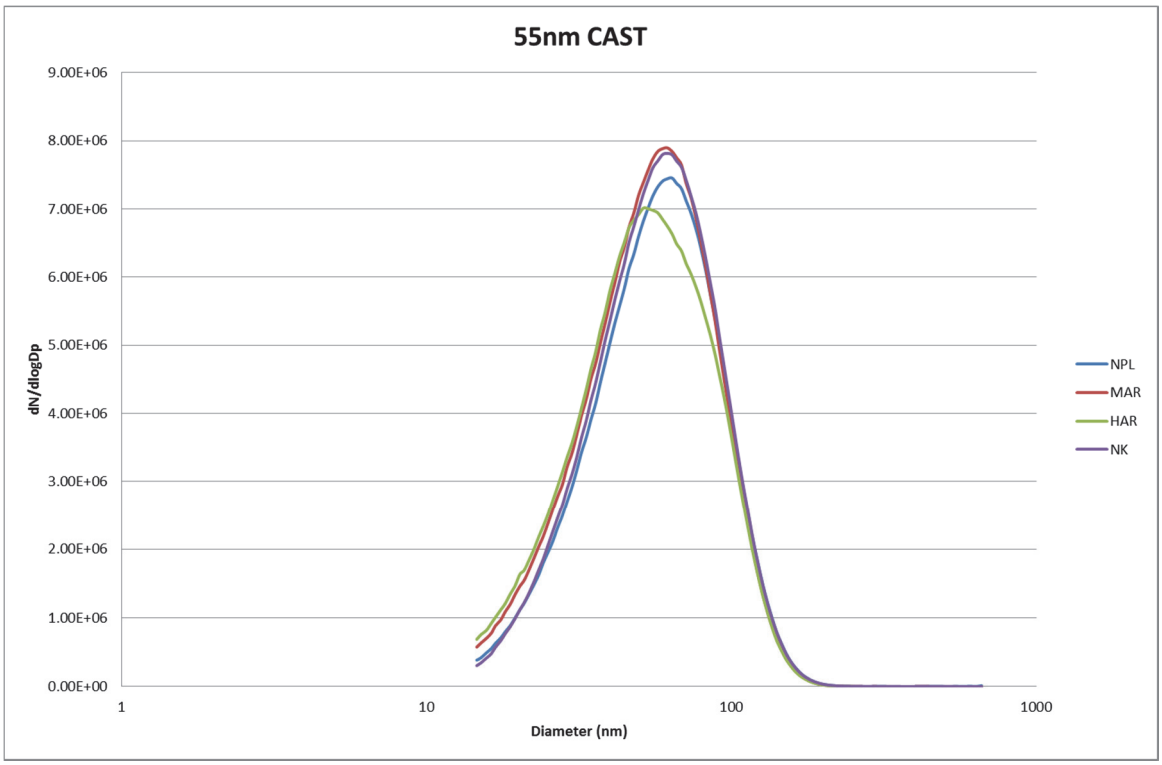



**Figure 4-15 Graph showing the particle size distributions recorded from a nominally 55nm diameter CAST soot input**

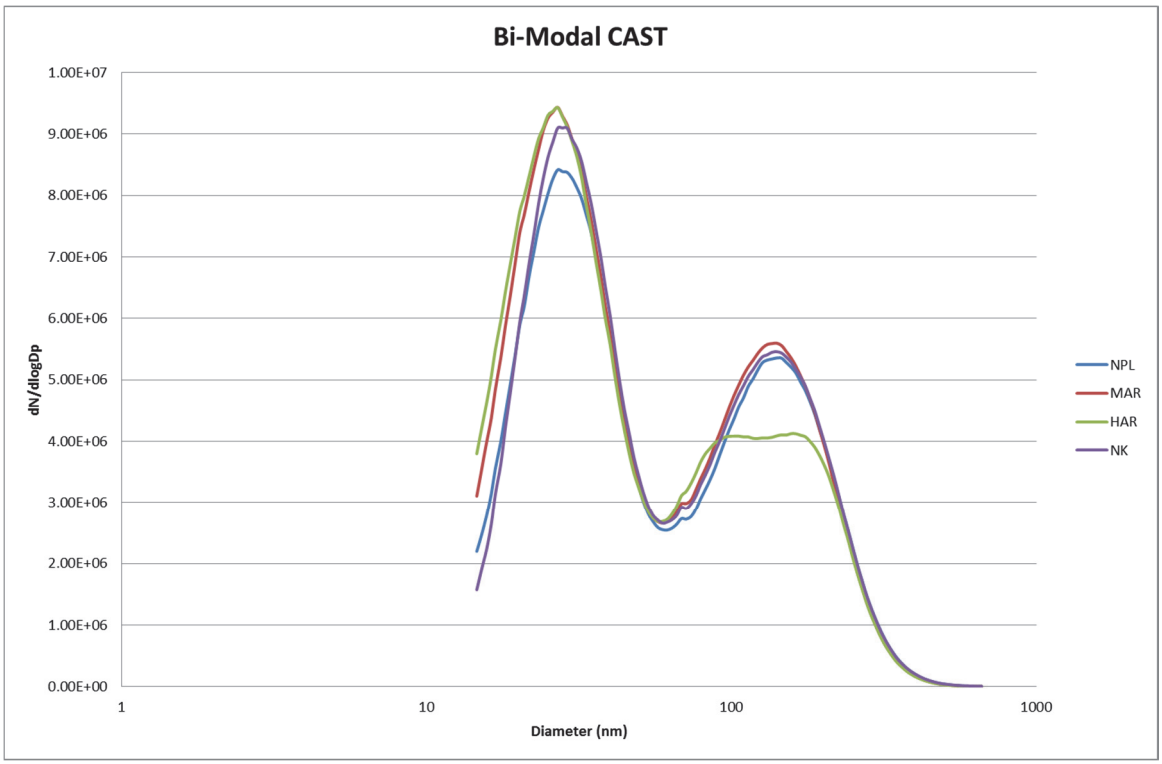



**Figure 4-16 Graph showing the particle size distributions recorded from a Bi-modal CAST soot input**

## 4.5 POLLUTION EPISODES

During 2014 a few pollution incidents occurred and the most relevant to the measurements performed in this network are described below.

### 4.5.1 $PM_{10}$ and $PM_{2.5}$ episode mid-March 2014

London and South East England were affected by a widespread pollution episode in mid-March that affected much of North-East Europe. A high pressure system slowed the circulation of air across this area and cold, foggy nights that further hampered pollution dispersion.

From the UK perspective, the episode first impacted on 12 March with widespread moderate particle concentrations across London and South East England. Further feeds of ground level continental air caused the episode to intensify on 13 March with $PM_{2.5}$ reaching "very high", the top level of the UK air quality index.

"High" $PM_{10}$ and $PM_{2.5}$ concentrations continued on 14 March before a return to a westerly airflow pushed the polluted air eastwards and began to disperse this over Europe on 15 March.

This episode produced some of the highest $PM_{10}$ concentrations to affect London in the last few years; the mean background $PM_{10}$ in London reached its greatest concentration since 15 March 2012. Tracing back London's air during this episode shows that air flowed across northern Germany, the Netherlands and Belgium before reaching the UK. This is reflected in the composition of particles measured which showed a dominance of nitrate and organic particles, consistent with distant traffic emissions that have been chemically aged in the atmosphere [8]. Figure 4-17 shows hourly concentrations of $PM_{10}$, $NO_3^-$, $SO_4^{2-}$ and $NH_4^+$ at North Kensington during the episode.

### 4.5.2 $PM_{10}$ and $PM_{2.5}$ episode early April 2014

On 31 March, the arrival of an air mass which had travelled up through France led to the importation of Saharan Dust. The import was, however, brief and the particles that have a health impact ($PM_{10}$ and $PM_{2.5}$) are much smaller than the visible Saharan dust deposits.

The light southerly winds that arrived in the UK between 31 March and 3 April had travelled over France at low altitude for around three days, accumulating urban and industrial pollution. Once they arrived over the UK, local emissions added to the pollution mix.

Throughout the episode exhaust emissions, both continental and local, were identified as a major component of the pollution.

Although this episode attracted significant press and public interest, pollution levels were actually higher during the previous episode of mid-March when levels reached 'Very High' in some areas of London [8]. Figure 4-18shows hourly concentrations of $PM_{10}$, $NO_3^-$, $SO_4^{2-}$, $NH_4^+$ and $Ca^{2+}$ during this late-March/early-April episode at North Kensington; an increase of $Ca^{2+}$ concentrations can be noticed between 2 April and 4 April.

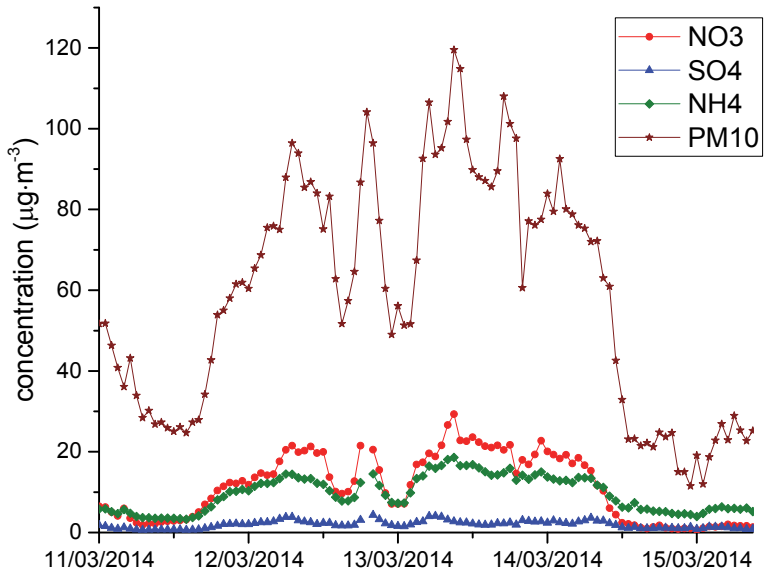



**Figure 4-17 $PM_{10}$, $NO_3^-$, $SO_4^{2-}$ and $NH_4^+$ hourly concentrations during the mid-March pollution episode at North Kensington**

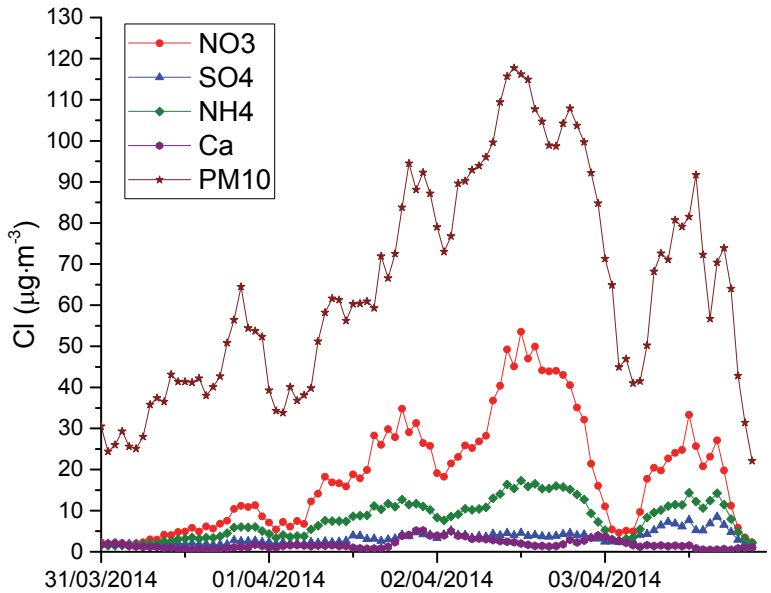



**Figure 4-18 $PM_{10}$, $NO_3^-$, $SO_4^{2-}$, $NH_4^+$ and $Ca^{2+}$ hourly concentrations during the late-March/early-April pollution episode at North Kensington**

## 4.6 LONG TERM TRENDS

### 4.6.1 Carbon measurements

Figure 4-19 shows the long term trends in annual averages for OC/EC/TC measurements.

There is a general decrease of total 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]. This is thought to be due to the increased proportion of low emission buses (hybrid and fuel cell / hybrid) in the London bus fleet [9]. In addition, all of London's Euro II and III diesel buses were retro-fitted with engine exhaust particulate filters by the end of 2011. Also in 2012 the vehicles types affected by the London Low Emission Zone (LEZ) was increased to include large vans, minibuses and other specialist diesel vehicles. Vehicles entering the LEZ must be Euro III or higher to be compliant with the requirements. In addition, the requirements for lorries, buses, coaches, licensed private hire and specialist heavy vehicles changed from Euro III to Euro IV. These changes may have also reduced black carbon/elemental carbon emissions from road transport.

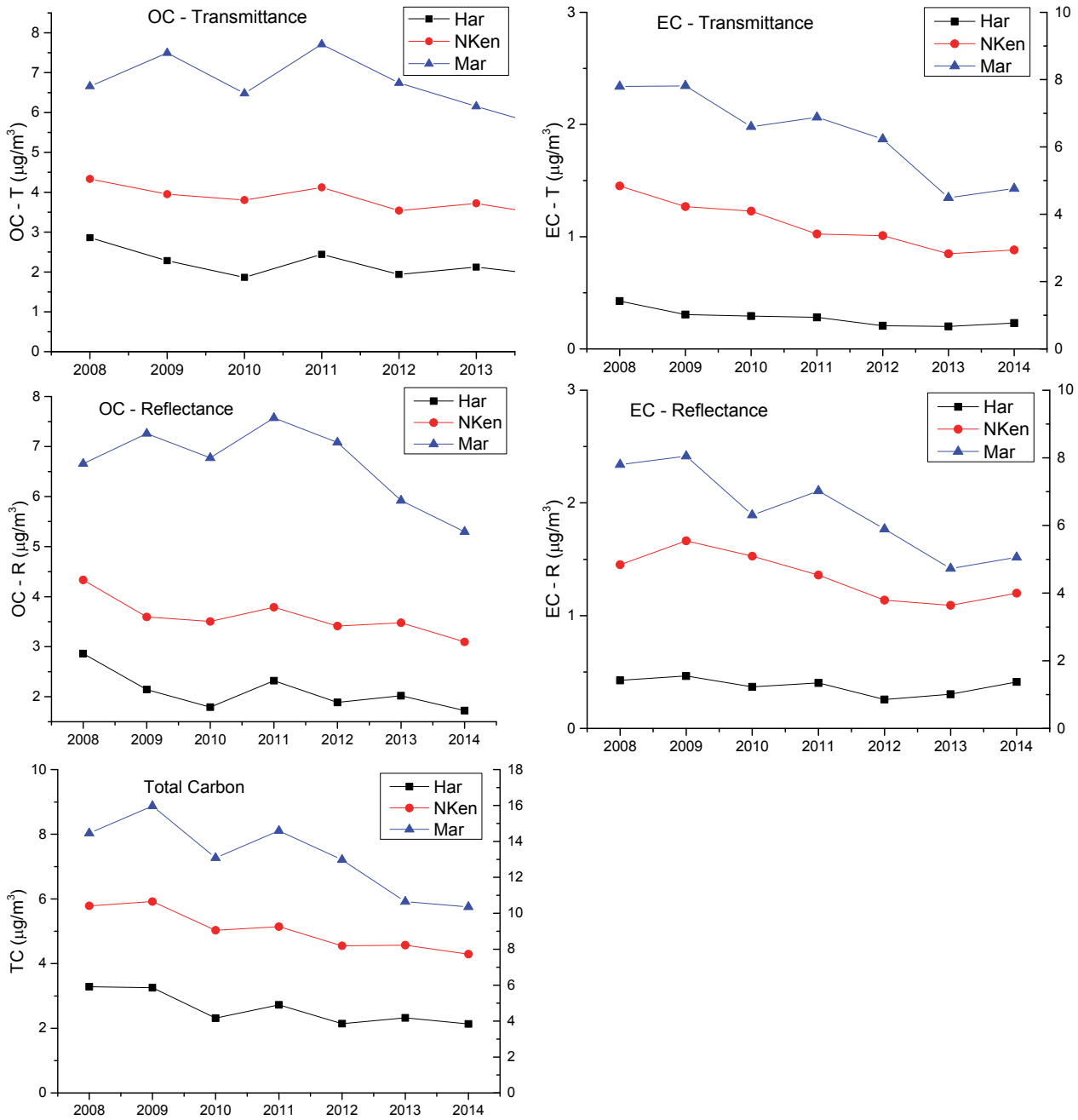



**Figure 4-19 Annual trends for OC/EC/TC measurements. EC and TC values for Marylebone Road are shown on the right-hand axis**

### 4.6.2 Ion measurements

Figure 4-20 shows long-term trend for the anion species. Between 2003 and 2010, the anion concentrations were derived by using a manual method, and a common trend across the three sites can be seen. After the installation of the automatic instruments, some discontinuity can be observed.

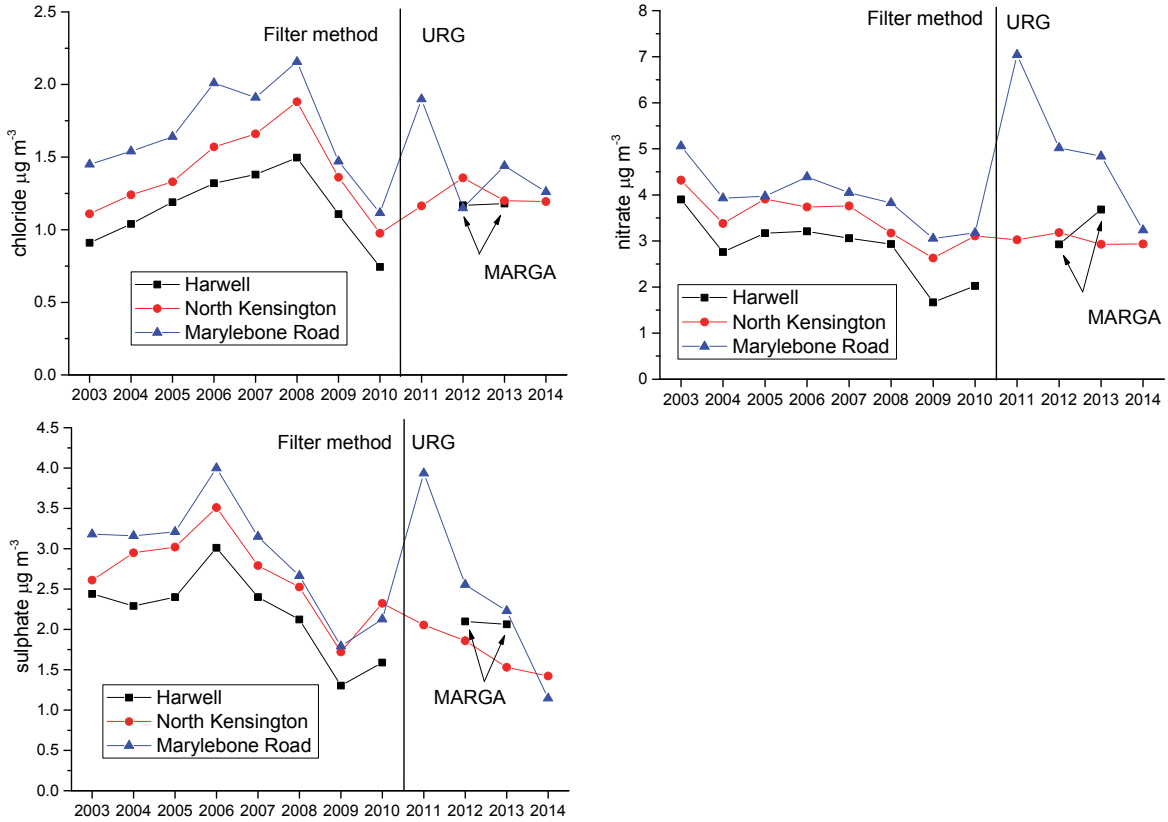



**Figure 4-20 Anion long-term annual trends (clockwise chloride, nitrate and sulphate). Note: data capture for Marylebone Road in 2013 is only 22%. The 2012 and 3013 data for Harwell have been derived from the MARGA measurements.**

### 4.6.3 Particle number concentrations

Figure 4-21 shows long-term annual trends for CPC measurements at all sites. The particle number concentrations have continued to decrease slowly 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) [10].

Legislation enacted in June 2007 [11] 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) [12] 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 [13] 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.

Given the simultaneous drop of concentration at Birmingham centre, it is probable that the reduction is a combination of change in fuel composition and the introduction of the London LEZ.

As mentioned in the previous section, in January 2012 the LEZ became more restricted: buses and coaches have to meet the 'Euro 4' emissions limit for particulates while vans, minibuses, horseboxes, motor-caravans, utility vehicles and pick-ups affected by the scheme will have to meet the 'Euro 3' emissions limits for particulates. This could explain the further reduction in numbers in 2012. Drivers most probably anticipated the introduction of all phases of the LEZ and emissions reduction happened before the respective threshold dates. However, changes to vehicle numbers and inter annual variability in meteorological factors may also have had an influence.

Long-term monthly trends are shown in Figure 4-22 along with long-term monthly trends from the SMPS total number concentrations. It can be seen how the SMPS concentrations do not follow the same trends and do not show the drops after 2007/2012. This may be because most of the particles produced by combustion processes are outside the size range covered by the SMPS instruments (< 16 nm).

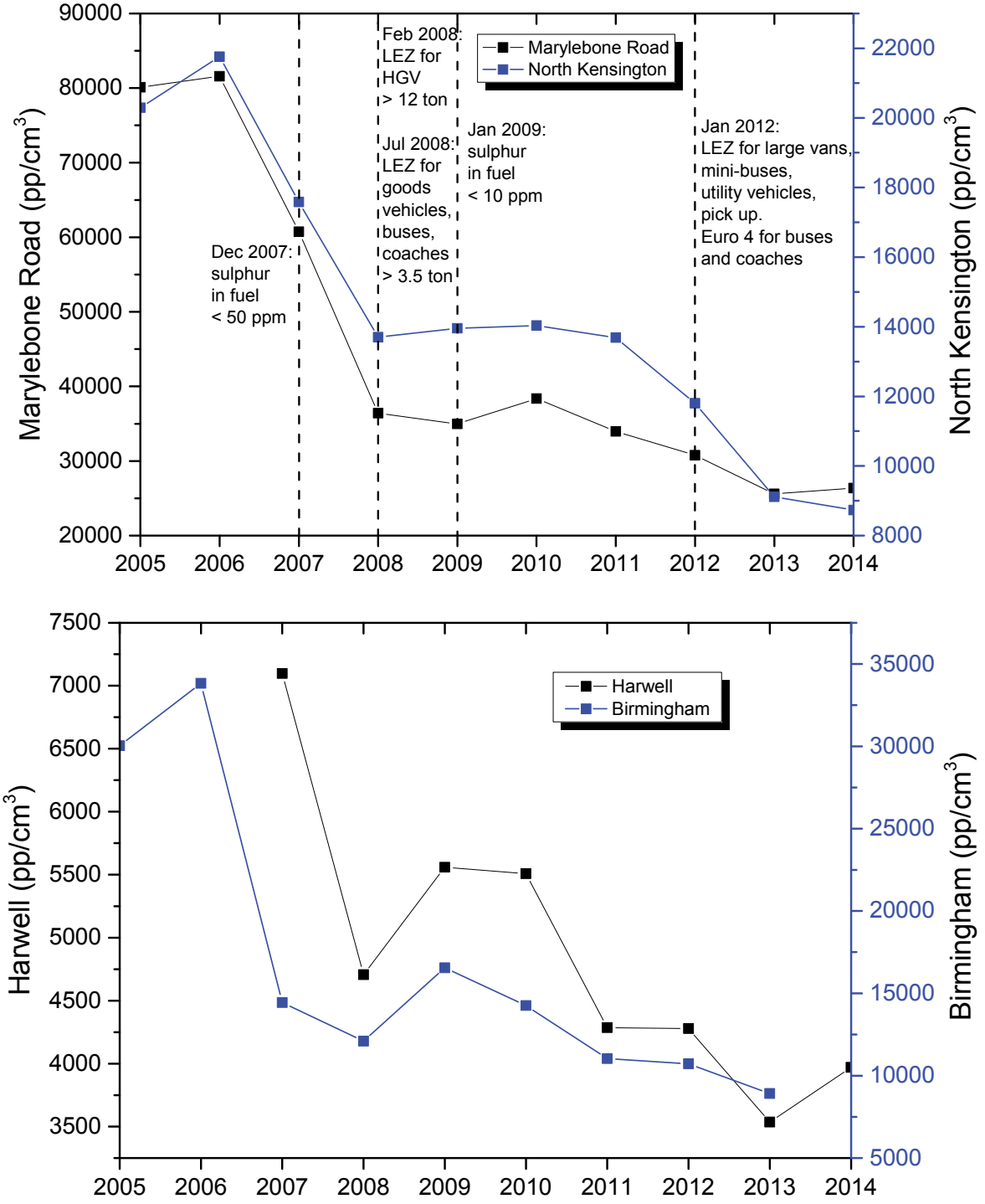



**Figure 4-21 CPC long-term annual trends at all sites (no data are available in 2014 for the Birmingham site)**

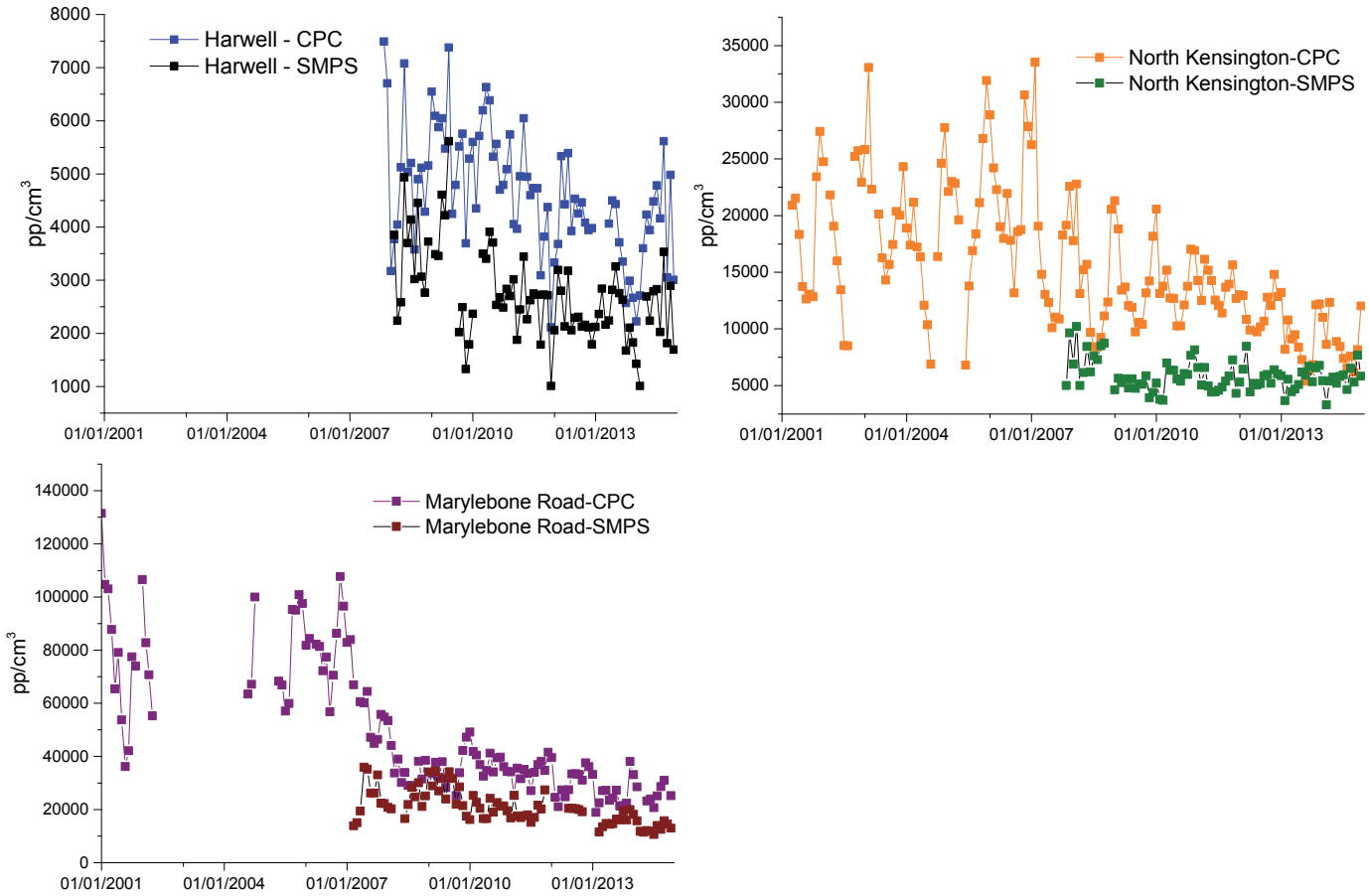



**Figure 4-22 CPC and SMPS long-term monthly trends at all Network sites**

## 4.7 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 [14,15,16].

### 4.7.1 Profiles for anion and cation species

Figure 4-23 shows the profiles for $Cl^-$, $Na^+$ and $Mg^+$ concentrations at North Kensington and Marylebone Road. 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 4-24 indicates the existence of both $(NH_4)_2SO_4$ 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 4-25).

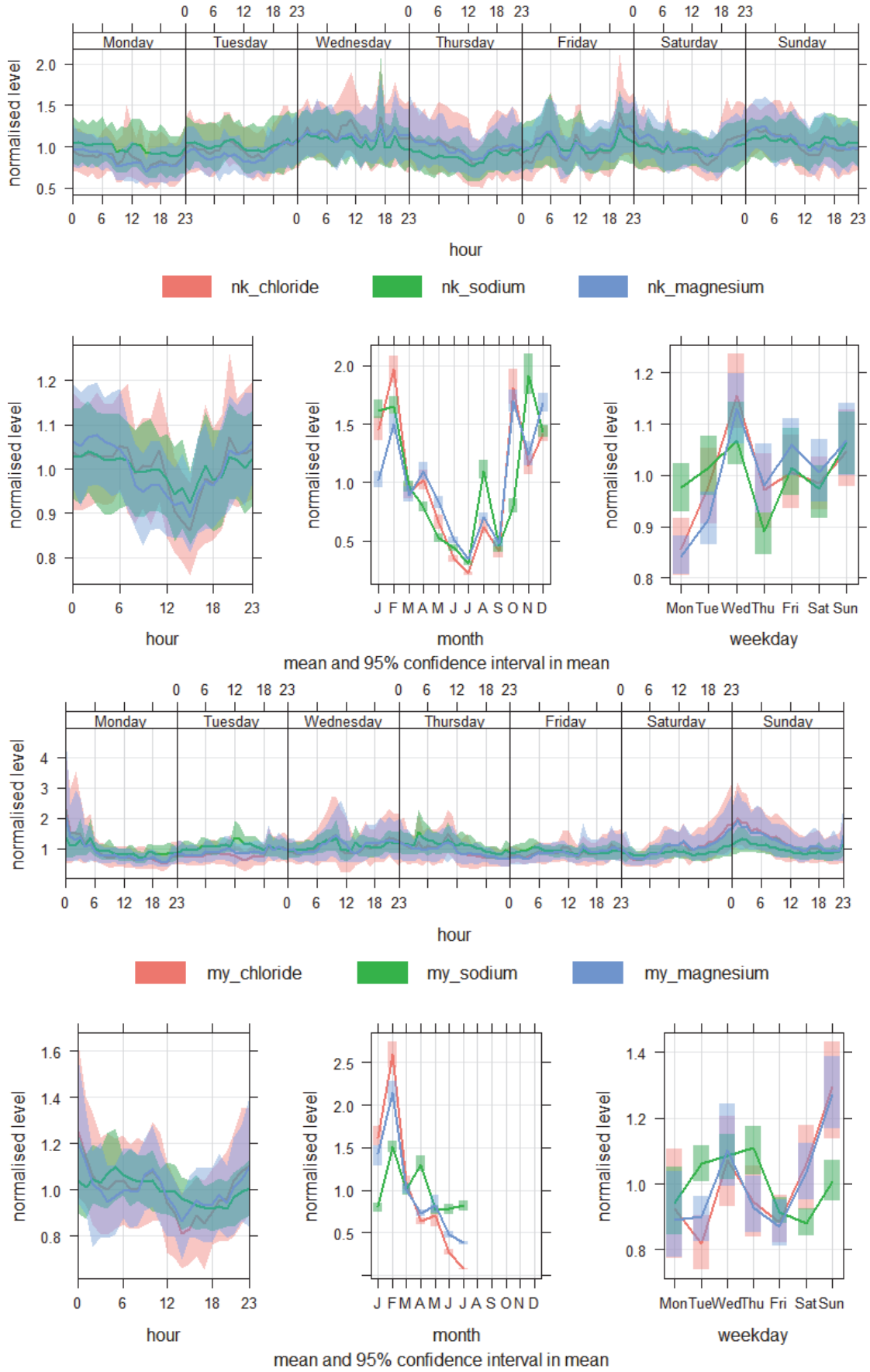



**Figure 4-23 Diurnal, weekly and monthly profiles for $Cl^-$ and $Mg^+$ concentrations during 2014 at North Kensington (top) and Marylebone Road (bottom).**

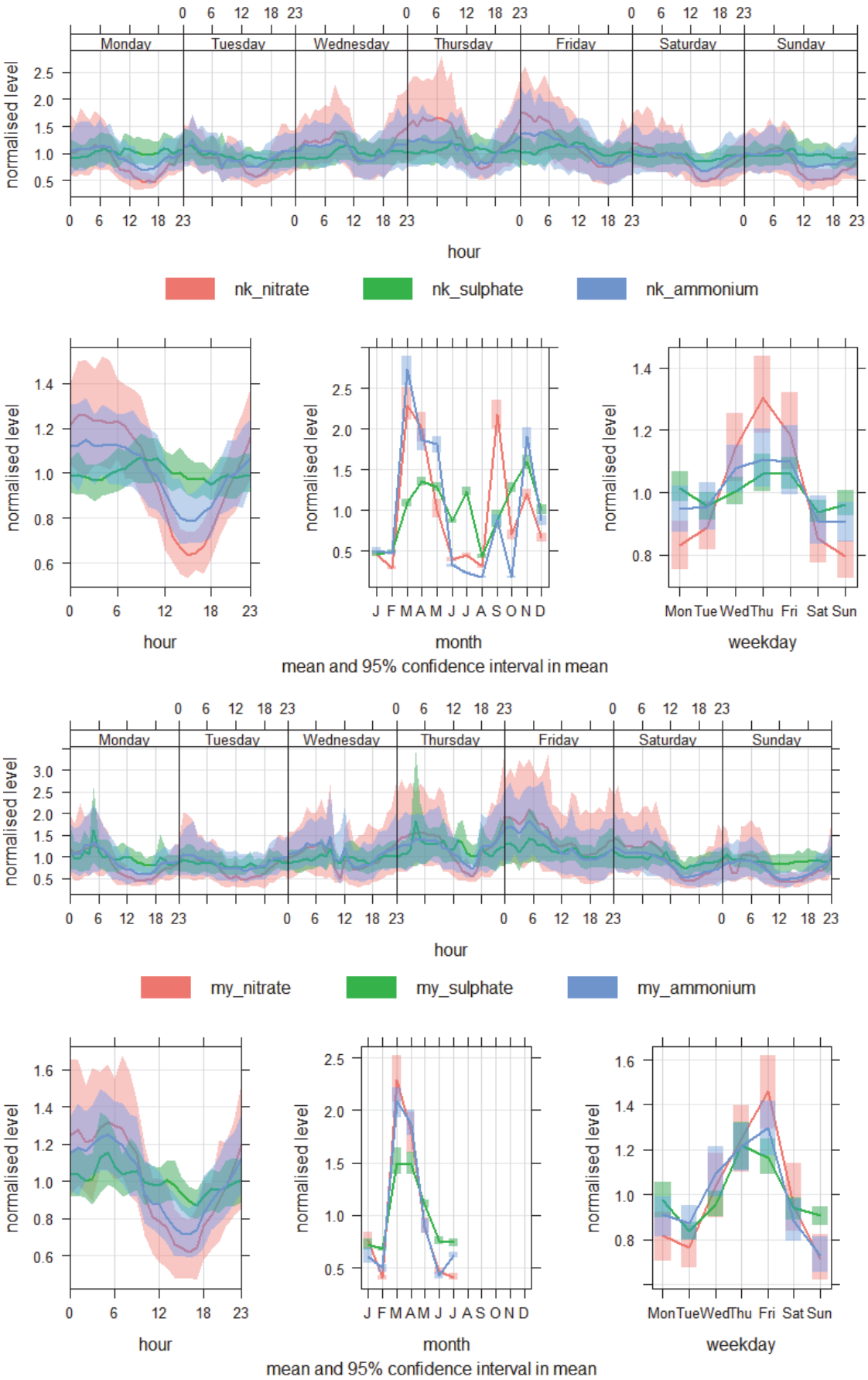



**Figure 4-24 Diurnal, weekly and monthly profiles for $NO_3^-$, $SO_4^{2-}$ and $NH_4^+$ during 2014 at North Kensington (top) and Marylebone Road (bottom)**

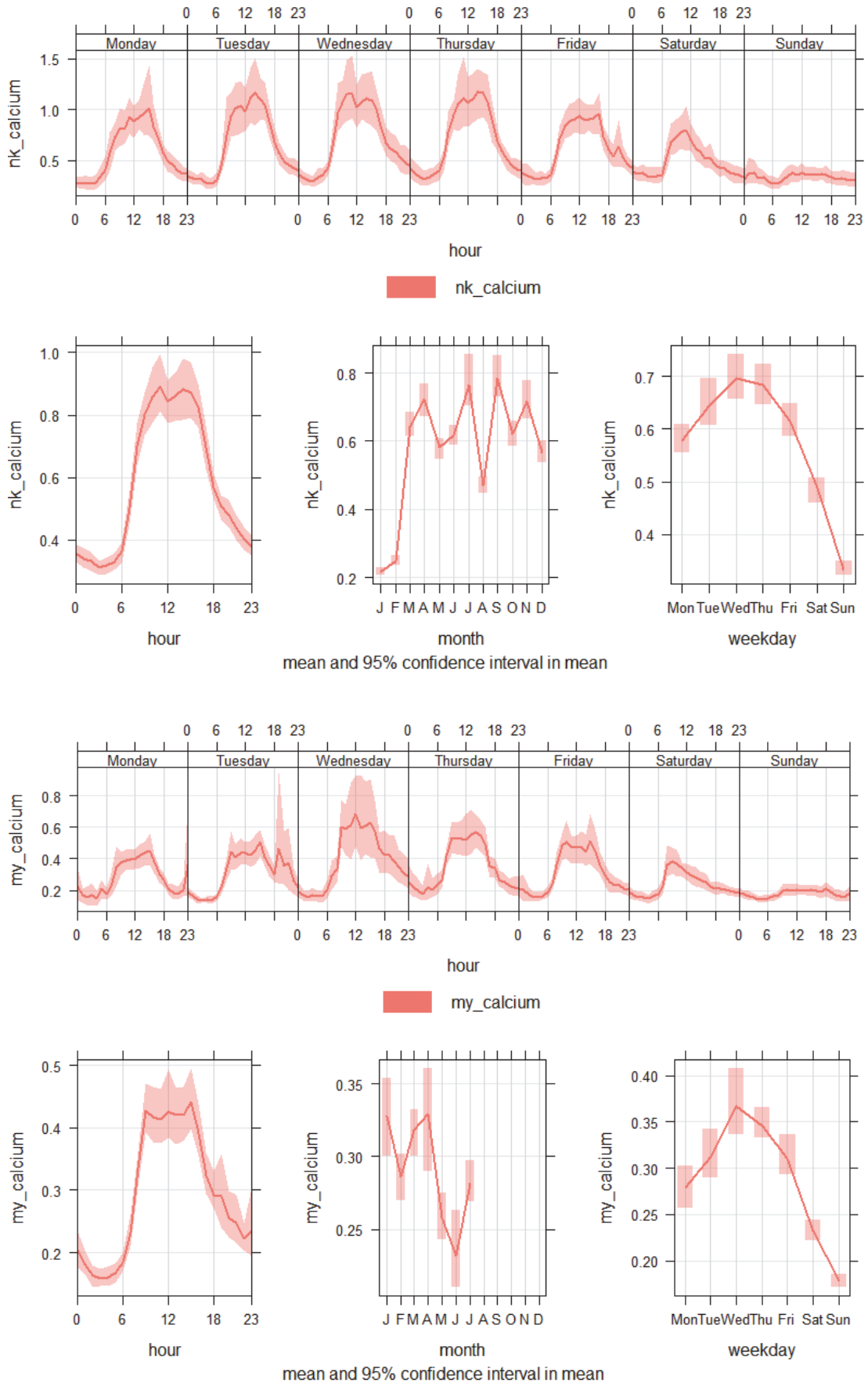



**Figure 4-25 Diurnal, weekly and monthly profiles for $Ca^{2+}$ during 2014 at North Kensington (top) and Marylebone Road (bottom)**

### 4.7.2 Profiles for number concentrations

At rural sites like Harwell, the diurnal profile is similar for all days of the week (see Figure 4-26 (top)). Concentrations show a minimum at 06:00 and an increase during the day, probably due to particle formation, which usually occurs during the day by photochemical processes. The monthly trend shows a maximum in spring and autumn and a minimum in winter.

At the urban 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.

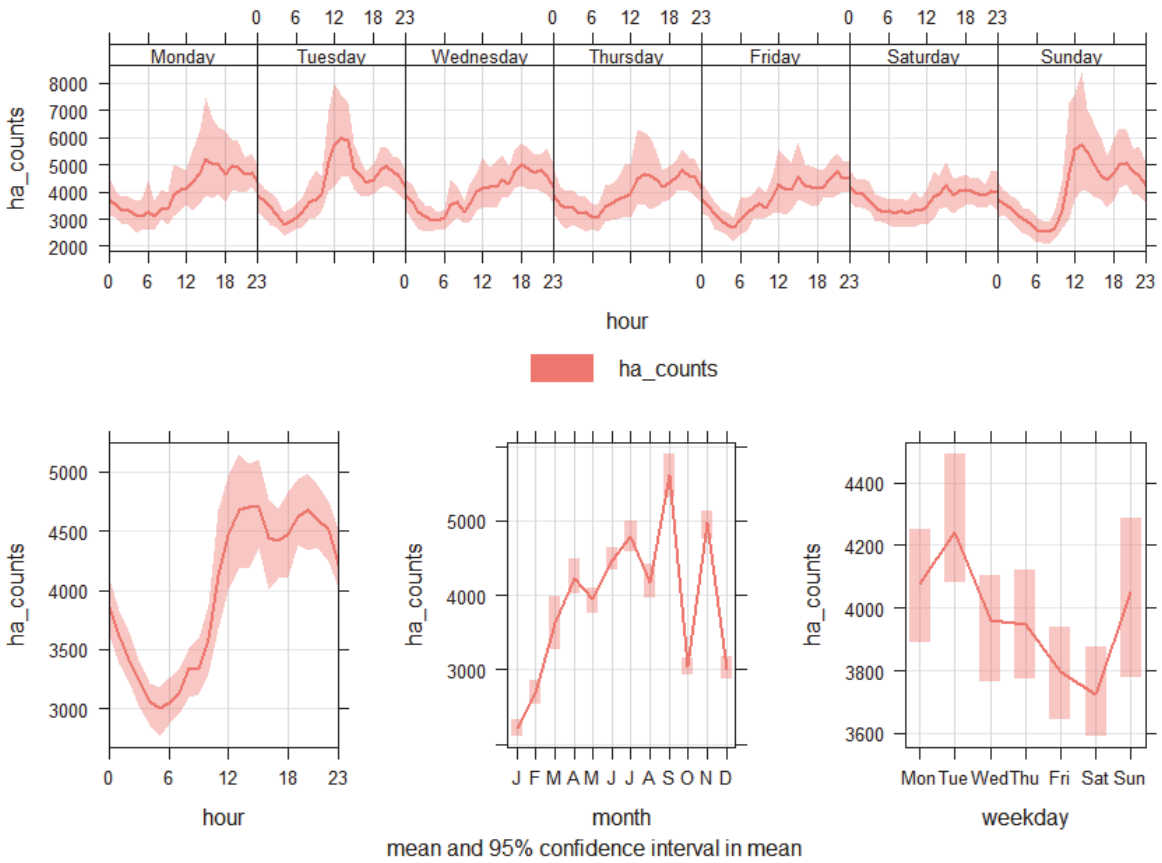



**Figure 4-26 Diurnal, weekly and monthly profiles for number concentrations at in 2014 at Harwell**

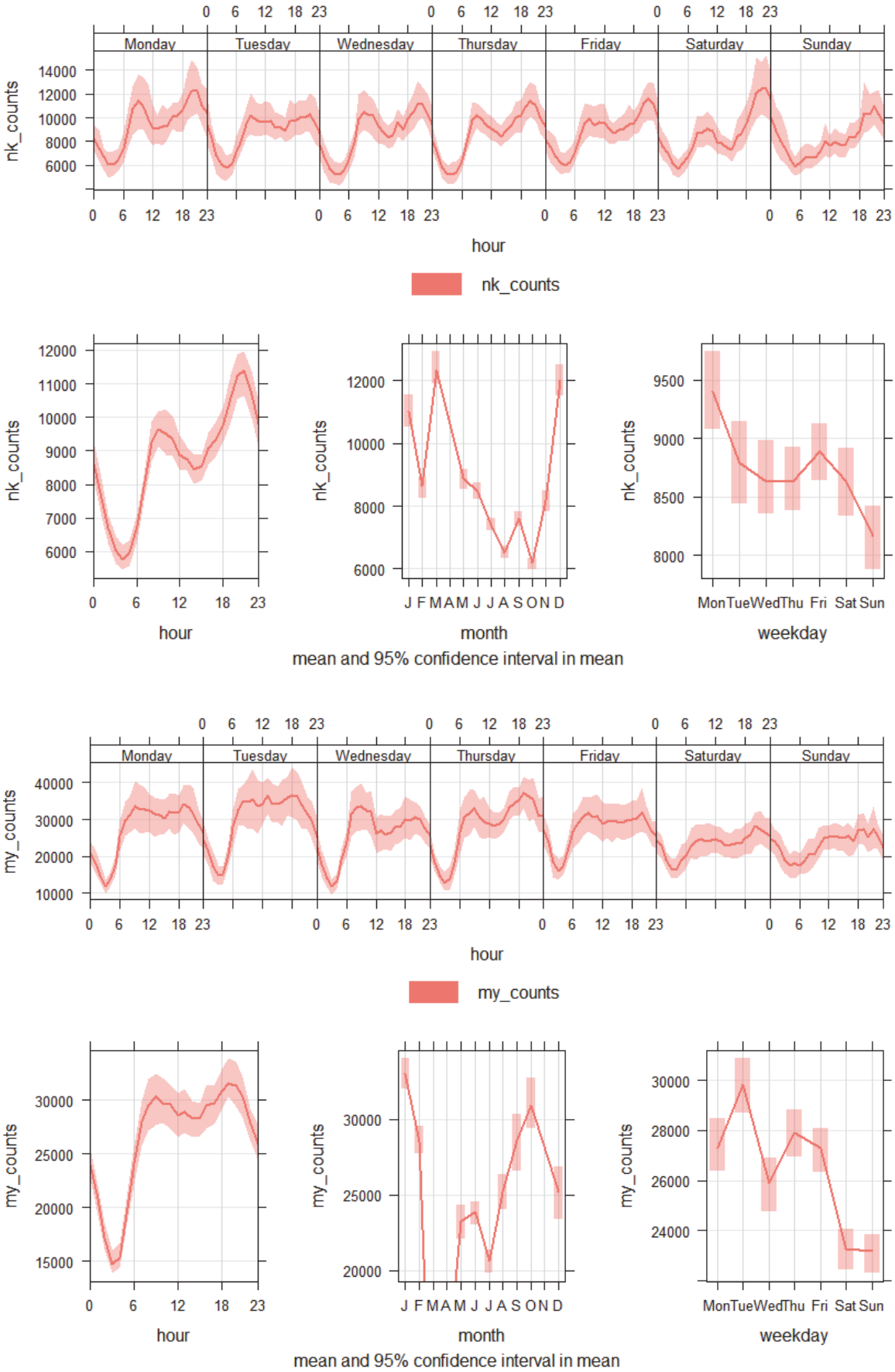



**Figure 4-27 Diurnal, weekly and monthly profiles for number concentrations at in 2014 at North Kensington (top) and Marylebone Road (bottom)**

## 4.8 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 this network. The data capture for the meteorological masts during 2014 was 100%. Wind roses are shown in Annex 1.

# 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 $PM_{10}$ 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 buses, coaches and 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. 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. So far the following papers have been published:

- D. E. Young, J. D. Allan, P. I. Williams, D. C. Green, R. M. Harrison, J. Yin, M. J. Flynn, M. W. Gallagher, and H. Coe (2015) Investigating the annual behaviour of submicron secondary inorganic and organic aerosols in London. Atmos. Chem. Phys., 15, 6351–6366, 2015. doi:10.5194/acp-15-6351-2015
- D. E. Young, J. D. Allan, P. I. Williams, D. C. Green, R. M. Harrison, J. Yin, M. J. Flynn, M. W. Gallagher, and H. Coe (2015) Investigating a two-component model of solid fuel organic aerosol in London: processes, PM1 contributions, and seasonality. Atmos. Chem. Phys., 15, 2429–2443. doi:10.5194/acp-15-2429-2015
- S. Visser, J. G. Slowik, M. Furger, P. Zotter, N. Bukowiecki, R. Dressler, U. Flechsig, K. Appel, D. C. Green, A. H. Tremper, D. E. Young, P. I. Williams, J. D. Allan, S. C. Herndon, L. R. Williams, C. Mohr, L. Xu, N. L. Ng, A. Detournay, J. F. Barlow, C. H. Halios, Z. L. Fleming, U. Baltensperger, and A. S. H. Prévôt. Kerb and urban increment of highly time-resolved trace elements in PM10, PM2.5 and PM1.0 winter aerosol in London during ClearfLo 2012. Atmos. Chem. Phys., 15, 2367-2386, 2015. doi:10.5194/acp-15-2367-2015
- Bohnenstengel S.I., Belcher S.E., Allan J.D., Allen G., Bacak A., Bannan T.J., Barlow J.F., Beddows D.C.S., Bloss W.J., Booth A.M., Chemel C., Coceal O., Di Marco C.F., Faloon K.H., Fleming Z.L., Furger M., Geitl J.K., Graves R.R., Green D.C., Grimmond C.S.B., Halios C., Hamilton J.F., Harrison R.M., Heal M.R., Heard D.E., Helfter C., Herndon S.C., Holmes R.E., Hopkins J.R., Jones A.M., Kelly F.J., Kotthaus S., Langford B., Lee J.D., Leigh R.J., Lewis A.C., Lidster R.T., Lopez-Hilfiker F.D., McQuaid J.B., Mohr C., Monks P.S., Nemitz E., Ng N.L., Percival C.J., Prévôt A.S.H., Ricketts H.M.A., Sokhi R., Stone D., Thornton J.A., Tremper A.H., Valach A.C., Visser S., Whalley L.K., Williams L.R., Xu L., Young D.E., Zotter P. (2014) Meteorology, air quality, and health in London: The ClearfLo project. Bulletin of the American Meteorological Society DOI: 10.1175/BAMS-D-12-00245.1

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. As part of Traffic, King's purchased a high time resolution XRF instrument which is capable of measuring a wide range of elements and has been deployed at Marylebone Road during 2014 and 2015.

### 5.1.3 Defra and other National Monitoring activities

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

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

Black Carbon Measurements

There are currently 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 $PM_{10}$ 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).

## 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, appears to be effectively on hold. 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, $SO_2$, NOx, VOCs, $NH_3$ and $CH_4$.

### 5.2.2 CEN standards

2014 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 $PM_{10}$ standard EN 12341:1998, and the gravimetric $PM_{2.5}$ standard EN 14907:2005, now published together as EN 12341:2014. 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). 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 Technical Specification CEN/TS 16450:2013 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 went for CEN Enquiry, to be upgraded to a full EN standard, in June 2015.

EN 12341:2014 may change relatively soon in the light of validation work to check various specific parts of the documents that was completed in early 2015. This may affect the allowed filter material. Currently a large range including quartz, glass fibre, PTFE and PTFE-coated glass fibre are allowed.

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, and manufacturers are producing variations of their products to meet them.

   The TS is due to be submitted as a draft for TC approval in January 2016.

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.

   The draft has been extended over the year, but no timescale for completion has been set.

**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).

Validation work is currently underway in both areas. The work packages being performed are:

- WP1: Literature review
- WP2: Lab tests
- WP3: Field tests
- WP4: Statistical evaluation

The current progress is as follows:

WP1 The final draft of the literature review has been approved by the working groups and publication is imminent.

WP2 Inter-laboratory comparisons have been performed.

WP3 Sampling has being performed at 6 field locations along with parallel sampling using automatic analysers.

WP4 The first interim reports on the working groups' progress have been approved by the working groups and sent to CEN. The statistical analysis of the field data has been completed and reported to CEN.

The method described in the standard for the analysis of ions deposited on filters will be Ion Chromatography. It is likely that the EUSAAR2 thermal protocol with transmission OC/EC split point determination will be adopted as the standard analysis protocol for OCEC. Currently the Network uses the Quartz protocol. In 2012 NPL analysed filters using both the EUSAAR2 and Quartz protocols and found no significant difference could be identified in TC – a reassuring check of the analysis system [17]. More recent unpublished measurements made at NPL suggest that a change to the EUSAAR-2 protocol will lead to step change reductions in EC of around 6% at Marylebone Road, 20% at North Kensington, and 25% at Harwell, with corresponding increases in OC of about 5% at all sites.

## 6 TOPIC REPORT – MEASUREMENTS OF COOKING ORGANIC AEROSOLS

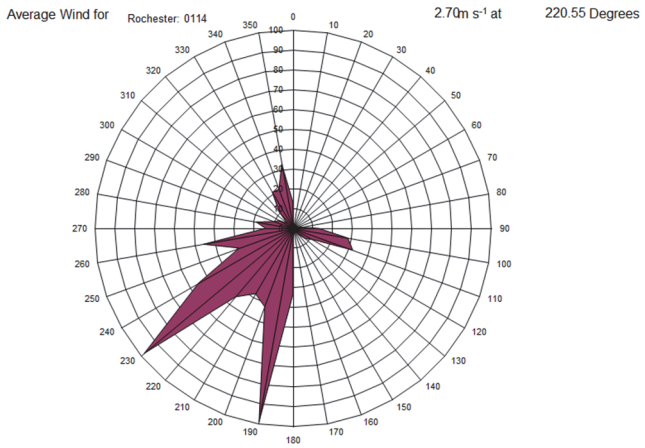
One Topic Report was produced in 2014 describing measurements of cooking organic aerosols.

The methods used to quantify cooking aerosol in the atmosphere were reviewed and these included the use of individual tracer compounds, the use of multiple tracers in a Chemical Mass Balance Model and the analysis of aerosol mass spectrometry data by Positive Matrix Factorisation.

As a broad generalisation, concentrations measured by the AMS/PMF technique usually exceed those measured by other methods. All measurement methods have very significant weaknesses and there are good reasons to believe that the AMS/PMF method may systematically overestimate airborne concentrations of cooking aerosol. Nonetheless, the collection of more quantitative data depends upon the development of more advanced techniques. Measured concentrations in the atmosphere, both by tracer, CMB and AMS/PMF techniques, show huge variation between locations and seasons. Given the uncertainty in the measurement methods, it is not possible to draw any general conclusions from these data. In an unpublished study conducted in the UK in 2012, mean concentrations of food cooking aerosol at the London North Kensington site were estimated as 0.44 $\mu g\ m^{-3}$ in the $PM_{2.5}$ size fraction by a CMB model and 0.87 $\mu g\ m^{-3}$ over the same period by the AMS/PMF technique. Daily concentrations measured by the two techniques were strongly correlated but with the AMS/PMF method measuring systematically higher. At the rural Harwell site, the CMB method estimated an average concentration of 0.13 $\mu g\ m^{-3}$. The overall conclusions is that, despite considerable difficulties in quantification, it seems probable that cooking aerosol represents of the order of 5% of $PM_{2.5}$ at an urban background location in the UK and considerably less at a rural site.

# ANNEX 1. WIND ROSES AT ROCHESTER

## January 2014

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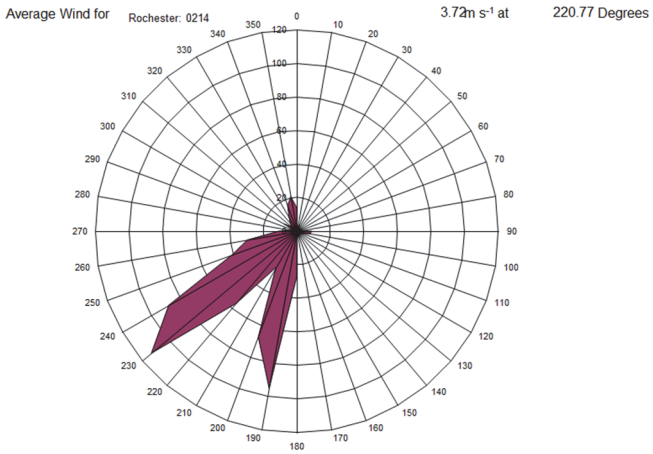


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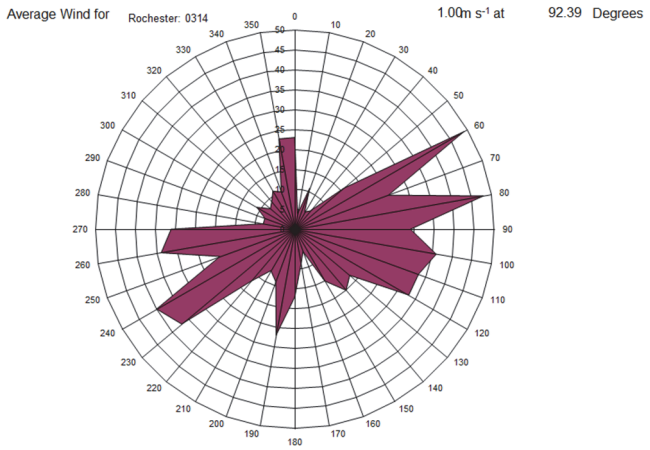


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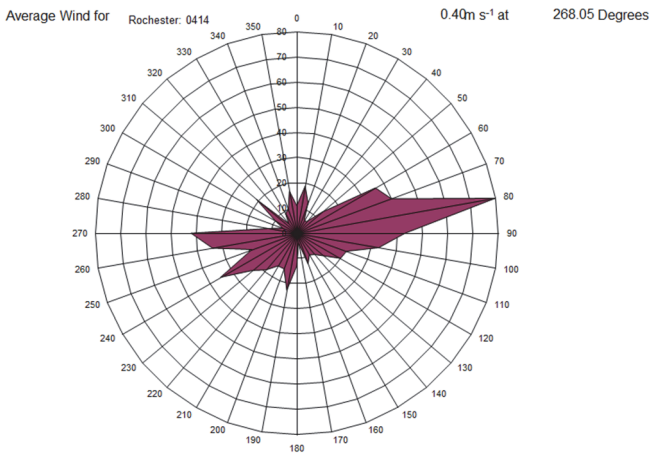


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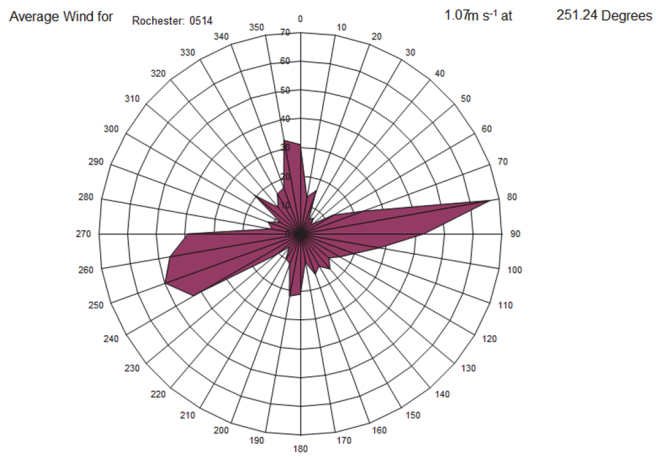


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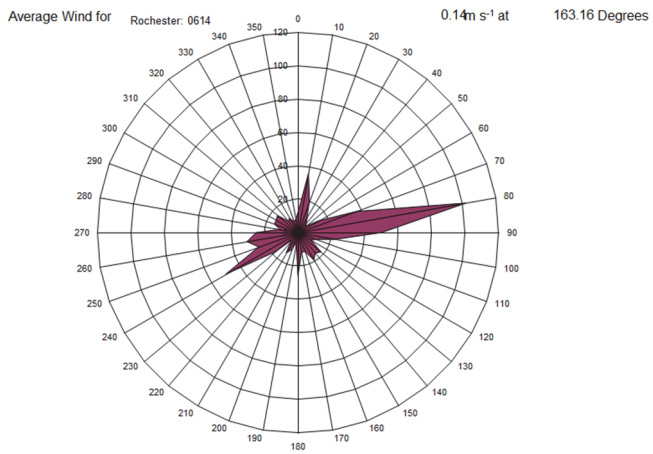

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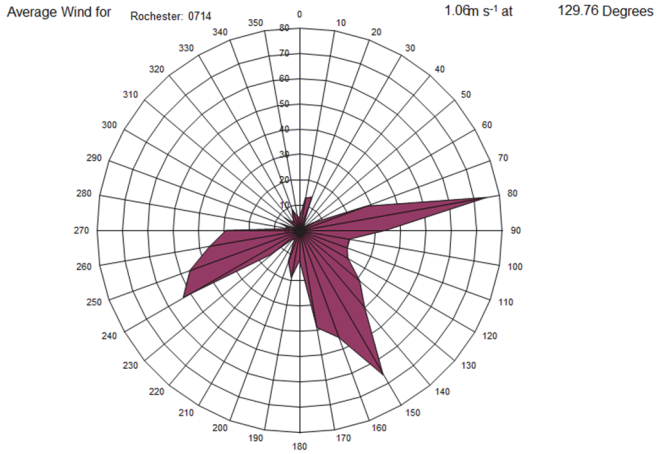


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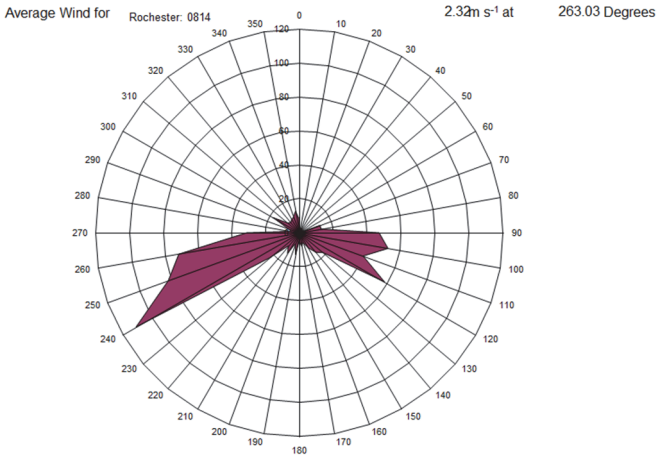


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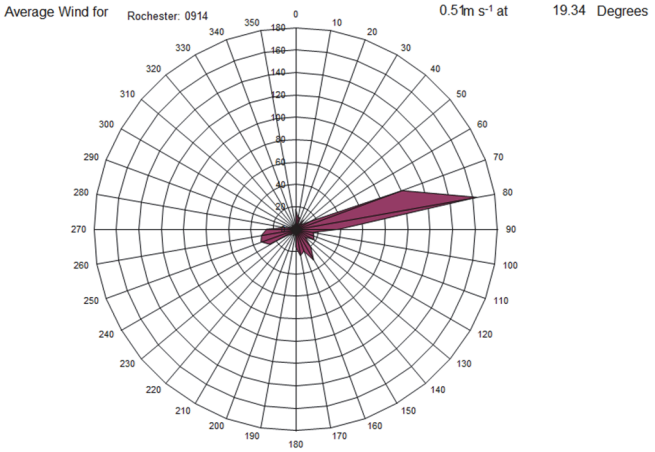


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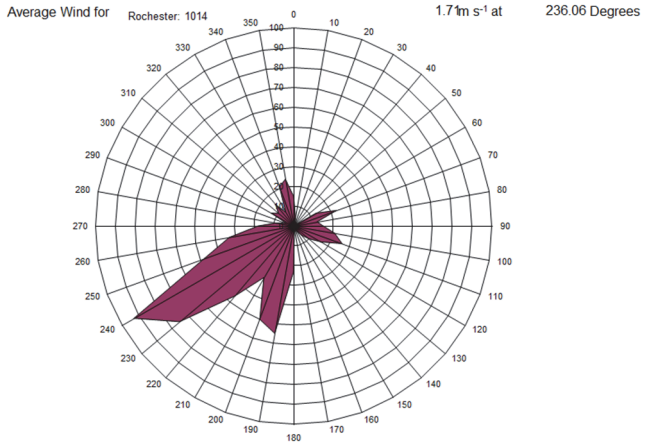


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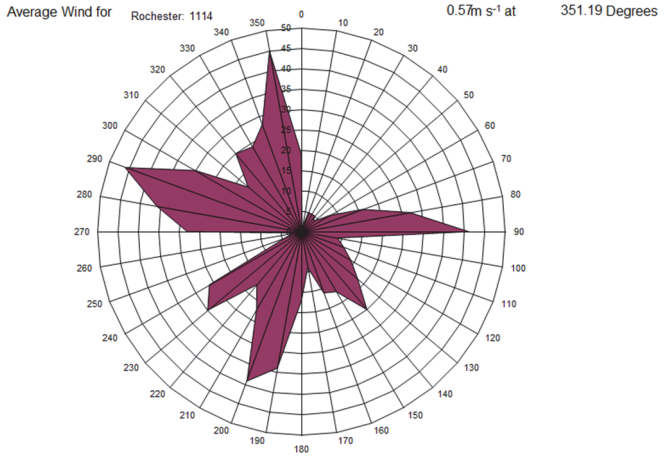


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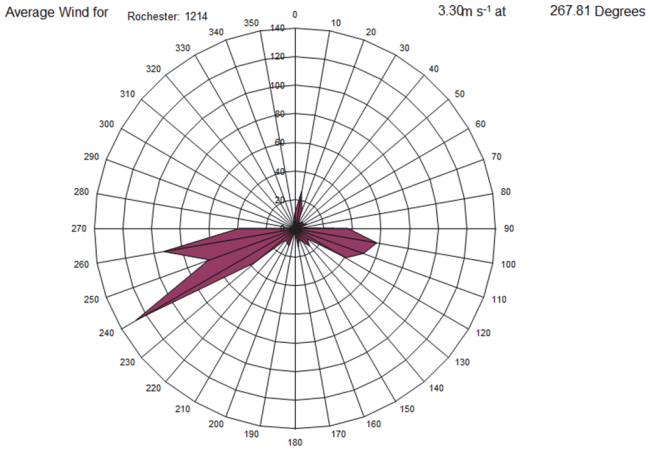

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