

**Airborne Particulate Concentrations and Numbers in the United
Kingdom (phase 3)
Annual report 2015**

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Approved on behalf of NPLML by
Martin Sené, Operations Director

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1 INTRODUCTION

The UK Airborne Particulate Concentrations and Numbers Network (AQ21636) currently 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/cation concentrations.

This report shows a summary of the 2015 data collected within this network, along with main findings, a comparison with previous years and a comparison with measurements carried out in other networks.

2 NETWORK OPERATION

2.1 OVERVIEW

The operation of the network in 2015 was structured in the same way as the previous year, with the CPC in Birmingham still not 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.

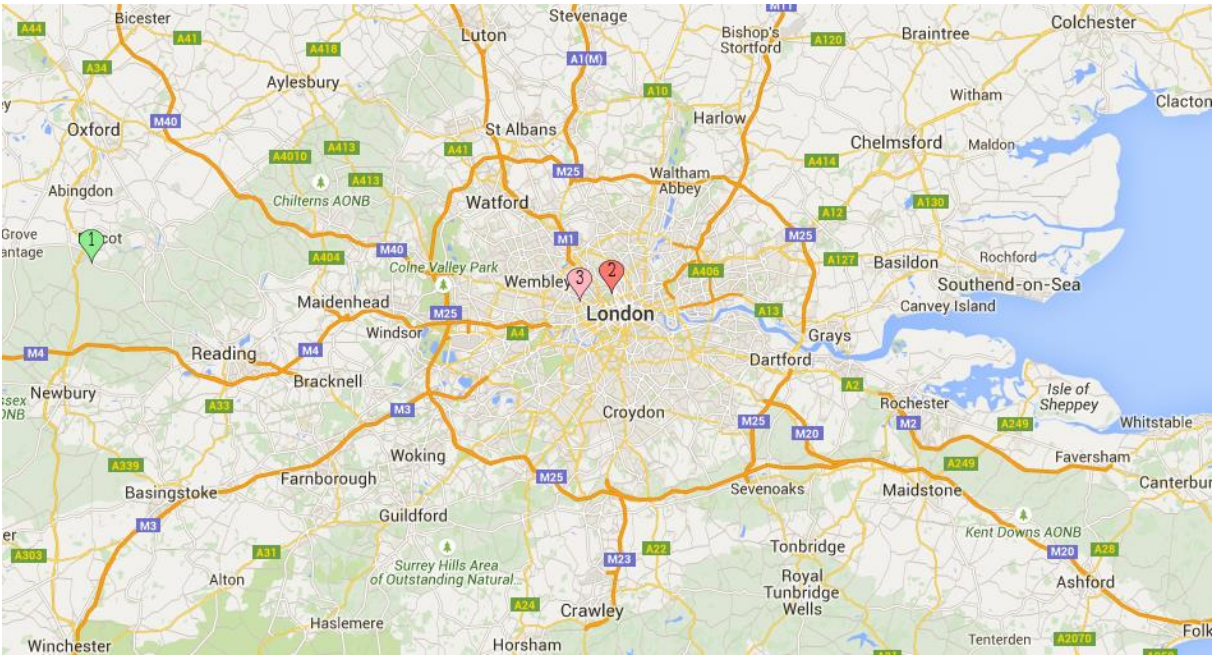
2.2 NETWORK STRUCTURE

The measurement programme during 2015 is shown in Table 2-1. Wind speed and direction are reported for the Rochester site.

Table 2-1 Network structure in 2015

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>.



- 1 Harwell
- 2 Marylebone Road
- 3 North Kensington
- 4 Auchencorth Moss

Figure 2-1 Network sites in 2015

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 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_{10} 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 **Error! Reference source not found.**), which use Nafion driers. Humidity sensors have been installed and are logged by the computers.

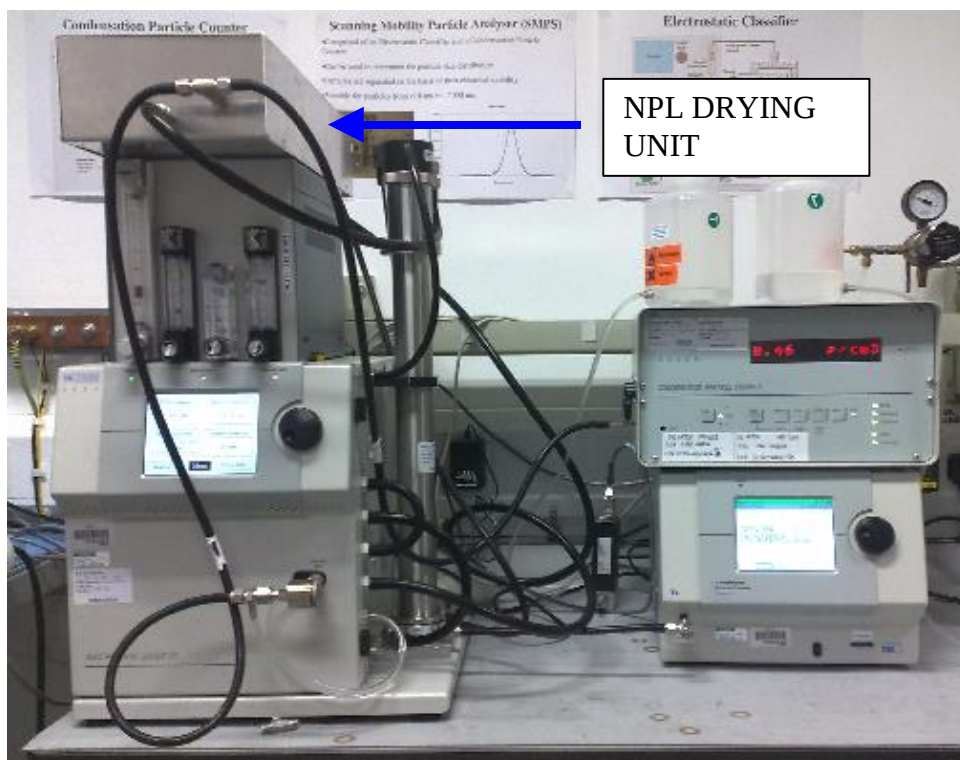


Figure 2-2 Typical configuration of CPC, SMPS and NPL drying unit at the Network sites

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.

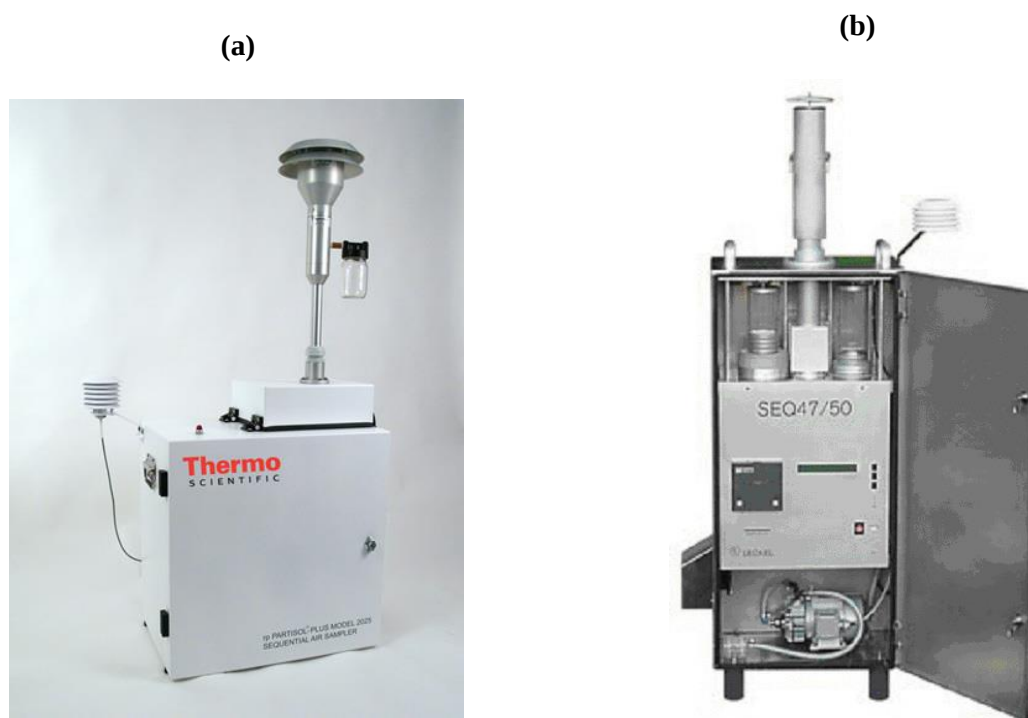


Figure 2-3 Thermo Partisol 2025 sampler (b) Leckel SEQ47/50 sampler



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

2.3.4 Aethalometer (Black carbon $PM_{2.5}$)

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

The 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 ‘UVP’ 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 Virkkula² 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 2015 Black Carbon Network report.³



Figure 2-5 Magee Scientific aethalometer

2.3.5 URG – AIM 9000B (PM₁₀ anion and cation measurements)

The URG – AIM (Ambient Ion Monitor) 9000-B (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 2100 Thermo Fisher Ion chromatograph (IC), which has its own eluent 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 (PM₁₀)

4.1.1 OC/EC/TC time trends

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.

The annual data capture for the Partisol 2025 instruments in 2015 were 94%, 96% and 97% 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 all 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.

Some of the pollution episodes that occurred during 2015 can be identified in the graphs:

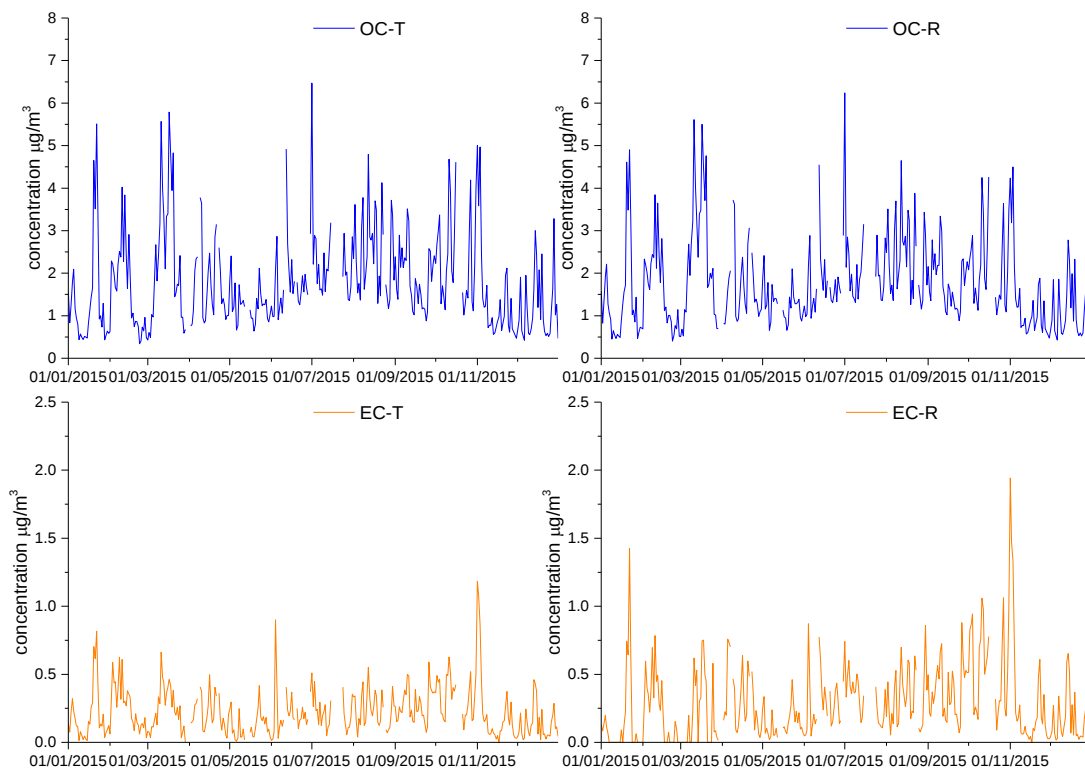
1. **End January:** cold and still weather conditions led to a build-up of local emitted pollutant causing “moderate” to “high” PM₁₀ concentrations on 19 and 20 January at some sites in London. On 23 January the wind direction changed bringing with it air which had previously passed over heavy-industrialised areas of Eastern-Europe. This caused a combination of local and long-range pollution. Analysis of the chemical composition of the particulate indicates that

this was driven by an influx of ammonium nitrate (NH_4NO_3) often linked to agricultural sources on the continent (see Section 4.3).

2. **Mid-February:** London experienced wintertime smog conditions with low cloud, low temperatures and most importantly, low wind speeds persisting through the week and preventing dispersion of local emissions. Adding to this, a gradual increase in imported pollution from the near continent raised the overall levels.
3. **Mid-March:** between the 17 and the 20 March, a high pressure system centred over Scandinavia resulted in settled conditions in south-east England and light easterly to south-easterly winds. Consequently, air arriving from the north of continental Europe mixed with local emissions to produce a widespread particulate episode across the whole region.
4. **Early April:** widespread 'moderate' PM_{10} and $\text{PM}_{2.5}$ was measured across London and south-east England on the 8 and 9 April due to a high pressure system over southern England and the northern part of continental Europe resulting in low wind speeds and accumulation of pollutants.
5. **Late October – Early November:** The episode was caused by still, calm, foggy conditions leading to poor pollutant dispersion. On both days, wind speeds were low, leading to accumulation of locally emitted particulate. Air mass back trajectories show that air was incoming from Europe throughout the weekend but this added little to the measured concentrations; in central London, over $\frac{3}{4}$ of the particle pollution was produced in the urban area. An additional factor to consider during this episode is a possible increase in local particulate sources from bonfires and fireworks.

(Source: London air website - <http://www.londonair.org.uk/>)

Harwell



North Kensington

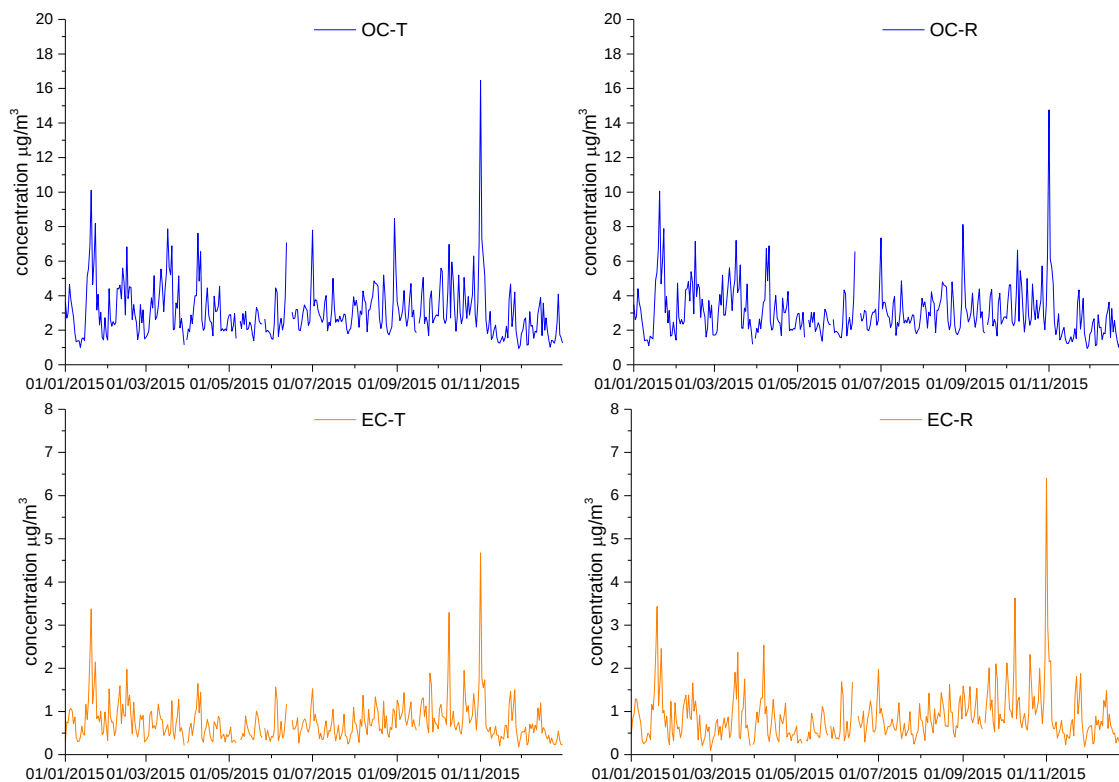


Figure 4-1 PM₁₀ OC and EC concentrations at Harwell (top) and North Kensington (bottom) during 2015

Marylebone Road

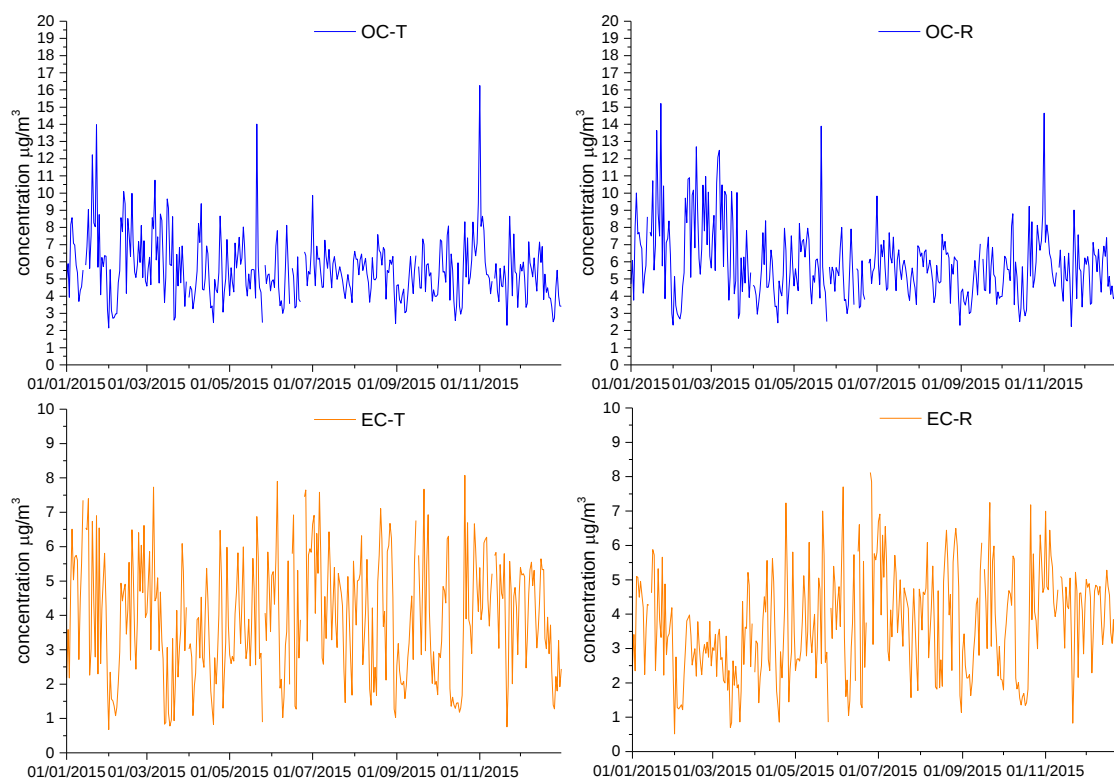


Figure 4-2 PM_{10} OC and EC concentrations at Marylebone Road during 2015

Total Carbon

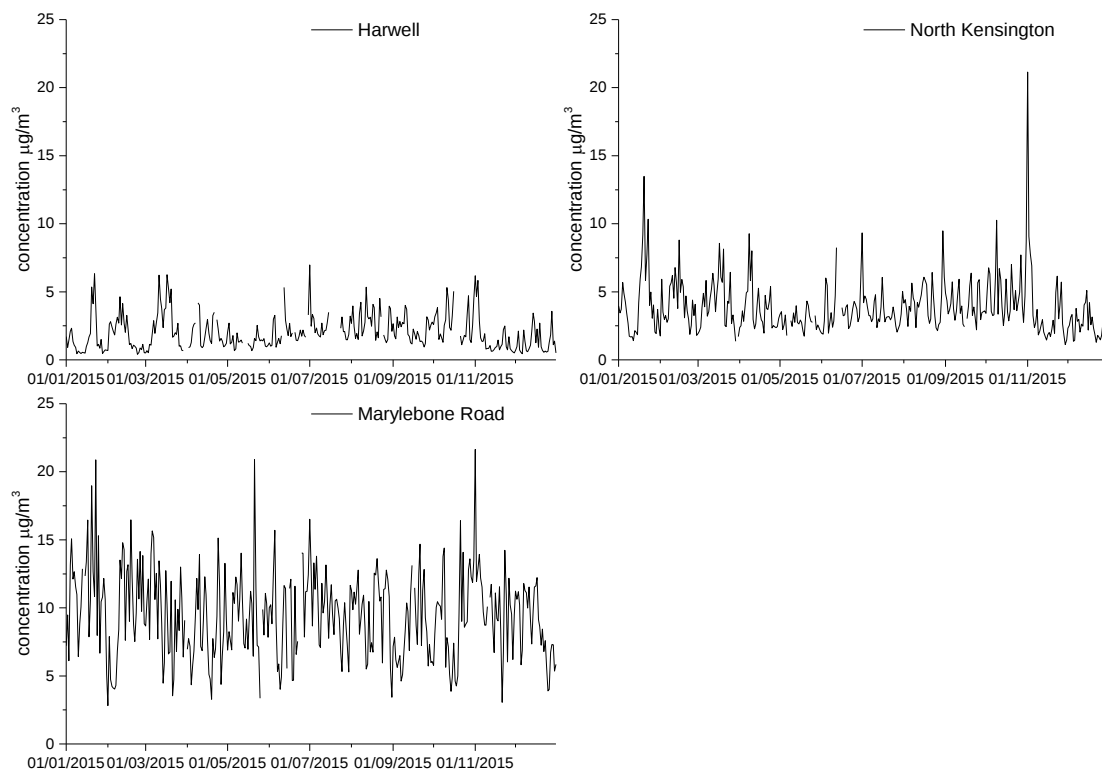


Figure 4-3 PM_{10} TC concentrations at Harwell, North Kensington and Marylebone Road during 2015

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

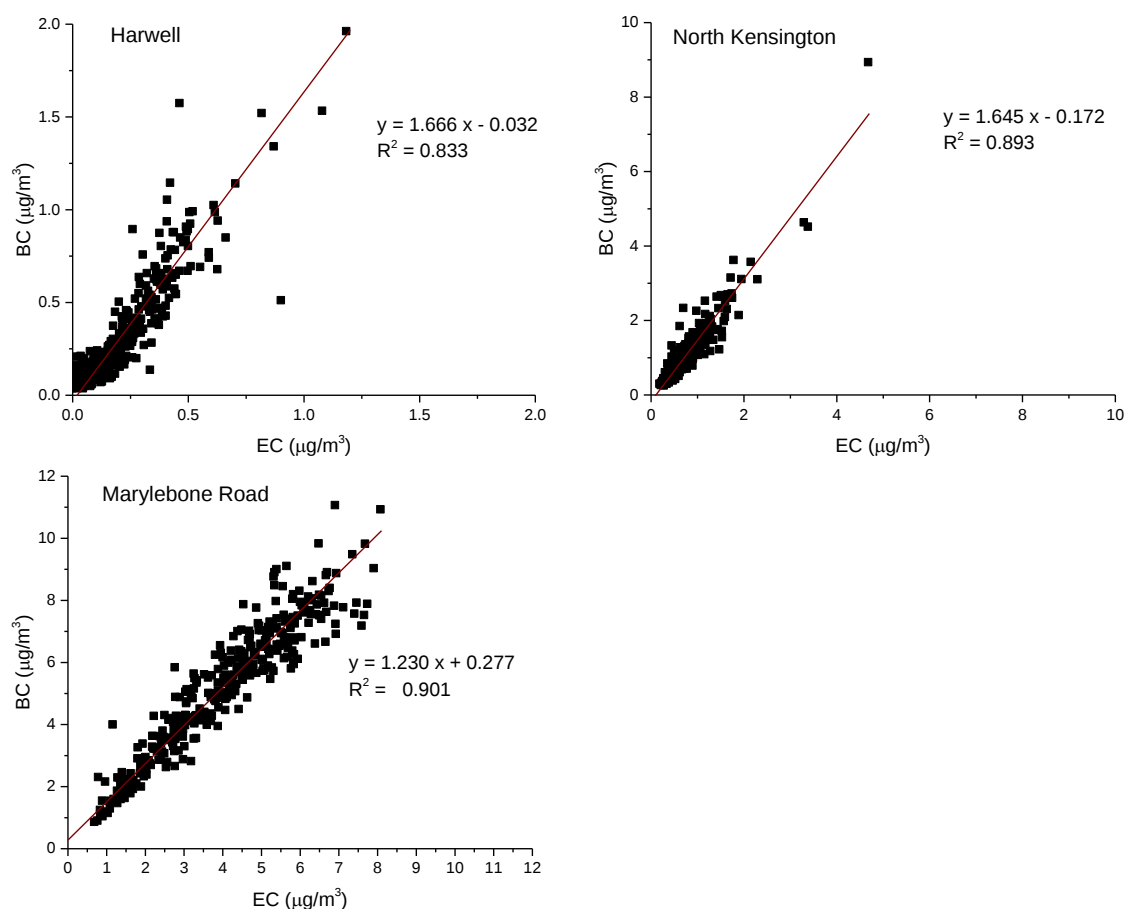


Figure 4-4 Comparison between PM_{2.5} BC and PM₁₀ EC (TOT) at the 3 sites in 2015

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

Table 4-1 Relationship between Black Carbon (PM_{2.5}) and Elemental Carbon (PM₁₀) and the three Network sites

Year	Harwell		North Kensington		Marylebone Road	
	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	$1.43 x + 0.01$	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	$1.68 x - 0.00$	0.872	$1.32 x + 0.25$	0.819
2015	$1.67 x - 0.03$	0.833	$1.64 x - 0.17$	0.893	$1.23 x + 0.28$	0.901

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 1 September 2011 and the sampler at Auchencorth Moss since 17 November 2011. Data capture for 2015 was 99% for Harwell and 98% for Auchencorth Moss. Figure 4-5 and Figure 4-6 show the time series for these measurements since the installation of the samplers.

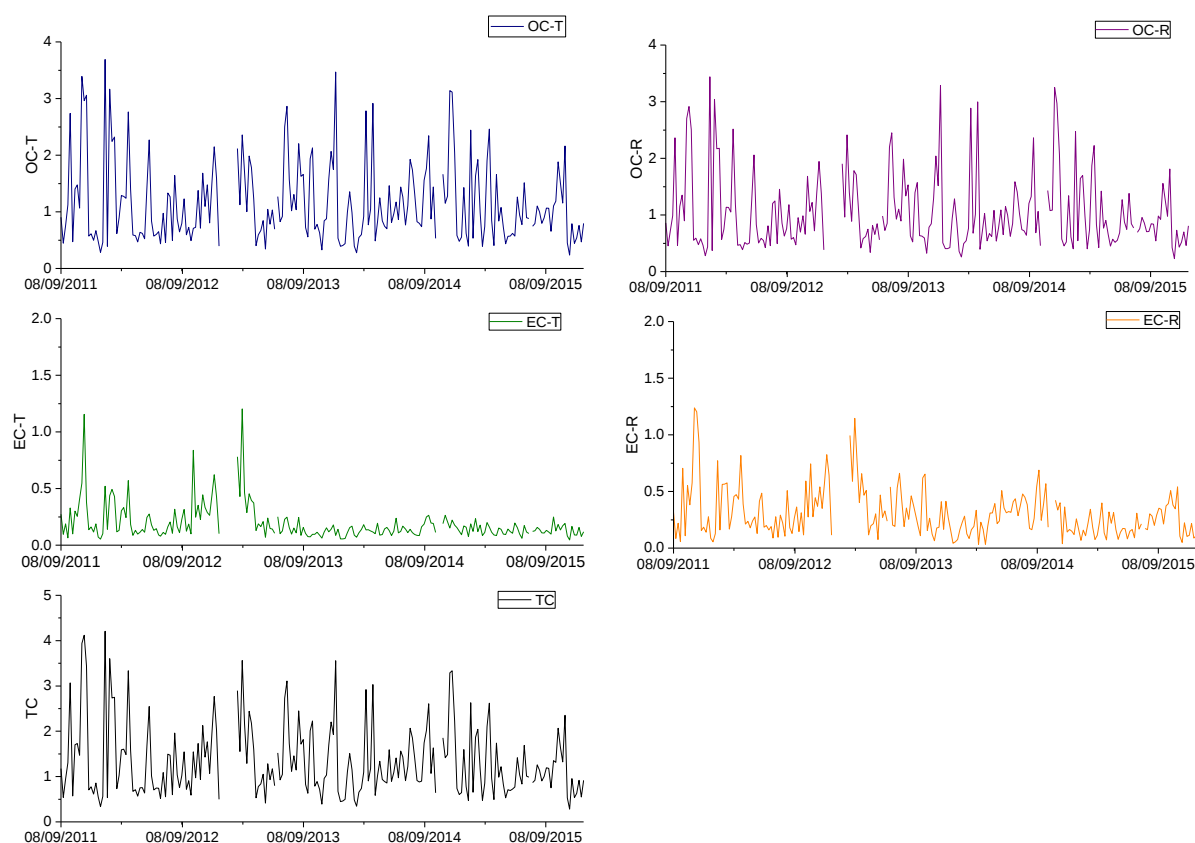


Figure 4-5 Time series of OC, EC and TC in the PM_{2.5} fraction at Harwell since the installation of the sampler (weekly samples) (µg/m³)



Figure 4-6 Time series of OC, EC and TC in the PM_{2.5} fraction at Auchencorth Moss since the installation of the sampler (weekly samples) (µg/m³)

The PM_{2.5} carbon concentrations at Harwell were compared with weekly averages from the PM₁₀ 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 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 (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 PM₁₀.

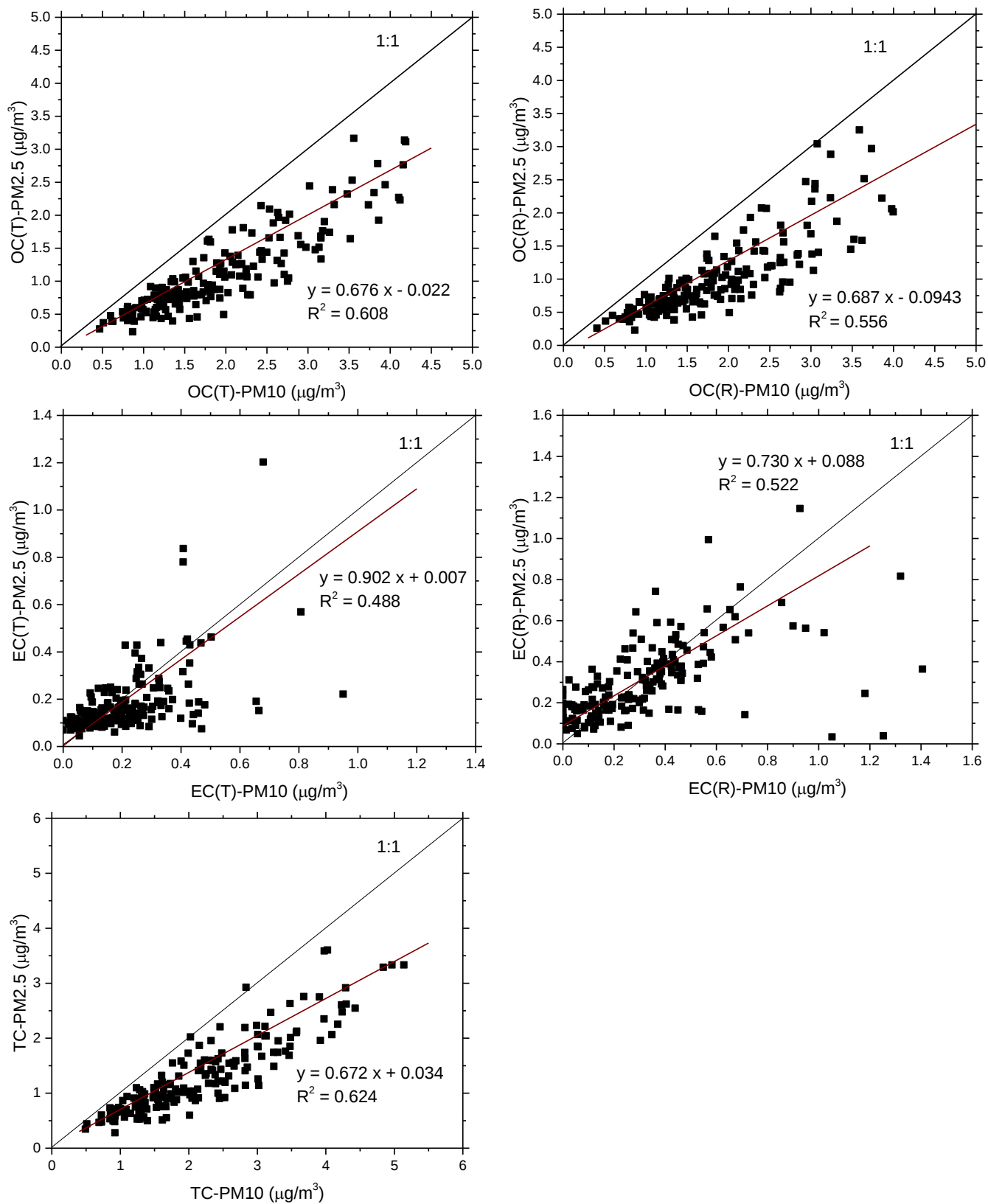


Figure 4-7 Comparison between PM₁₀ OC/EC weekly averages and PM_{2.5} OC/EC at Harwell

4.3 AUTOMATIC PM₁₀ 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 (NO₃⁻), sulphate (SO₄²⁻), sodium (Na⁺), ammonium (NH₄⁺), potassium (K⁺), magnesium (Mg²⁺) and calcium (Ca²⁺) 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 in operation, under a different Network.

The annual data capture was 53% for Marylebone Road and 65% for North Kensington.

The lower data capture at Marylebone Road and the large gap in the data were due to a major breakdown in the anion chromatograph which required the system to be sent to Thermo Fisher for repair. Figure 4-8 and Figure 4-9 show the times series for all the ion concentrations at the two sites.

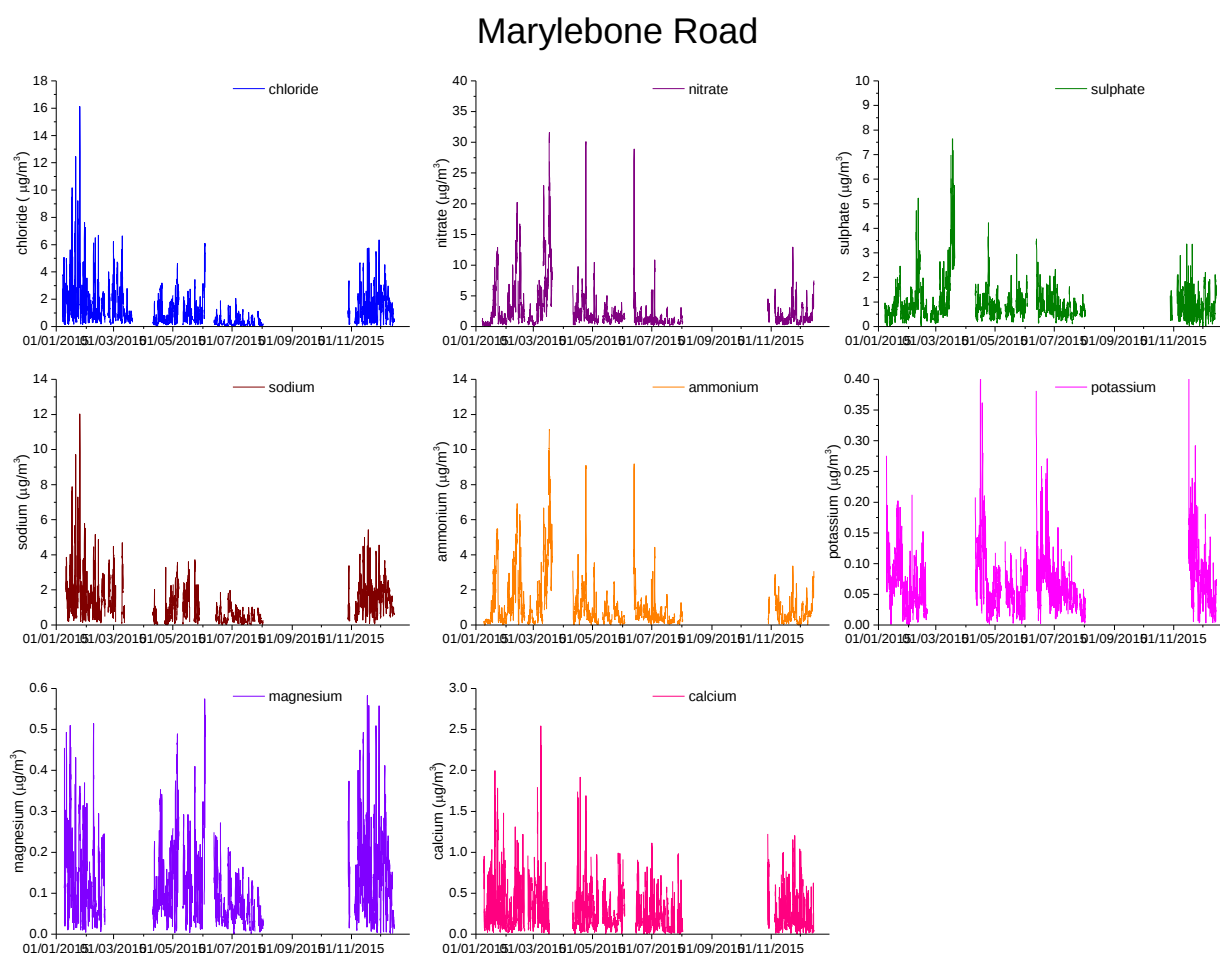


Figure 4-8 Time series for ion concentrations at Marylebone Road in 2015

North Kensington

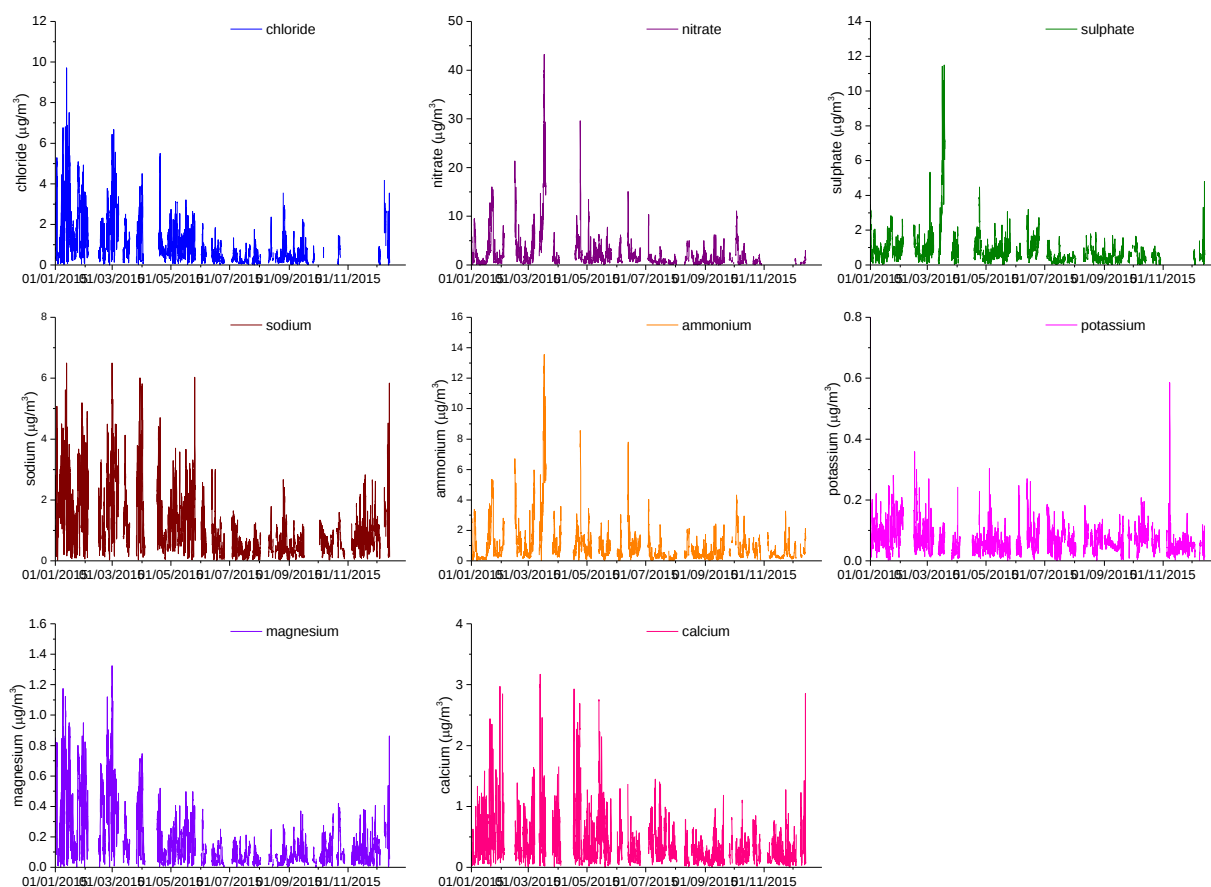


Figure 4-9 Time series for ion concentrations at North Kensington in 2015

Figure 4-10 shows the pollution episode on 19 – 23 January described in Section 4.1.1. It can be noticed the increase of NH_4NO_3 on 23 January when the wind direction changed bringing air from Eastern Europe and possibly emissions from agriculture activities in the continent.

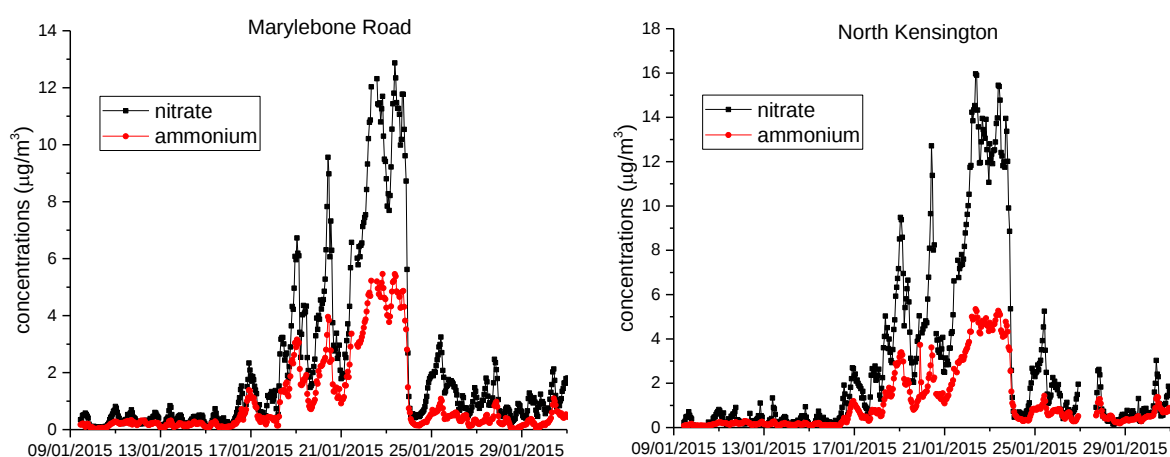


Figure 4-10 Pollution episode on 19 – 23 January 2015 at the two sites in London. The ammonium nitrate (NH_4NO_3) is thought to be linked to agriculture emissions.

Figure 4-11 instead shows the pollution episode in mid-February at Marylebone Road, which caused hourly NO_3^- concentrations to reach values of about $20 \mu\text{g}/\text{m}^3$ on 12 February. This episode was dominated by ‘moderate’ PM_{10} concentrations at roadside sites, like Marylebone Road, due to cold and

still conditions. Continentally driven particulate episodes are marked by an influx of very fine particles in the $PM_{2.5}$ fraction which can travel vast distances. During these types of episodes, where $PM_{2.5}$ makes up a larger fraction of overall PM_{10} concentrations, similar particulate concentrations are seen at roadside and background sites. Locally driven episodes, however, tend to be dominated by the larger PM_{10} fraction. As its main source is traffic, these episodes tend to affect roadside locations.⁷

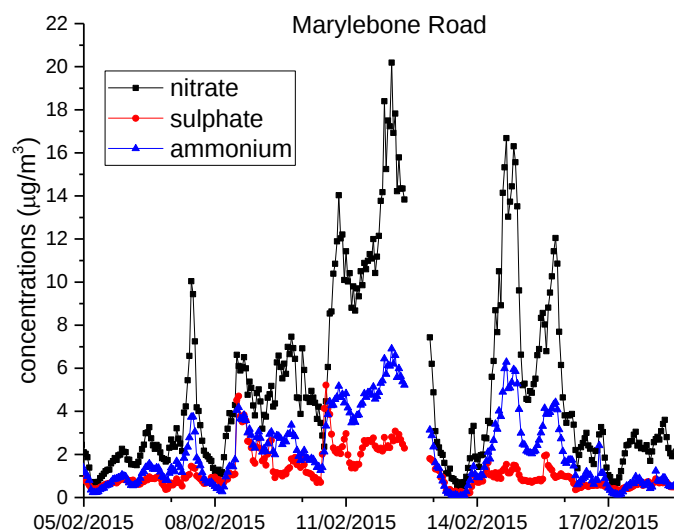


Figure 4-11 Pollution episode on 9 – 15 February 2015 at Marylebone Road.

Two more main pollution episodes affected London in mid-March and early April; however, both instruments were not fully operational at the beginning of April.

Figure 4-12 shows the concentration of NO_3^- , SO_4^{2-} and NH_4^+ at Marylebone Road during the mid-March episode. Nitrate concentrations reached values as high as $30 \mu g/m^3$; this is likely to have been due to the springtime application of slurry and fertiliser in agricultural regions on the near-continent. The presence of some SO_4^{2-} in the measured particulate indicated a contribution from both local and distant combustion sources. This type of long-range transport episode has become common at this time of year.⁷

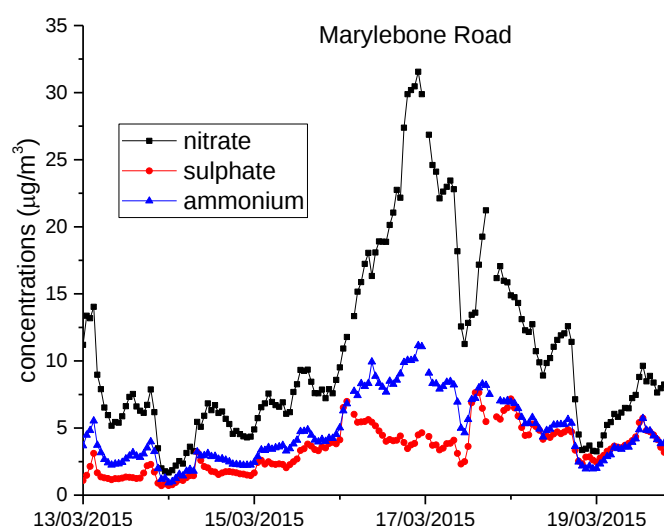


Figure 4-12 Mid-March 2015 pollution episode at Marylebone Road

Higher concentrations of Cl^- , Na^+ and Mg^{2+} are found at both sites at the beginning of the year. January and February were characterised by heavy rain and strong winds coming from the west; it is then possible that sea-salt aerosols dominated the chemical composition over this period of the year.

Higher K^+ concentrations on 1 January and on the evenings of 6 and 7 November at North Kensington are also noteworthy; these are due to fireworks for the New Year and fireworks/bonfires in occasion the Guy Fawkes Night on 5 November.

4.4 PARTICLE NUMBERS AND SIZE DISTRIBUTIONS

4.4.1 Particle number concentrations

Time series of hourly particle number concentrations (between about 7nm and several microns in diameter) measured at network sites during 2015 are shown in Figure 4-13. The plots have been shown on the same scale.

The reasons for the main data gaps were:

- **Harwell:** The instrument was removed for service/calibration on 3 February and re-installed on 2 March. The laser failed on 15 October; the instrument has been permanently removed from site.
- **North Kensington:** The instrument was removed for service/calibration on 4 February and re-installed on 23 February.
- **Marylebone Road:** The instrument was calibrated in October 2014 following a fault which required the replacement of the pump. It was, however, removed from site on 22 February due to butanol flooding and re-installed on 26 March. Upon calibration in February 2016, the CPC was found to be largely and erratically under-reading in both single-particle and photometric modes and the laser failed soon afterwards. The fault with the laser is believed to have started sometime in August; for this reason only the data until 31 July have been submitted to the UK-Air data archive.

The average annual data captures for the CPC instruments during 2015 were 83%, 92% and 81% respectively for Harwell (up to 15 October), North Kensington and Marylebone Road (up to 31 July).

For the purpose of this report, the long-term ratio between total number concentrations from the SMPS data and CPC data was used for the Harwell and Marylebone Road datasets to complete the time series after the instruments broke down, as shown in Figure 4-13. The uncertainty for these extra data, however, cannot be accurately estimated, hence they have not been included in the datasets submitted to the UK-Air website.

A few periods of low concentrations can be noticed in the trend at Marylebone Road, specifically between 1 – 8 February and 10 – 20 October. The same behaviour can also be observed in the EC trends in Figure 4-2 at different times of the year, in the Black Carbon and NO_x concentrations at the same site and, to a lesser extent, at North Kensington. The reason for these periods of low concentrations are thought to be due to a change of wind direction: when the wind blows from N/NW, it brings cleaner air coming from Regent's park, at north of the site. Marylebone Road is considered a street canyon, therefore wind speed and wind direction affect significantly the air quality within the street.

Figure 4-14 shows a plot of wind and number concentrations rose at Marylebone Road during 2015 using modelled wind data from UK-Air. The plot clearly shows that low concentrations occur when the wind blows from N/NW.

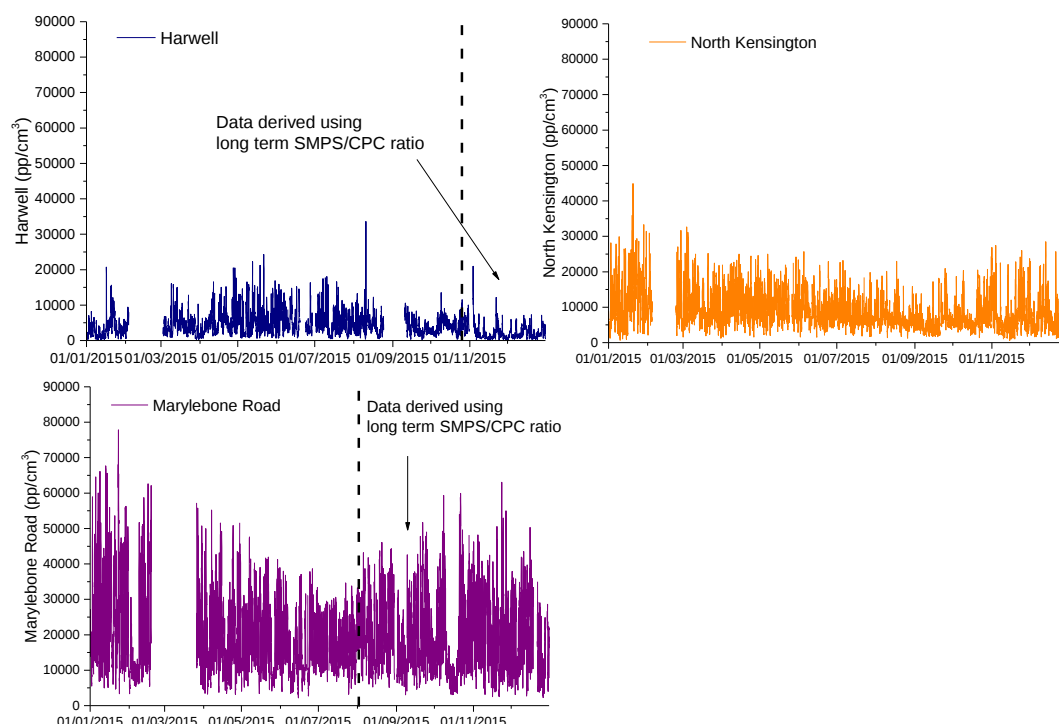


Figure 4-13 Time series of number concentrations during 2015 at the Network sites. The data from when the instruments at Harwell and Marylebone Road broke down (15 October and 31 July 2015 respectively) were calculated using the long-term SMPS/CPC ratio for the purpose of this report. These data have not been submitted to the UK-Air data archive.

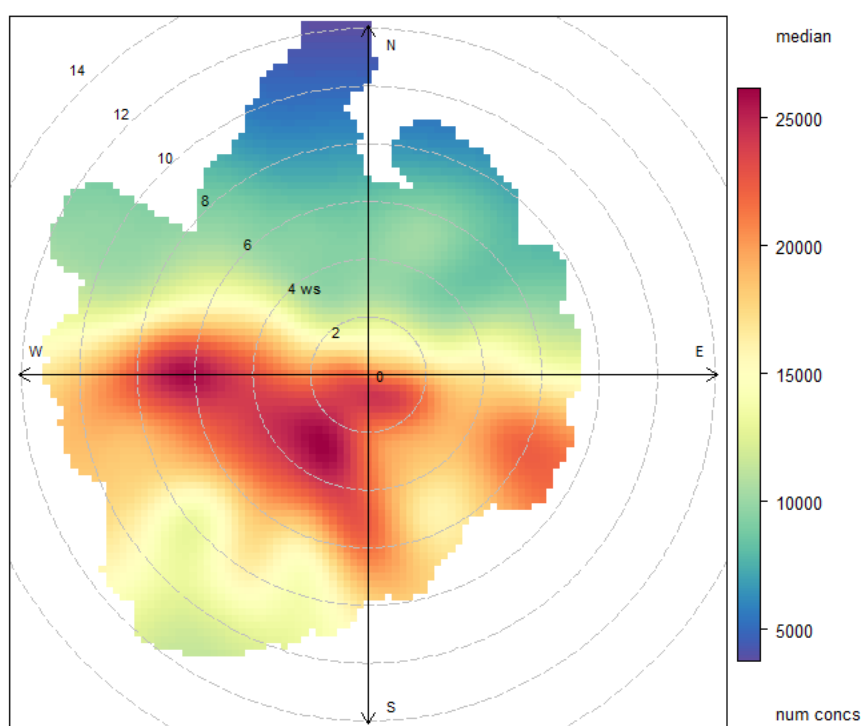


Figure 4-14 Wind rose against number concentrations at Marylebone Road in 2015. Lowest concentrations are recorded when the wind blows from N/NW.

The TSI 3022A is an old model that has been discontinued by TSI. Currently in the network there is one fully operational CPC at North Kensington. A Technical Specification is being produced by CEN TC 264 WG 32 for CPC instruments (see Section 5.2.2 for details); therefore new CPCs will be purchased in the near future to replace this old model in the network.

4.4.2 Particle size distributions

The SMPS instruments generate particle number size spectra between 16 nm and 605 nm. The annual data captures for the SMPS instruments during 2015 were 74%, 83% and 89% respectively for Harwell, North Kensington and Marylebone Road.

The reasons for the main data gaps were:

- **Harwell:** The instrument was removed for service and calibration on 3 February and reinstalled on site on 24 February. In August the CPC showed low concentrations because of a laser failure and was sent to TSI for repair; it was re-installed on 11 September.
- **North Kensington:** Instrument was removed for calibration at NPL on 4 February and was reinstalled on site on 23 February. The gap between 25 June and 28 July is due to a pump failure in the CPC.
- **Marylebone Road:** Instrument removed for calibration at NPL on 4 February and was reinstalled on site on 23 February. No major problems during the rest of the year.

The production of data from SMPS instruments is a complicated process, summarised schematically in Figure 4-15. 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 4-16. The overall effect of the two corrections is to increase the particle number counts at smaller sizes and to increase the total particle count.⁸

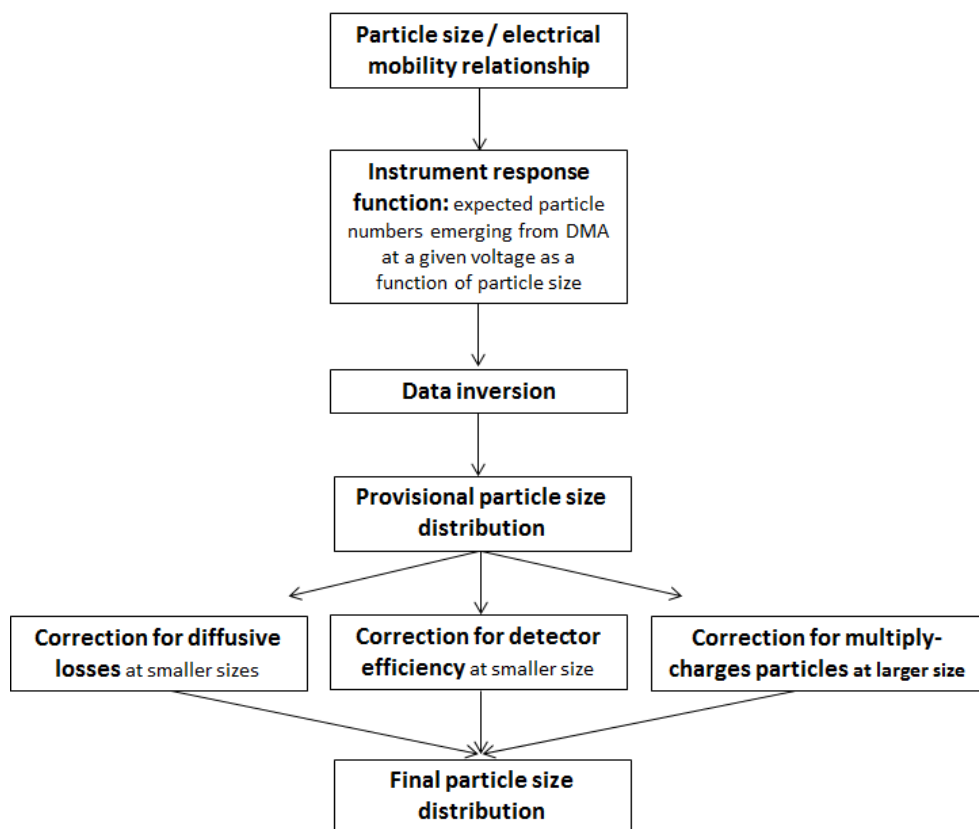


Figure 4-15 Schematic of the internal data processing of SMPS instrument in the Network

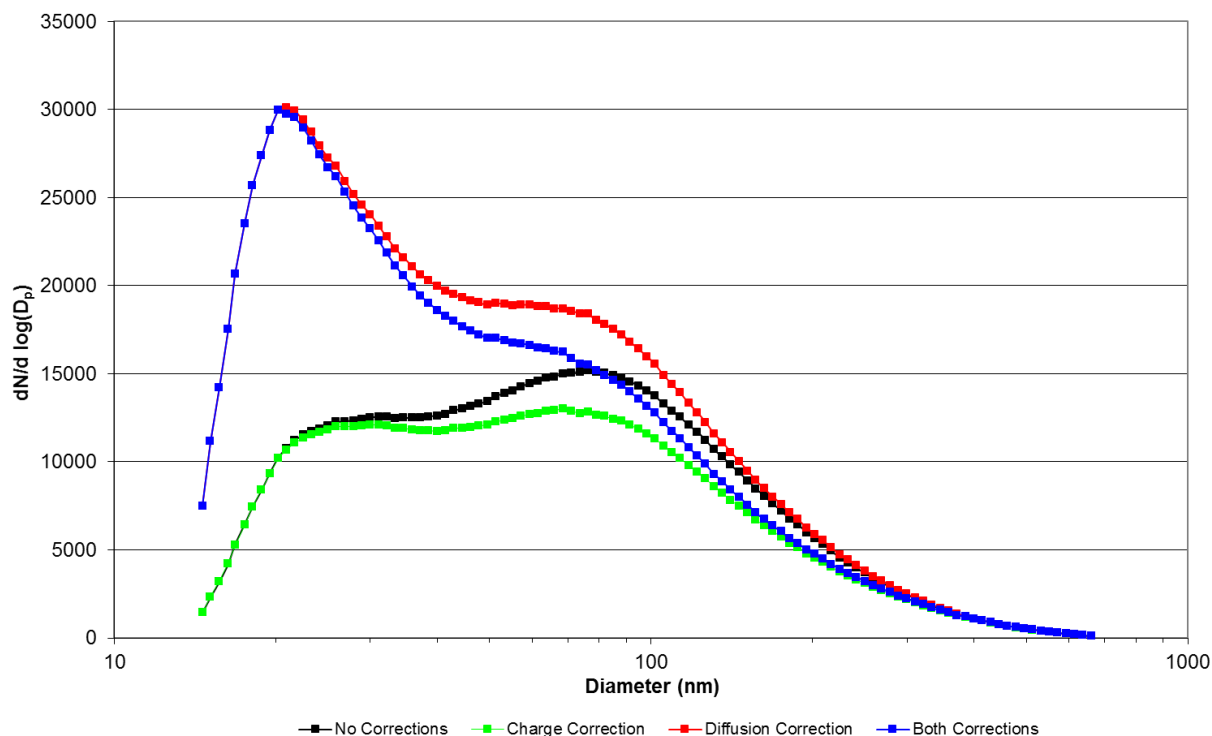


Figure 4-16 Effect of the multiple charge, the diffusion loss and their combined correction in the SMPS size spectrum

The counts in each particle size bin measured during 2015 are presented as monthly averages in the left-hand panels of Figure 4-17 and as an annual average in the right-panel.

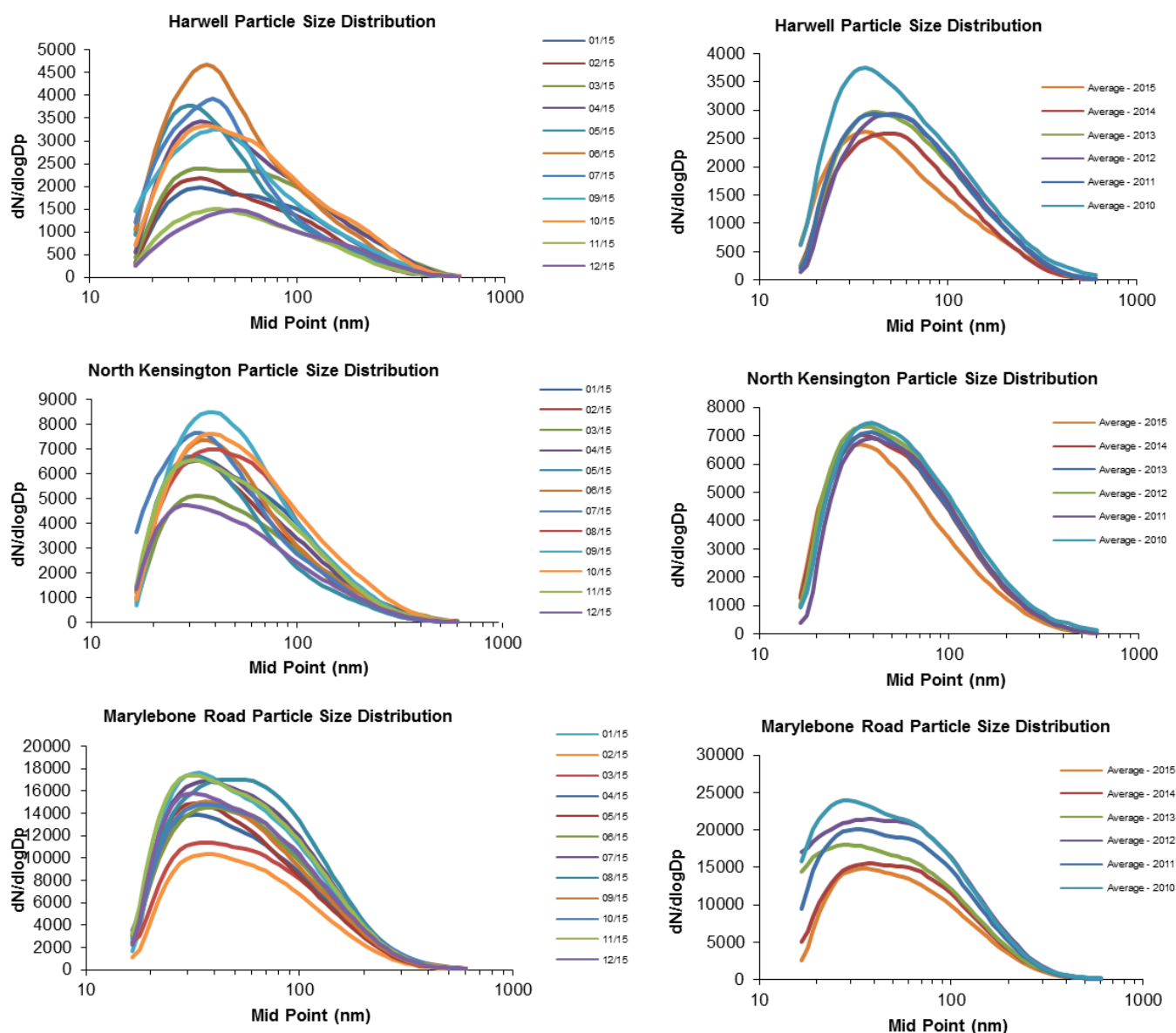


Figure 4-17 Monthly averaged particle size distributions at the Network sites during 2015 [left-hand panels] and comparison of the 2010, 2011, 2012, 2013, 2014 and 2015 annual-averaged size distributions [right-hand panels]

4.4.3 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 were used as calibration aerosols.

Experimental

The sites' SMPS units (consisting of TSI classifier 3080 and CPC 3775) were transported to NPL without their respective nuclear source (neutraliser). An in-house neutraliser (TSI 3077A) was therefore

shared with all SMPS units. The configuration used is shown in Figure 4-20. 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 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.

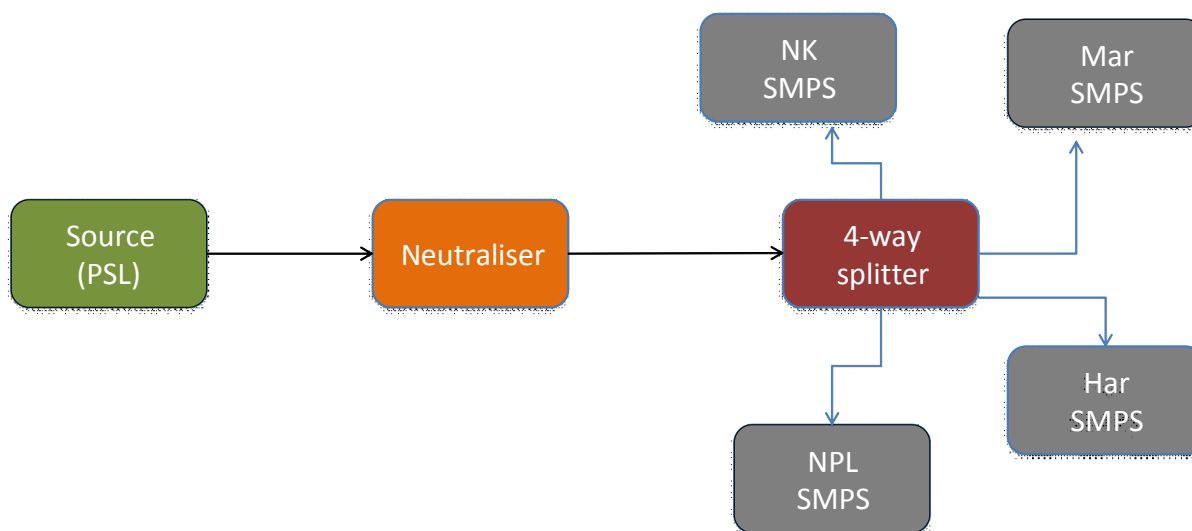


Figure 4-20 Schematic showing the parallel sampling of the four SMPS when connected to a flow splitter and fed with a single particle source (PSL) or the broader size range of the CAST (soot), conditioned with a single neutraliser.

Results and Discussion

In Table 4-7 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.

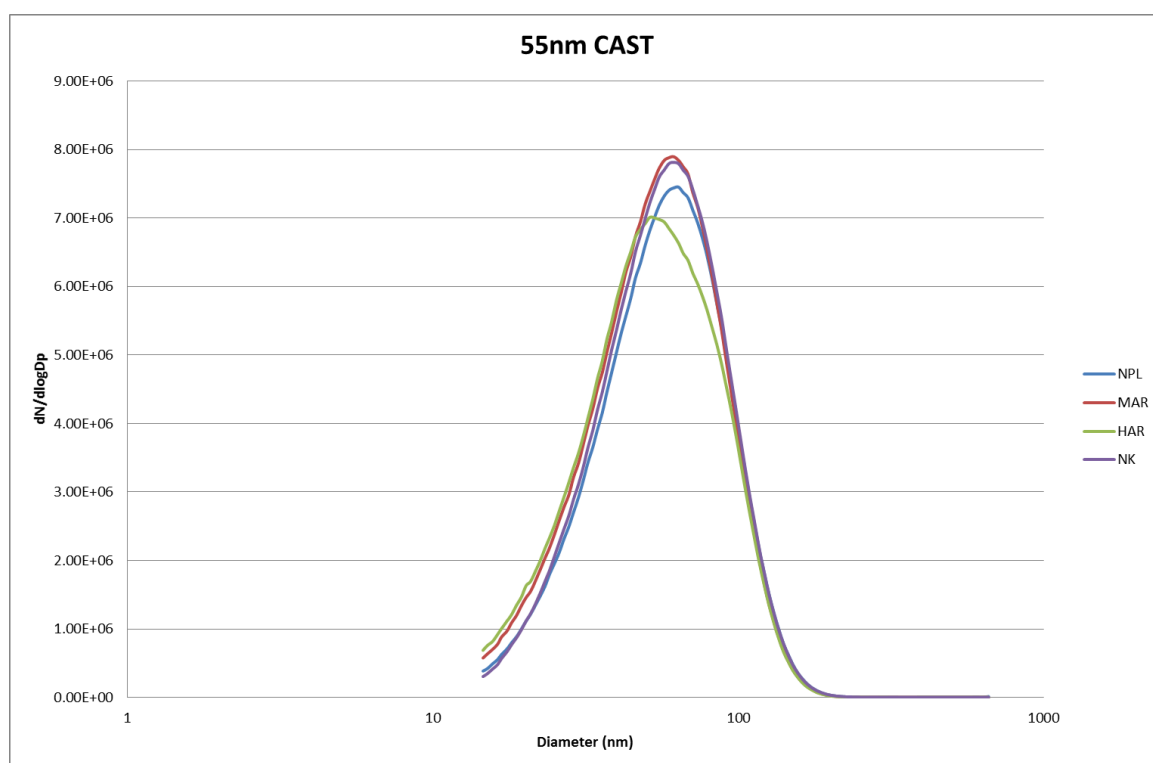
Figures 4-21 and 4-22 show the size distributions recorded for a 55nm single modal CAST input and a Bi-modal CAST input respectively.

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. The results for broad size distributions generally showed good agreement at the $\pm 5\%$ level for each size bin, $\pm 10\%$ 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 4-7 Comparison of SMPS measured distributions with polystyrene latex (PSL) nominal values.

		PSL				
		41	60	92	125	203
		± 4	± 4	± 3	± 3	± 5
Site		nm	nm	nm	nm	nm
Mar	Geometric mean	41.5	64.0	89.9	124.5	197.9
	Geometric st. dev.	1.11	1.08	1.07	1.05	1.05
Har	Geometric mean	41.4	63.8	89.6	124.0	197.6
	Geometric st. dev.	1.11	1.08	1.07	1.06	1.05
NK	Geometric mean	42.9	65.0	91.2	126.0	200.5
	Geometric st. dev.	1.11	1.07	1.06	1.06	1.05
Mean						
2015		41.9	64.3	90.2	124.8	198.7
Mean						
2014		42.0	64.1	90.2	124.8	199.4

**Figure 4-21 Graph showing the particle size distributions recorded from a nominally 55nm diameter CAST soot input**

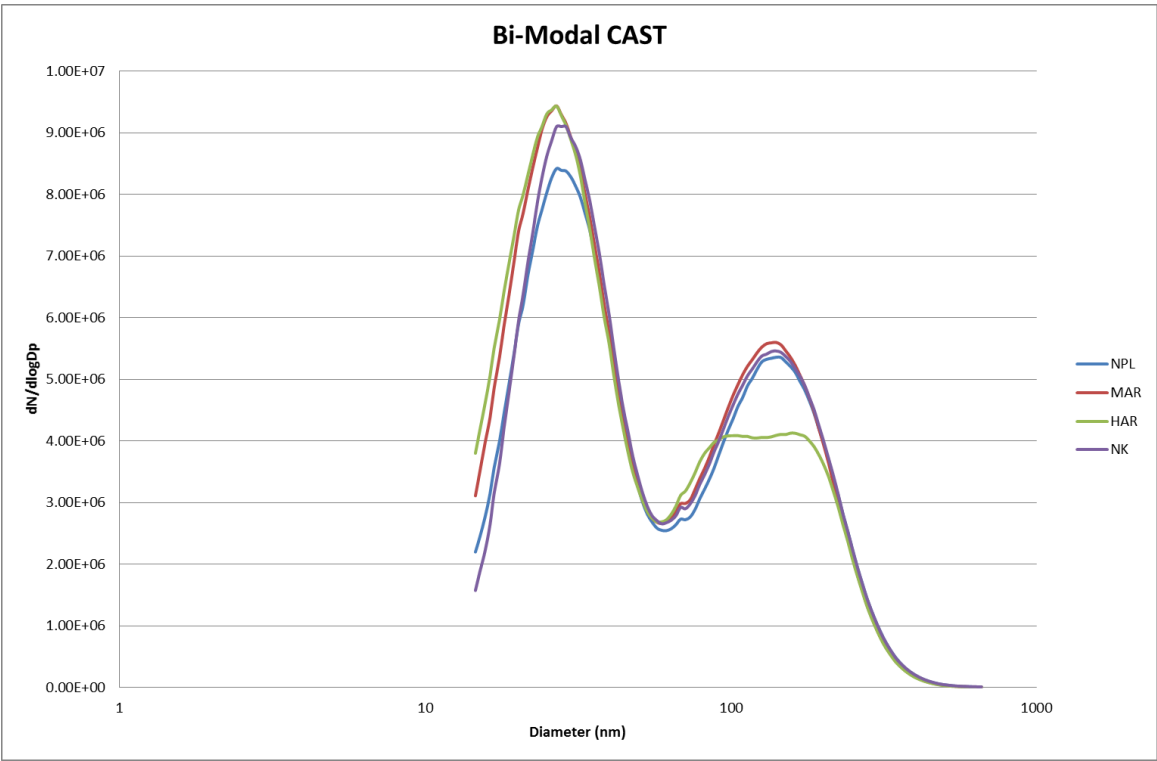


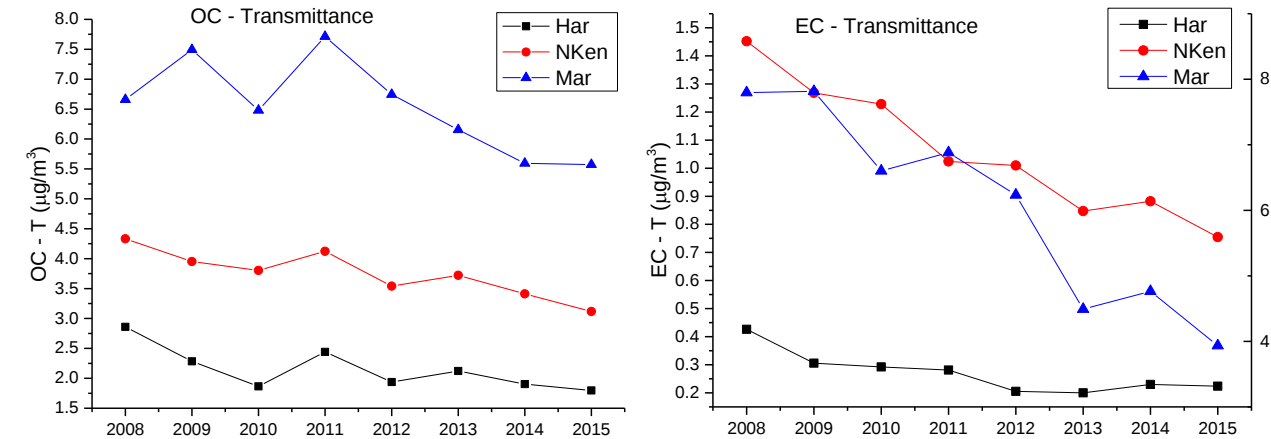
Figure 4-22 Graph showing the particle size distributions recorded from a Bi-modal CAST soot input

4.5 LONG TERM TRENDS

4.5.1 Carbon measurements

Figure 4-18 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.



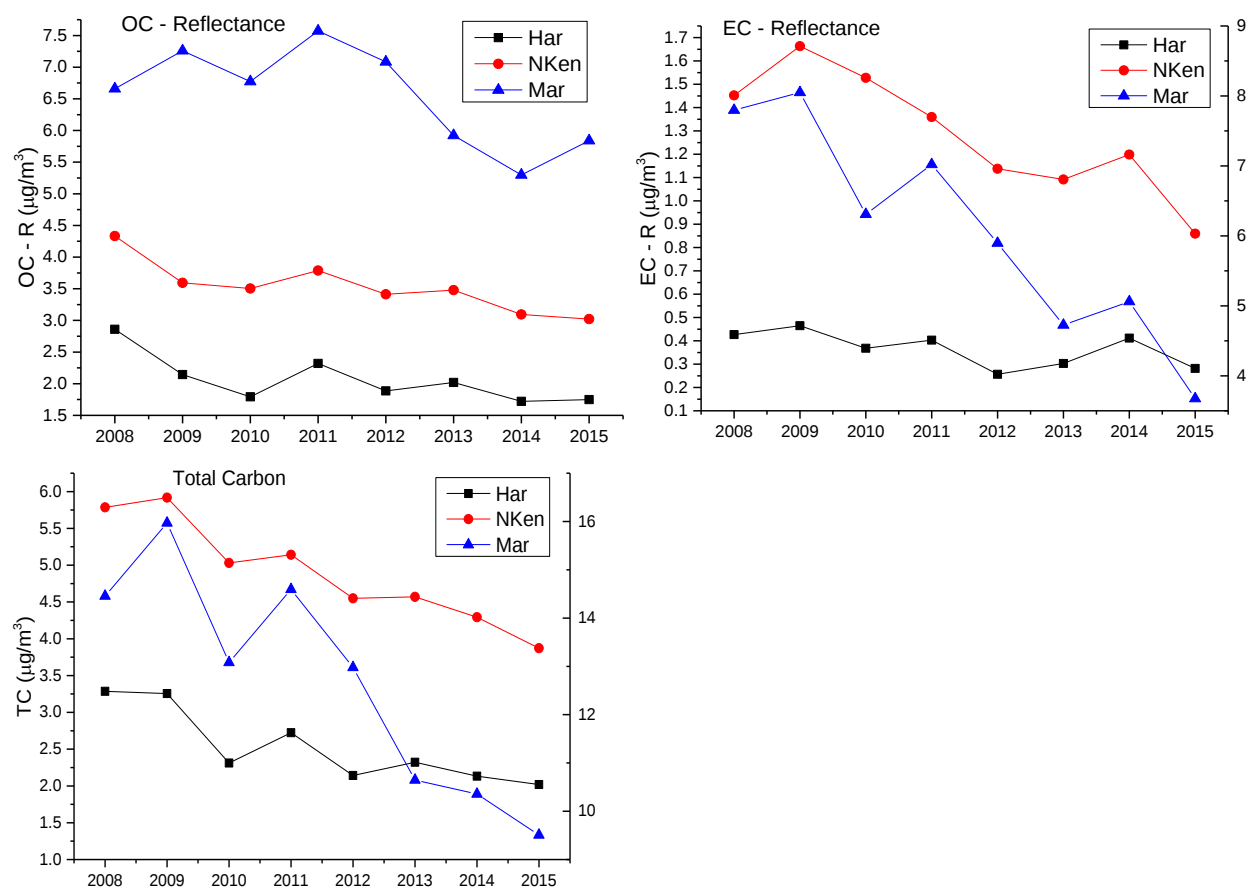


Figure 4-18 Annual trends for OC/EC/TC measurements. EC and TC values for Marylebone Road are shown on the right-hand axis

Figure 4-19 shows the annual Black Carbon and Elemental Carbon concentrations along with the average daily traffic flow past the site.

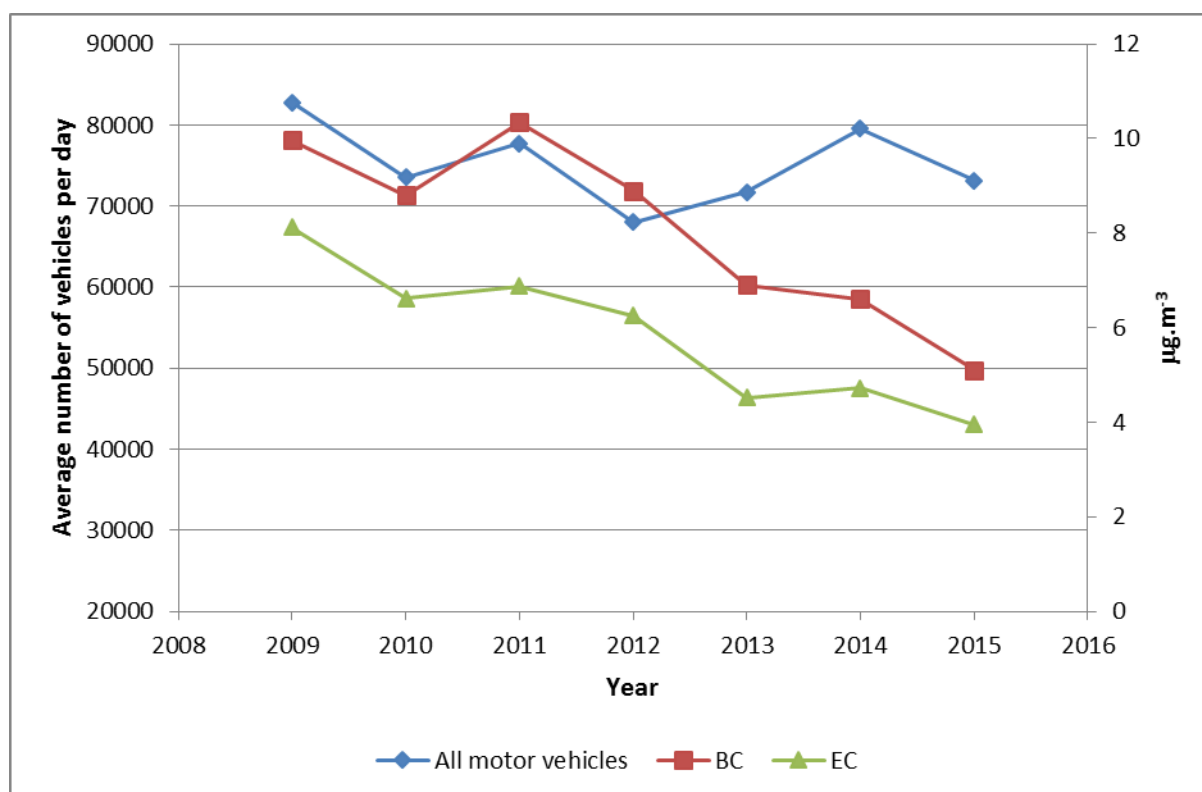


Figure 4-19 Annual Average Black Carbon, Elemental Carbon and Motor Vehicles per day at Marylebone Road for the period 2009 – 2015

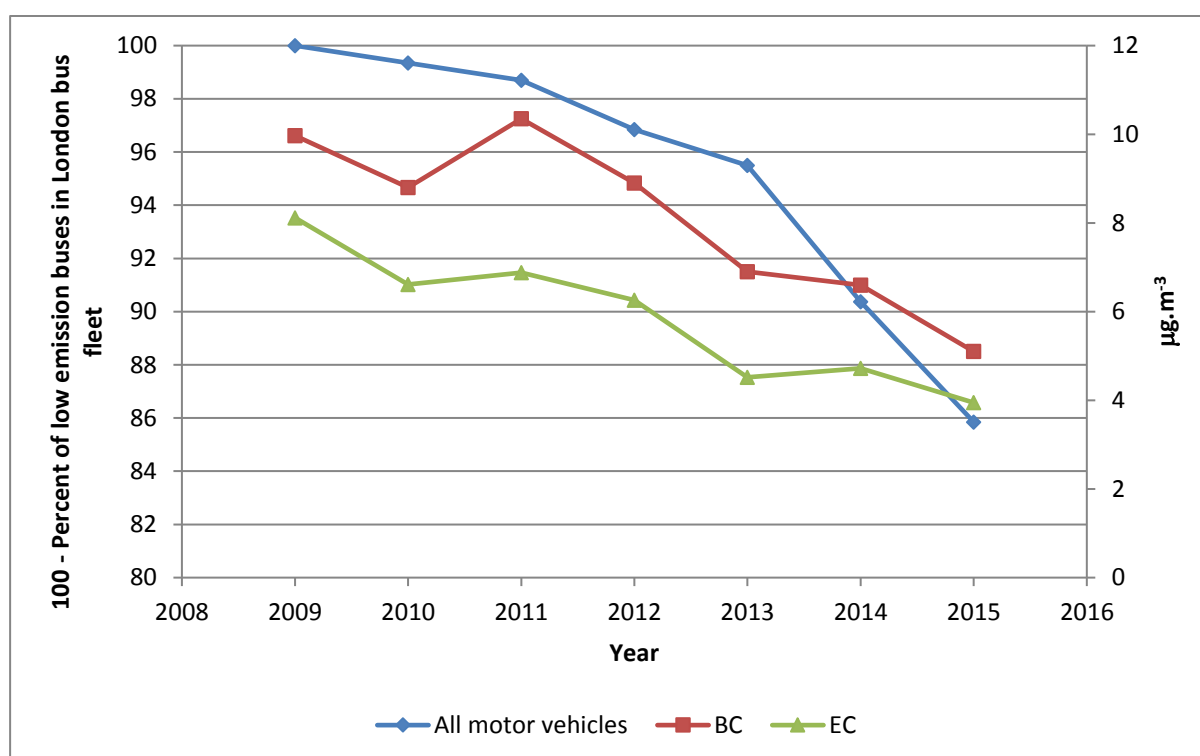
It can be seen that the changes in Black Carbon and Elemental Carbon concentrations follow changes in the total traffic flow for the years 2009 to 2012, but not for 2013 to 2015, which would indicate that the emissions per vehicle have reduced over the last 3 years. The drop in emissions per vehicle type may be linked to the increased proportion of low emission buses (hybrid and fuel cell / hybrid) in the London bus fleet.⁹ Table 4-2 shows the composition of the London bus fleet over the period 2010 to 2015. The bottom row of the table shows the percentage of low emission buses, which is a combination of the hybrid and fuel cell / hybrid bus numbers. 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, which would have also reduced Black Carbon emissions.

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 4-20 is Figure 4-19 replotted with the number of motor vehicles per day passing the Marylebone Road monitoring site replaced by [100 – percentage of low emission buses in the London bus fleet].

Table 4-2 Composition of London bus fleet, 2010 to 2015⁹

Bus Type	Drive train type	Number of buses					
		2010	2011	2012	2013	2014	2015
New Routemaster	Hybrid	0	0	5	8	168	432
Routemaster	Diesel	18	18	19	20	19	19
Artic	Diesel	320	260	0	0	0	0
Single deck	Diesel	2,676	2,670	2,661	2,608	2,606	2,662
	Fuel Cell/Hybrid	0	5	5	5	8	8
	Hybrid	27	27	33	28	23	23
	Electric	0	0	0	0	2	8
Double deck	Diesel	5,554	5,487	5,787	5,696	5,296	5,026
	Hybrid	29	79	233	352	643	799
TOTAL		8,624	8,546	8,743	8,717	8,765	8977
% low emission		0.65	1.30	3.16	4.51	9.63	14.15

**Figure 4-20 Annual Average Black Carbon, Elemental Carbon and 100 – percentage of low emission buses in the London bus fleet for the period 2009 – 2015.**

Assuming that the mix of buses passing the Marylebone Road site is representative of the whole London bus fleet, it is likely that the increase in low emission buses and changes to the LEZ from 2012, have led to reduced Black Carbon and Elemental Carbon concentrations.

4.5.2 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. After 2011 a general decrease can be observed at all sites.

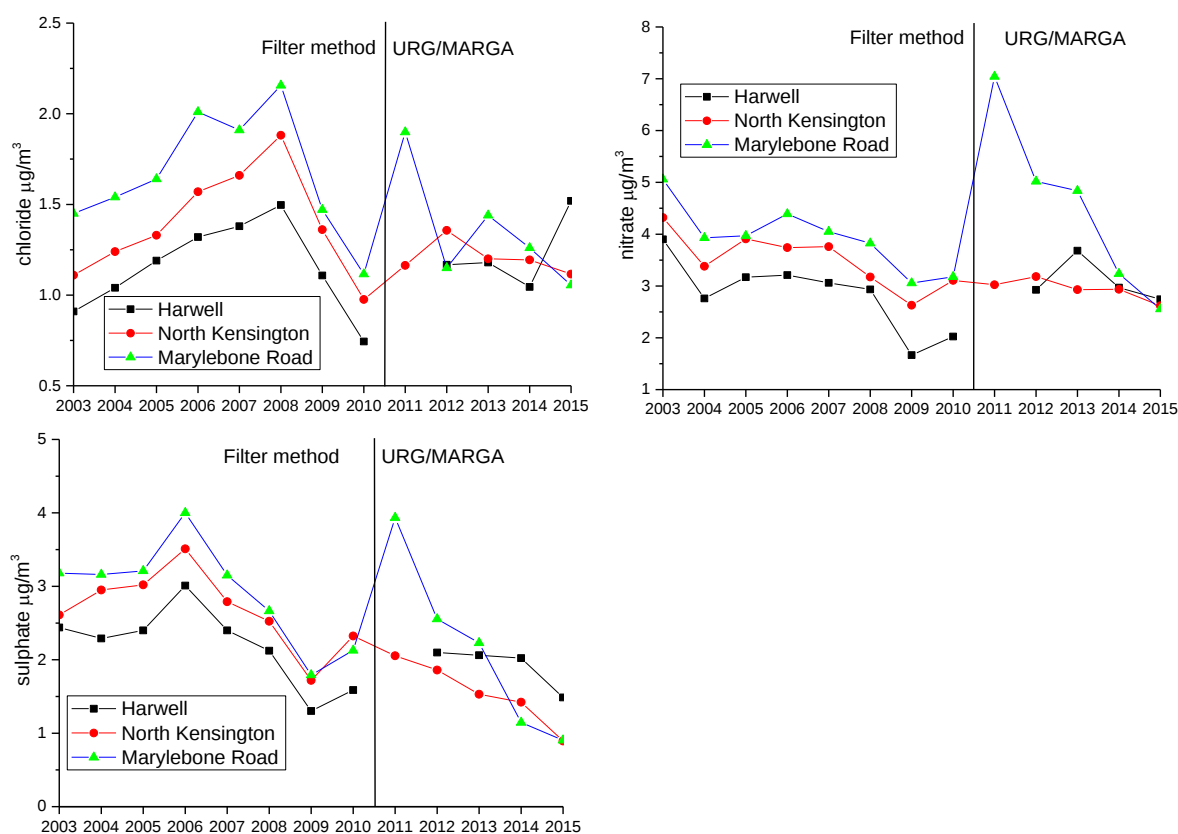


Figure 4-21 Anion long-term annual trends (clockwise chloride, nitrate and sulphate). The 2012 - 2015 data for Harwell have been derived from the MARGA measurements.

4.5.3 Particle number concentrations

Figure 4-22 shows long-term annual trends for CPC measurements at all sites. The averages for the Marylebone Road and Harwell sites have been calculated using the whole datasets. 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 2007¹¹ 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 2007¹³ 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.

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.

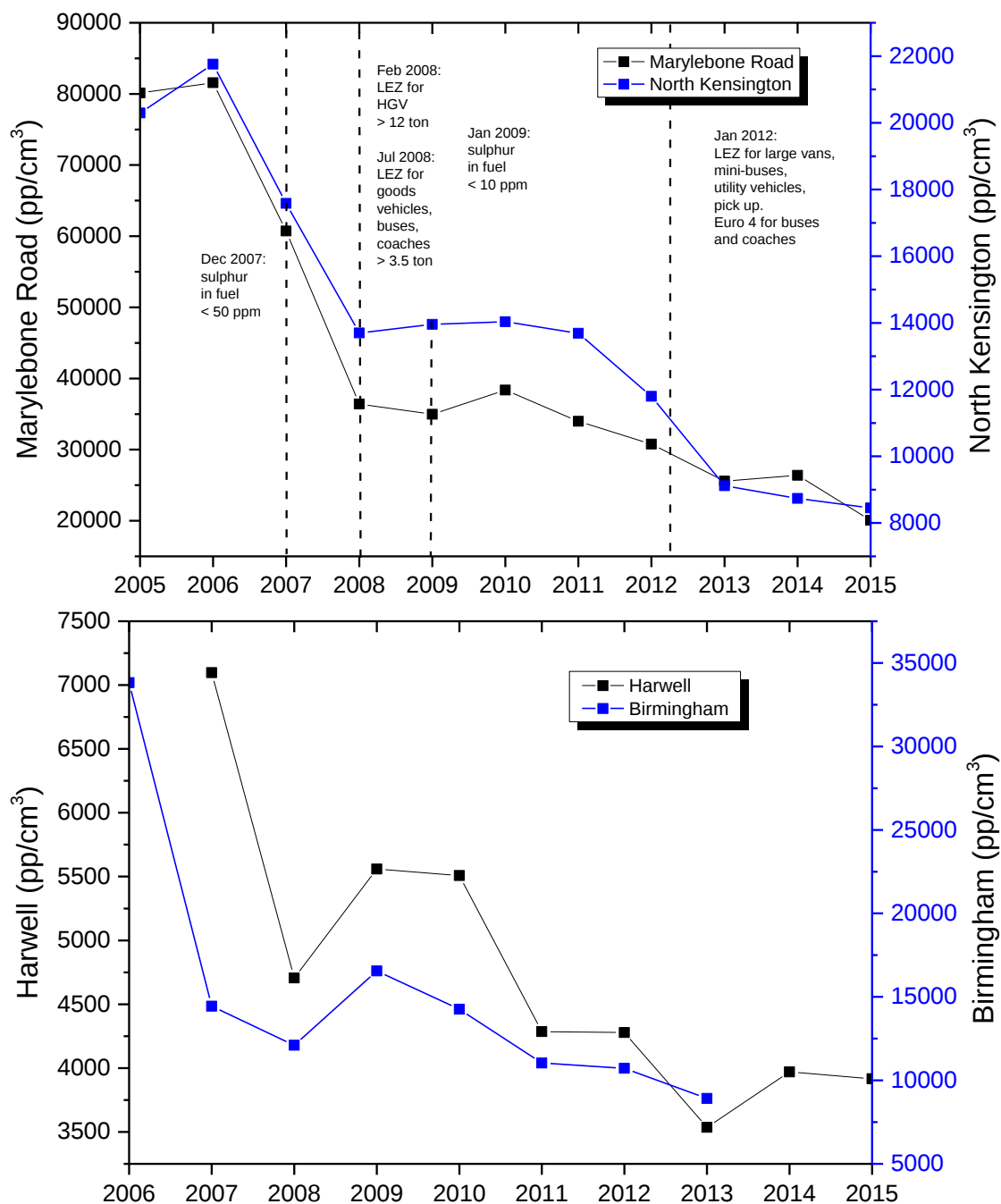


Figure 4-22 CPC long-term annual trends at all sites (no data are available in 2014-2015 for the Birmingham site)

Long-term monthly trends are shown in Figure 4-23 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).

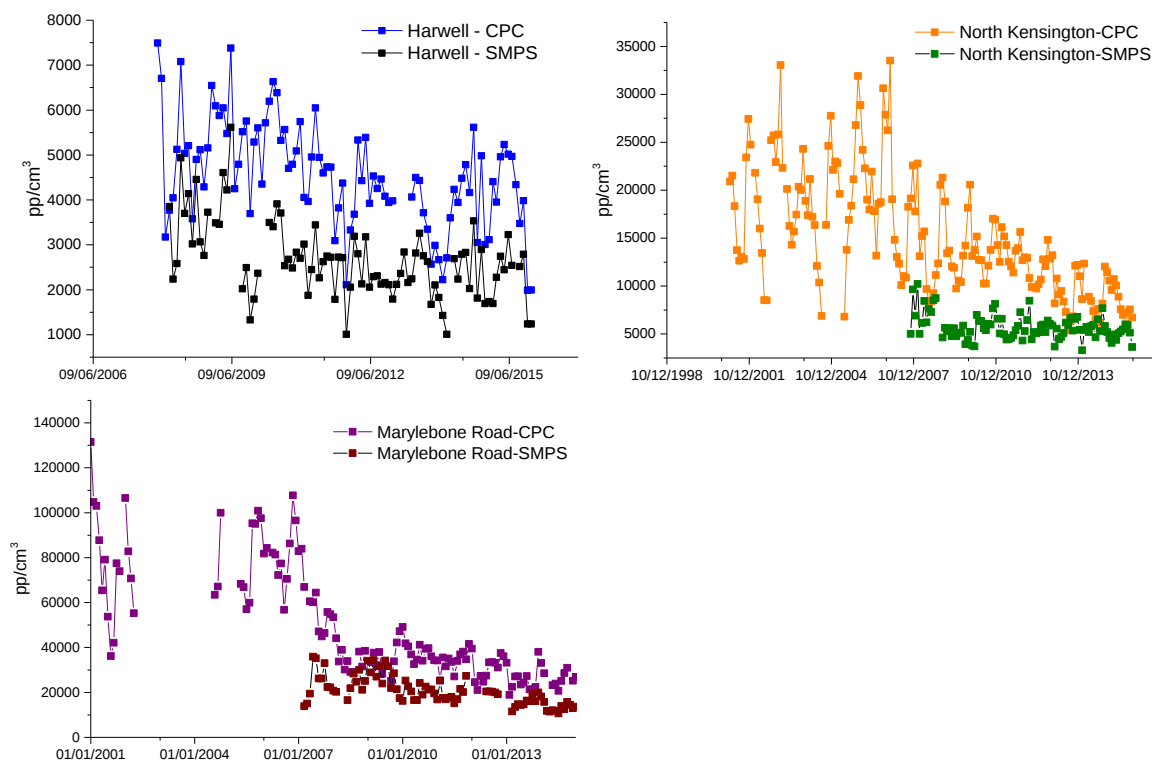


Figure 4-23 CPC and SMPS long-term monthly trends at all Network sites

4.6 DIURNAL, WEEKLY AND MONTHLY PROFILES

Diurnal, weekly and monthly profiles have been plotted for the hourly concentrations using the Openair tools.^{14, 15, 16}

4.6.1 Profiles for anion and cation species

The good correlation between SO_4^{2-} , NO_3^- and NH_4^+ in Figure 4-25 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.

Figure 4-25 shows the profiles for Cl^- , Na^+ and Mg^+ concentrations at North Kensington and Marylebone Road. There is a very good correlation between these three species, suggesting they derive from the same source, identifiable with sea salt.

Ca^{2+} profiles at both sites in Figure 4-26 show values characteristic of traffic contribution, possibly re-suspension of crustal material from road surfaces

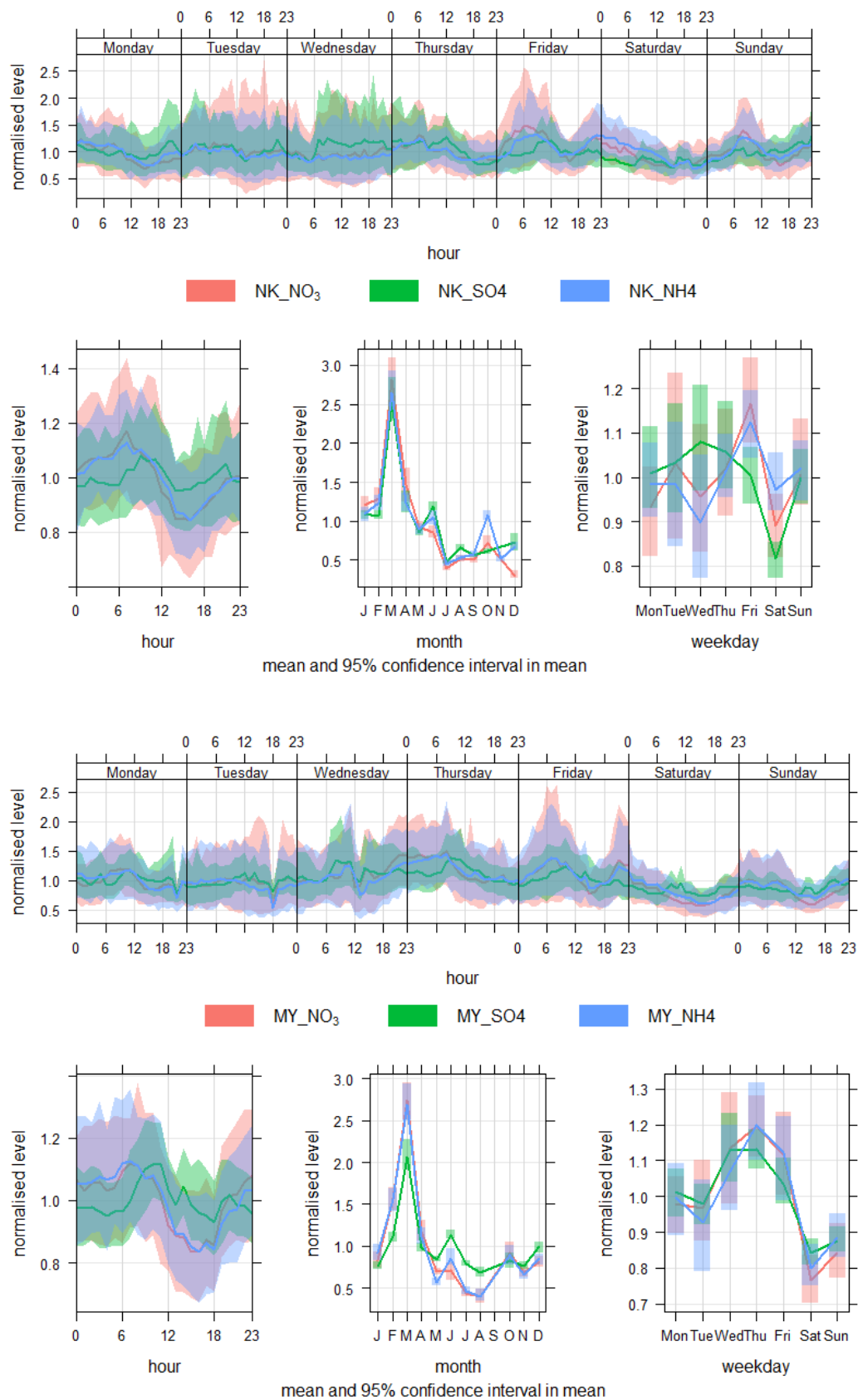


Figure 4-24 Diurnal, weekly and monthly profiles for NO_3^- , SO_4^{2-} and NH_4^+ during 2015 at North Kensington (top) and Marylebone Road (bottom)

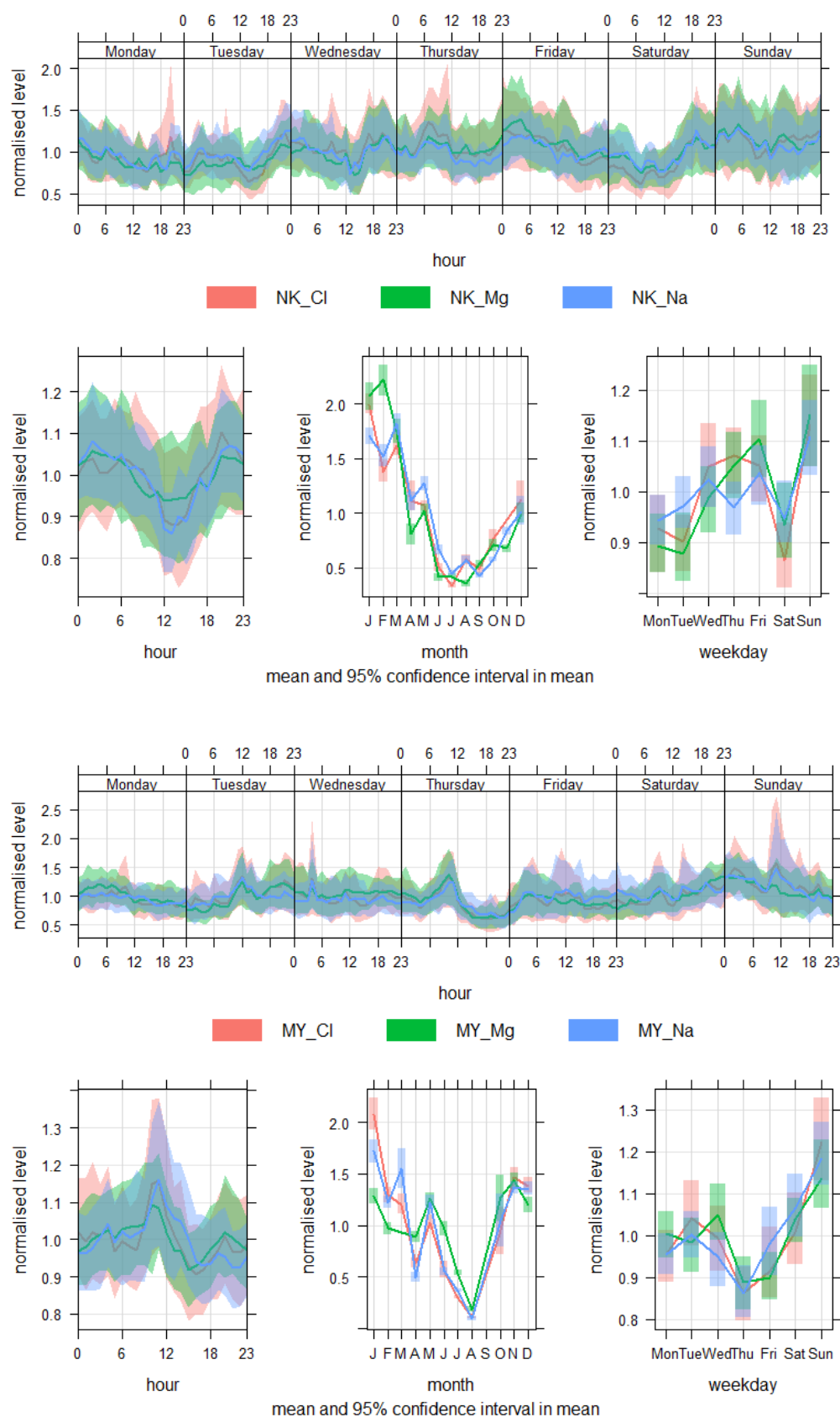


Figure 4-25 Diurnal, weekly and monthly profiles for Cl⁻, Na⁺ and Mg²⁺ concentrations during 2015 at North Kensington (top) and Marylebone Road (bottom).

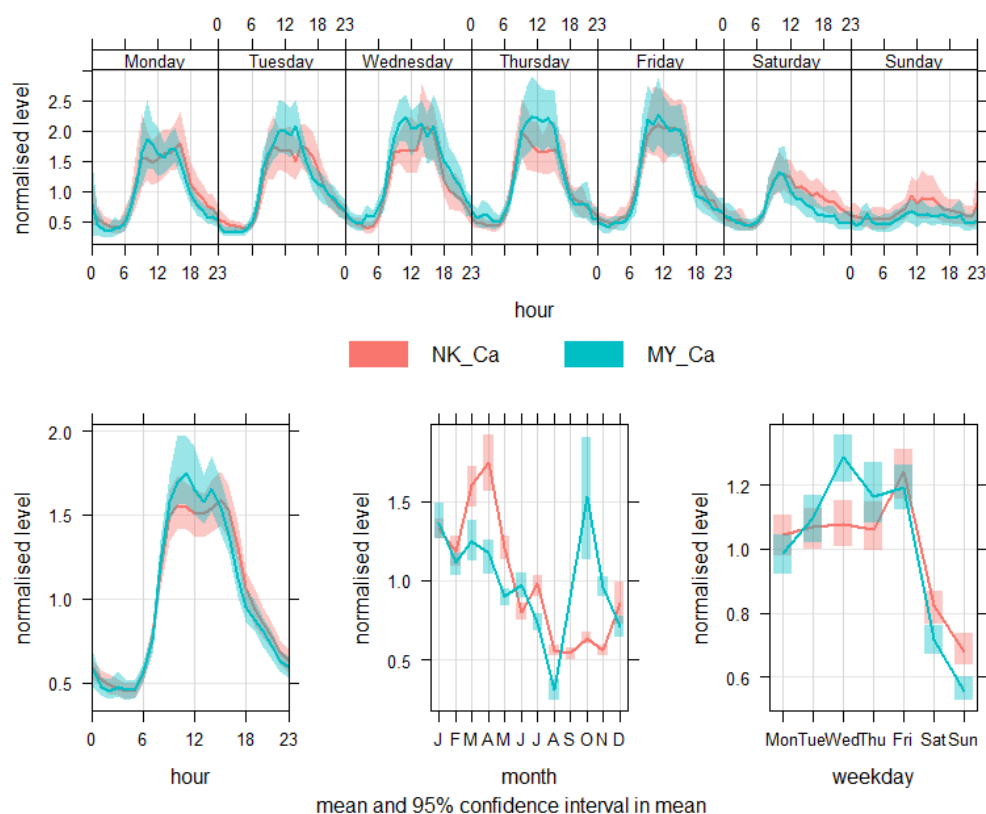


Figure 4-26 Diurnal, weekly and monthly profiles for Ca^{2+} during 2015 at North Kensington and Marylebone Road.

4.6.2 Profile for number concentrations

At rural sites like Harwell, the diurnal profile is similar for all days of the week (see Figure 4-27 (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.

At all sites the concentrations in both November and December were particularly low compared to previous years, probably due to the exceptionally high temperatures during these months (about 12°C on average).

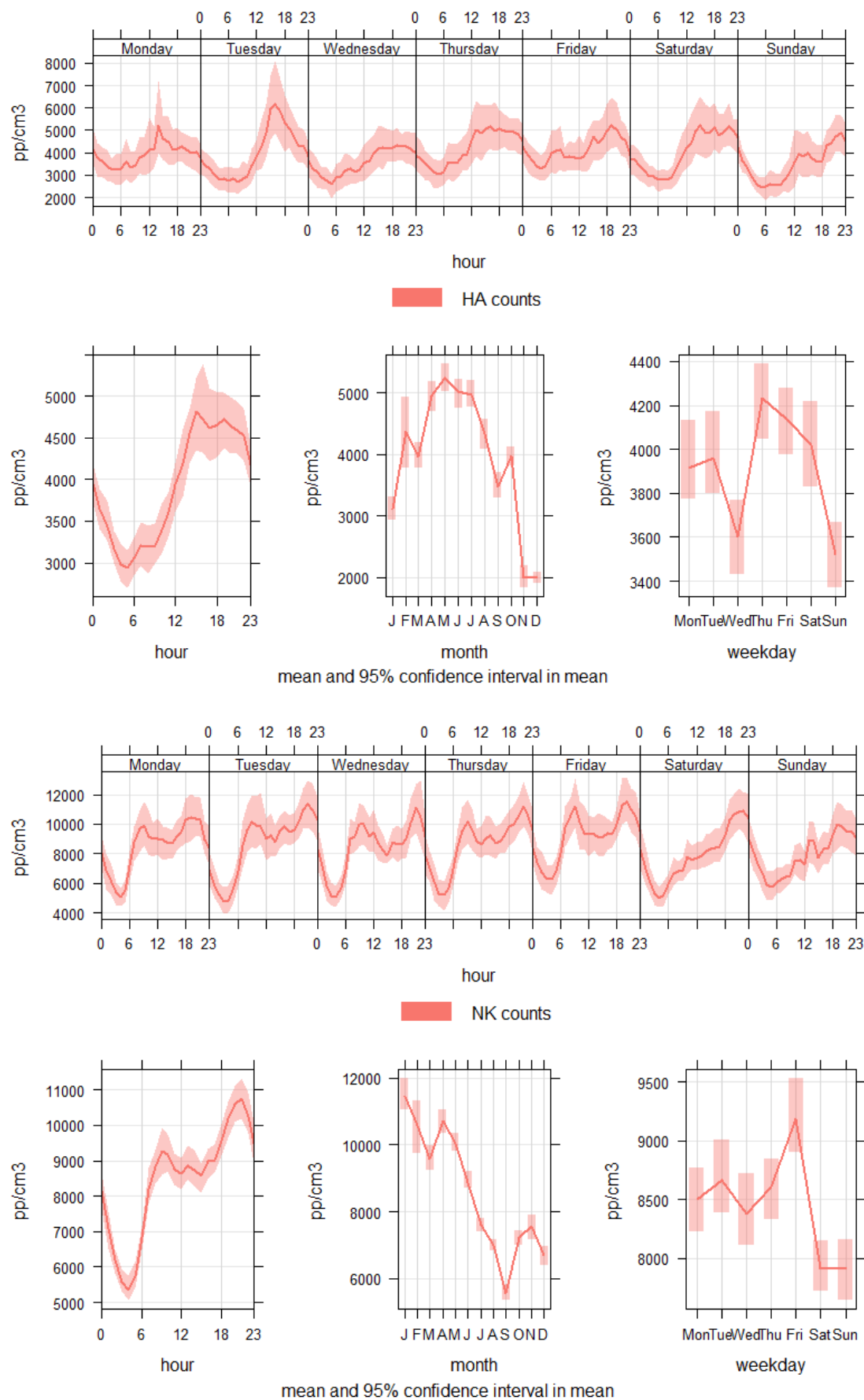


Figure 4-27 Diurnal, weekly and monthly profiles for number concentrations in 2015 at Harwell (top) and North Kensington (bottom)

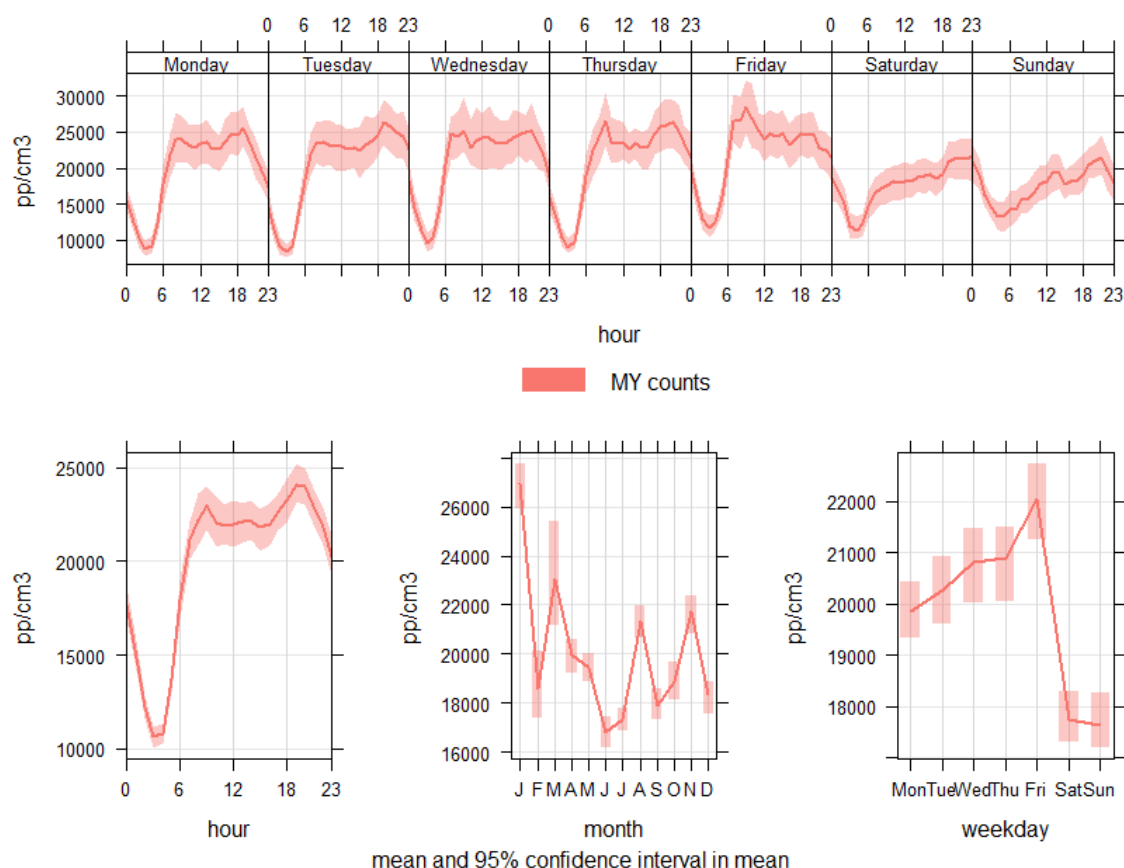


Figure 4-28 Diurnal, weekly and monthly profiles for number concentrations in 2015 at Marylebone Road

4.7 METEOROLOGICAL DATA

Although not a formal part of this measurement programme, meteorological data have been collated from the measurements made at Rochester as part of this network. The data capture for the meteorological masts during 2014 was 99%. Wind roses are shown in Annex 1.

5 UPDATE ON WIDER POLICY AND RESEARCH CONTEXT

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 where the combination of long range transport of PM from mainland Europe, combined with dense urban and vehicular sources lead to some of the highest concentrations of PM mass measured in the UK. An understanding of the chemical composition is therefore vital to understand these diverse sources of PM and the relative 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. The promotion of cleaner vehicles (taxis and buses) on these routes and across London will also require assessment using particle number concentrations. Other significant packages include the Mayor's Air Quality Fund, Low Emission Neighbourhoods, £1bn investment in cycling infrastructure and an Ultra Low Emission Vehicle Delivery Plan. Looking ahead, the London Mayor will also introduce the world's first Ultra Low Emission Zone (ULEZ) in September 2020 (an earlier date of 2019 is currently being proposed through consultation). This scheme will set new emissions standards for vehicles driving in central London; allowing only the newest, cleanest diesel vehicles in free of charge while non-compliant vehicles will face a charge. Assessing changes in PM concentrations due to these policies requires a detailed analysis using the chemical composition measurements made using this network at sites in this network.

5.1.2 Research Council Activities in London

ClearfLo was a large NERC-funded project involving 11 UK partners. Its ambition was 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 were undertaken between 2010 and 2013, complemented by more detailed Intensive Observation Periods (IOPs) during January/February and July/August 2012. The aims of the IOPs were to (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 was based on the existing measurements made for the PM network and AURN. A selection of the papers published which have relied on this network are shown below:

- Bohnenstengel, S.I., et al., Meteorology, Air Quality, and Health in London the ClearfLo Project. Bulletin of the American Meteorological Society, 2015. 96(5): p. 779-804.
- Ots, R., et al., Simulating secondary organic aerosol from missing diesel-related intermediate-volatility organic compound emissions during the Clean Air for London (ClearfLo) campaign. Atmospheric Chemistry and Physics, 2016. 16(10): p. 6453-6473.
- Visser, S., et al., Advanced source apportionment of size-resolved trace elements at multiple sites in London during winter. Atmospheric Chemistry and Physics, 2015. 15(19): p. 11291-11309.
- Visser, S., et al., Kerb and urban increment of highly time-resolved trace elements in PM₁₀, PM_{2.5} and PM_{1.0} winter aerosol in London during ClearfLo 2012. Atmospheric Chemistry and Physics, 2015. 15(5): p. 2367-2386.
- Young, D.E., et al., Investigating the annual behaviour of submicron secondary inorganic and organic aerosols in London. Atmospheric Chemistry and Physics, 2015. 15(11): p. 6351-6366.
- Young, D.E., et al., Investigating a two-component model of solid fuel organic aerosol in London: processes, PM₁ contributions, and seasonality. Atmospheric Chemistry and Physics, 2015. 15(5): p. 2429-2443.

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. 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 and in Wales during 2015 and 2016. A selection of key papers from this programme are listed below:

- Atkinson, R.W., et al., Short-term exposure to traffic-related air pollution and daily mortality in London, UK. *Journal of Exposure Science and Environmental Epidemiology*, 2016. 26(2): p. 125-132.
- Atkinson, R.W., et al., Short-term associations between particle oxidative potential and daily mortality and hospital admissions in London. *Int J Hyg Environ Health*, 2016. 219(6): p. 566-72.
- Beddows, D.C.S., et al., Receptor modelling of both particle composition and size distribution from a background site in London, UK. *Atmospheric Chemistry and Physics*, 2015. 15(17): p. 10107-10125.

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 (now moved to Chilbolton), 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, appears to be effectively on hold.

There was an associated development, with the publication of Commission Directive (EU) 2015/1480 “amending several annexes to Directives 2004/107/EC and 2008/50/EC, laying down the rules concerning reference methods, data validation and location of sampling points for the assessment of ambient air quality”. These are generally technical changes bringing references to EN standards up to date. The main change relating to sampling points is the inclusion of a requirement to have “at least 1 station in areas where exposure of the population to the highest concentrations of ozone is likely to occur”.

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

2015 has seen considerable CEN activity in the areas covered by this Network.

CEN TC 264 WG 15 published EN 12341:2014, gravimetric reference methods for PM₁₀ and PM_{2.5} (updating and combining EN 12341:1998 and EN 14907:2005), last year. 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 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 is in the process of being upgraded to a full EN standard. The final vote should be in April 2016, with publication by the end of 2016.

The WG plans to update EN 12341:2014 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 CEN/TS 16976 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. The first commercially-available instruments that comply with the specification are expected in 2016.

FprCEN/TS 16976 will be out for voting in Spring 2016. As a TS, only editorial comments and a yes/no/abstain vote are allowed, and it should be published by the end of 2016.

- 2) Standard methods for measuring particle number concentration over more limited size ranges, as used to form size distributions, ie SMPSSs, 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 has been carried out in both areas. The work packages performed were:

- 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 published as an internal CEN report. The WG 35 report has been converted into a scientific paper for publication. The paper is currently in open for interactive public discussion in Atmospheric Measurement Techniques.¹⁷

WP2 Two inter-laboratory comparisons have been performed. The first demonstrated the requirement to perform regular instrument calibrations to ensure satisfactory performance from the thermal / optical method. The second intercomparison showed good agreement between the 4 laboratories.

WP3 Sampling has been 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 is Ion Chromatography.

EUSAAR2 thermal protocol with transmission OCEC split point determination has been adopted as the standard analysis protocol for OCEC PM_{2.5} particulate matter collected on filters. Currently the Network uses the NIOSH transmission protocol. In 2012 NPL analysed filters using both the EUSAAR2 transmission and NIOSH transmission protocols¹⁸ and found that no significant difference could be identified in TC – a reassuring check of the analysis system. As expected, NIOSH gives somewhat lower EC values than EUSAAR II (with correspondingly higher OC values). These differences are of the order of 20% for EC and 5% for OC.

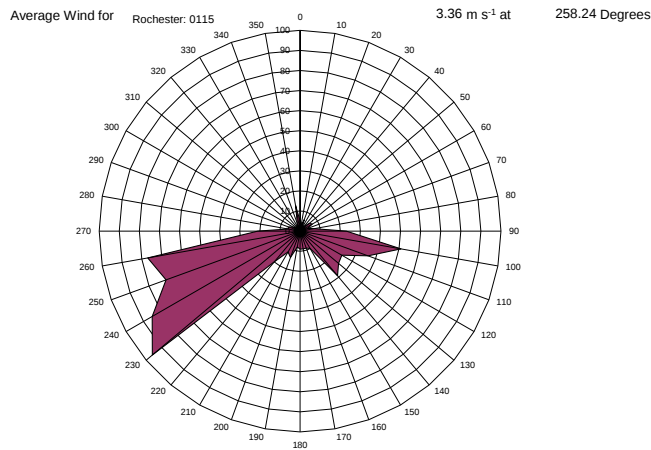
Protocols that have a lower maximum temperature during the inert-gas heating phase, such as the EUSAAR II protocol with a maximum of 650°C, tend to record significantly higher EC values than protocols such as NIOSH, with a maximum of 870°C, with correspondingly less OC, such that the sum of EC and OC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

The final draft of the proposed standard was finalised in May 2015 and sent for CEN enquiry. Suggested changes to the standard were received and have been implemented. The revised standard has been submitted to CEN for formal vote and subsequent publication. Publication is due in late 2016.

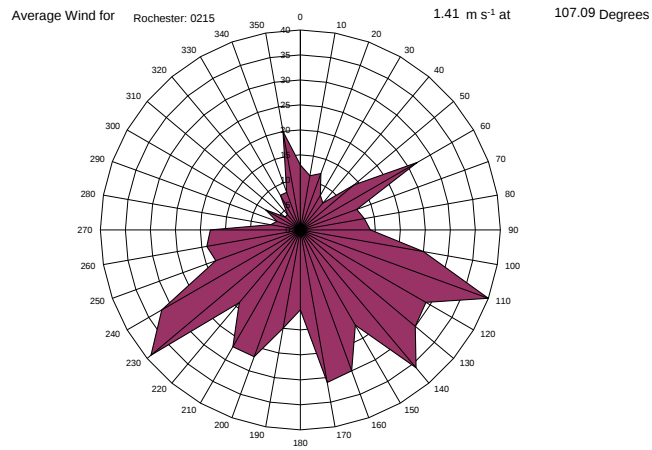
NPL will apply the EUSAAR2 transmission protocol for all filters exposed from 1 January 2016 onwards.

ANNEX 1 WIND ROSES AT ROCHESTER

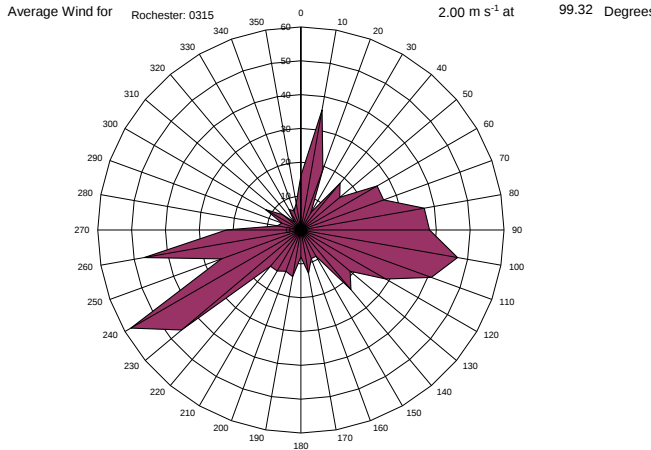
January 2015



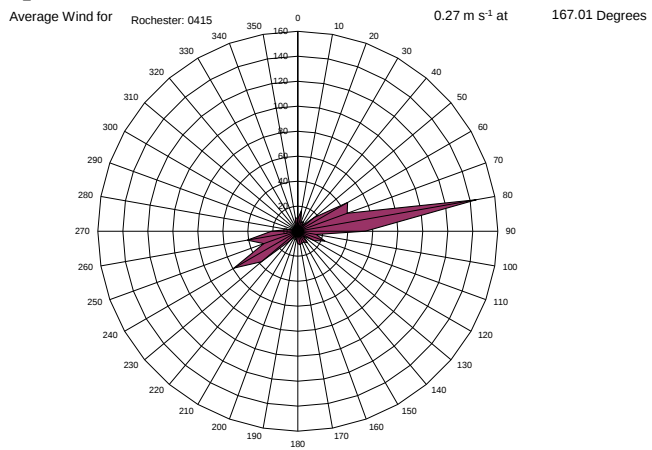
February 2015



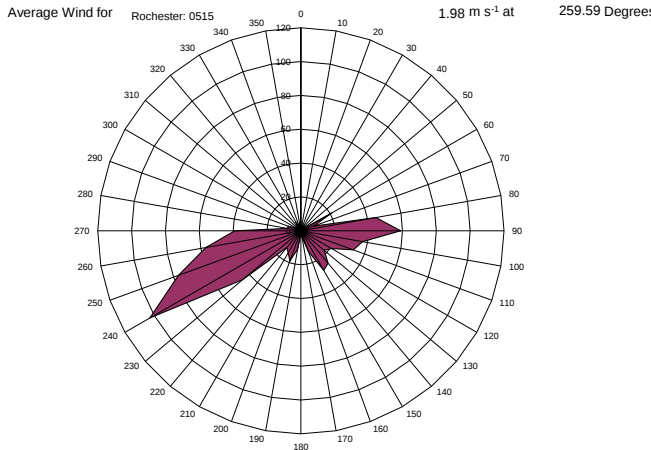
March 2015



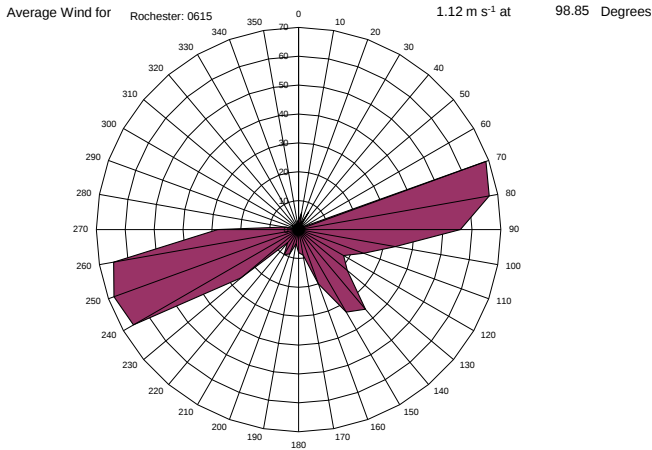
April 2015



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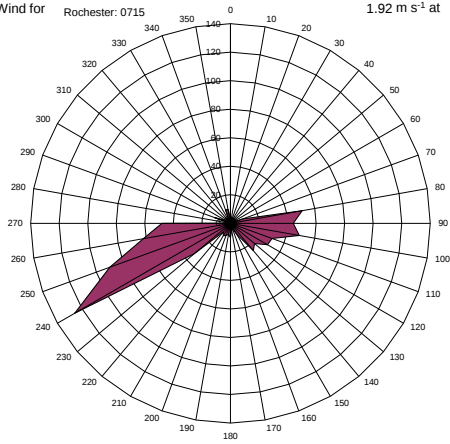


June 2015



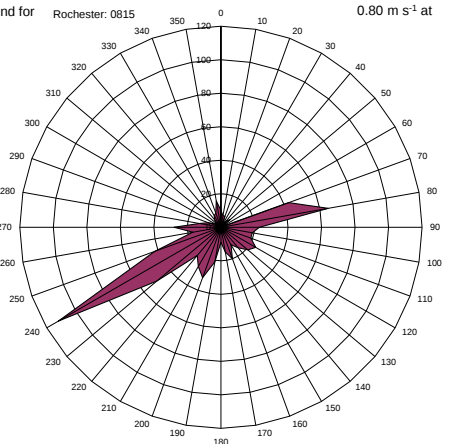
July 2015

Average Wind for Rochester: 0715 1.92 m s⁻¹ at 262.07 Degrees



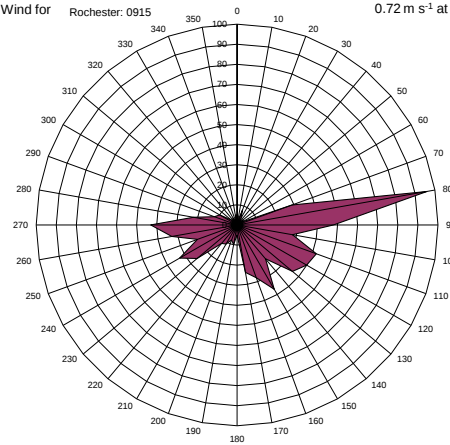
August 2015

Average Wind for Rochester: 0815 0.80 m s⁻¹ at 244.37 Degrees



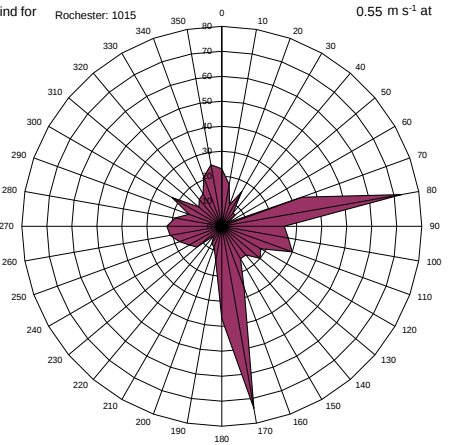
September 2015

Average Wind for Rochester: 0915 0.72 m s⁻¹ at 132.05 Degrees



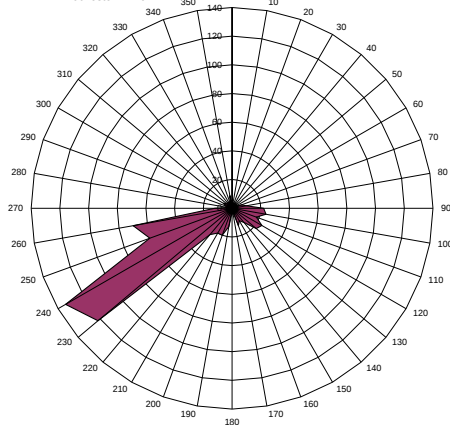
October 2015

Average Wind for Rochester: 1015 0.55 m s⁻¹ at 154.20 Degrees



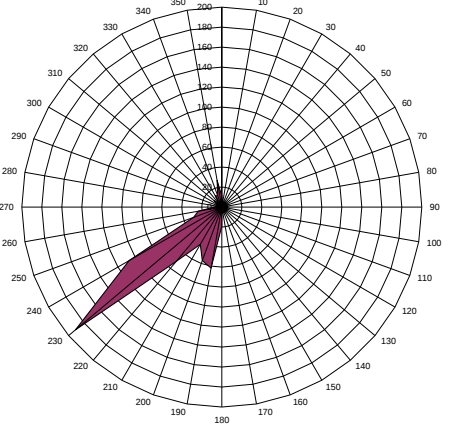
November 2015

Average Wind for Rochester: 1115 4.04 m s⁻¹ at 252.36 Degrees



December 2015

Average Wind for Rochester: 1215 3.80 m s⁻¹ at 224.56 Degrees



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- ¹⁷ Karanasiou, A., Minguillón, M. C., Viana, M., Alastuey, A., Putaud, J.-P., Maenhaut, W., Panteliadis, P., Močnik, G., Favez, O., and Kuhlbusch, T. A. J.: Thermal-optical analysis for the measurement of elemental carbon (EC) and organic carbon (OC) in ambient air a literature review, *Atmos. Meas. Tech. Discuss.*, 8, 9649-9712, doi:10.5194/amtd-8-9649-2015, 2015.
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