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

Annual report 2016

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1 INTRODUCTION

The UK Airborne Particulate Concentrations and Numbers Network 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 2016 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 2016 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 2016 is shown in Table 2-1.

Table 2-1 Network structure in 2016

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
Chilbolton (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	Chilbolton
2	Marylebone Road
3	North Kensington
4	Auchencorth Moss

Figure 2-1 Network sites in 2016

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 were 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 were 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) was 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. Its recommendations for sampling have been included in the CEN Technical Specification for CPC measurements, CEN/TS 16976.

The Harwell site was audited by a group from EUSAAR in November 2007 and a number of recommendations were made, most notably on the sampling inlet and regulating the humidity of the inlet air. New manifolds with PM_1 size selective cyclones were installed for the SMPS and CPC at Harwell and the other Network sites in late 2009 to meet these recommendations. The humidity of the sample air going to both the CPC and SMPS instruments is now controlled and monitored through drying units designed by NPL, which use Nafion driers. Humidity sensors have been installed and are logged by the computers.

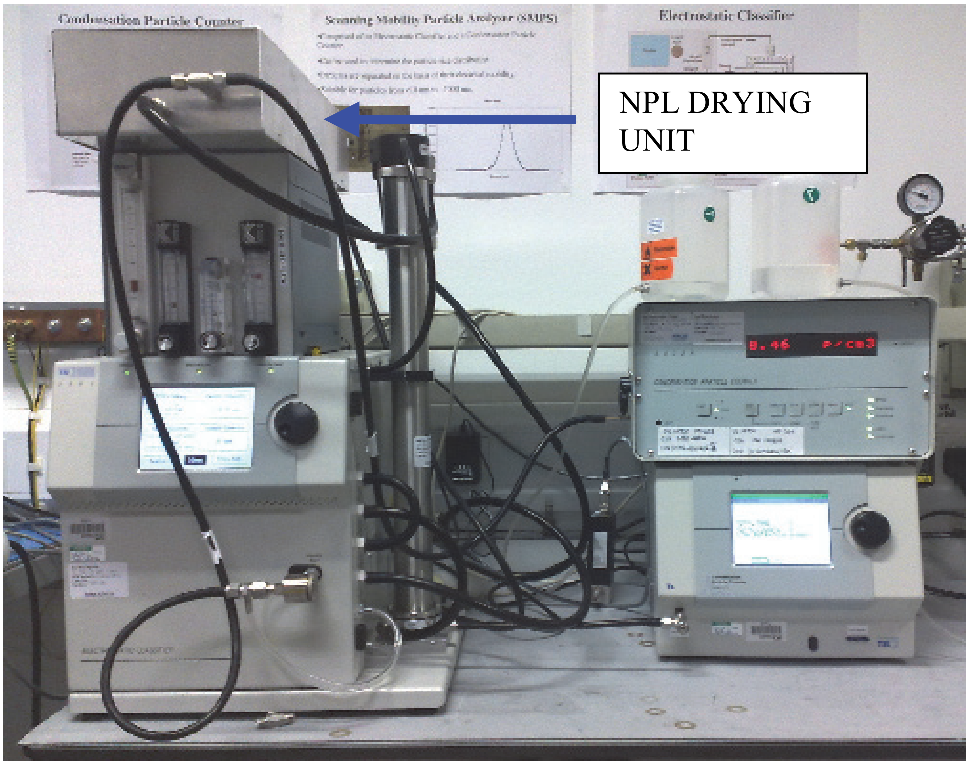


Figure 2-2 Typical configuration of CPC, SMPS and NPL drying unit at the Network sites

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.

The procedure 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 650°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 850°C in the presence of oxygen and helium. The protocol used is termed EUSAAR2.

The temperatures are calibrated using the Sunset Laboratories calibration kit.

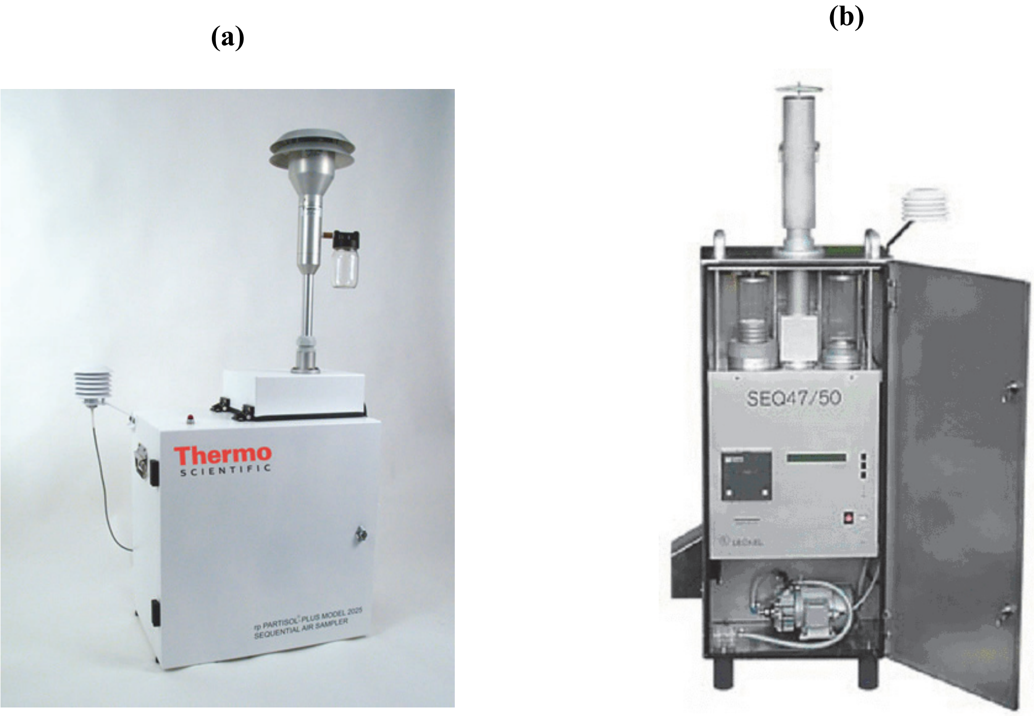


Figure 2-3 Thermo Partisol 2025 sampler (b) Leckel SEQ47/50 sampler

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 attenuation by 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, 880 nm and 370 nm. The 880 nm wavelength is used to measure the Black Carbon (BC) concentration of the aerosol, while the 370 nm 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 is that the Aethalometer under-reads at high filter tape loadings. To correct for this nonlinearity, the model developed by A Virkkula[1] 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 Chilbolton aethalometer are shown in the 2016 Black Carbon Network report.[2]

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 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 Chilbolton, North Kensington and Marylebone Road were serviced by the ESU, Air Monitors during 2016. 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: Chilbolton, North Kensington and Marylebone Road. The sampler previously stationed at Harwell was moved to Chilbolton and began sampling on 21 January 2016.

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 vehicle emissions.

The annual data capture for the Partisol 2025 instruments in 2016 were 90%, 90% and 99% respectively at Chilbolton, 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 for all the three sites. Concentrations for EC and OC are shown for thermal/optical transmission (TOT). Data are reported as the mass of carbon atoms per unit volume of air.

Some of the pollution episodes that occurred during 2016, as described by London air website http://www.londonair.org.uk/, can be identified in the graphs:

1. **End January:** A spell of cold, still weather allowed local emissions to build-up giving ‘moderate’ and ‘high’ PM_{10} and $PM_{2,5}$ particulate pollution across the south east on 19 and 20

January. Low wind speeds with air circulating over the south-east that had travelled through industrialised areas of the continent allowed particulate emissions to build

2. **March:** Low wind speeds and an influx of air from northern Europe resulted in elevated particulate levels across southern England between 10 and 13 March. The air arriving in London contained pollution from Germany and the Netherlands. This imported pollution was most likely from a mix of industrial, agricultural and urban sources. Relatively calm conditions also resulted in poor dispersion of our own local traffic emissions, contributing to elevated particulate. Days later, on 22 and 23 March, calm murky conditions resulted in elevated particulate levels across London as a result of local emissions.

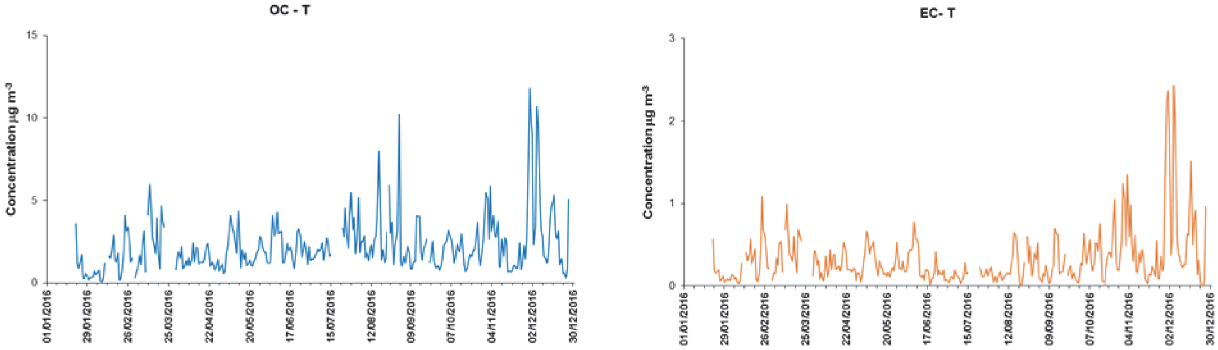
3. **Early May:**
   Fine, settled conditions with light south-easterly winds resulted at times in the import of a mix of industrial, agricultural, urban and traffic related pollution from the continent, to join with UK emissions. A change in the path of incoming air later on 7 May resulted in relatively cleaner air from the Mediterranean being imported and an end to the elevated particulate episodes of 6 and 7 May.

4. **End October:**
   On 25 October, a combination of imported particulates and poor dispersal of local emissions resulted in a build-up of PM_{10} particulate. That morning, a north-easterly air flow imported particulates from Germany and Holland. Later in the evening, air flow from the Calais region of France significantly added to the particulates imported. In addition, throughout the day, poor dispersal of local vehicular emissions in relatively calm local conditions helped push PM_{10} particulate to 'Moderate' at a number of sites. Concentrations dropped overnight and into the following day due to a change in wind direction to south-westerly and an increase in wind speed. 'Moderate' PM_{10} and $PM_{2.5}$ were measured in London during the weekend of Saturday 29 and 30 October. This was due to a combination of calm settled conditions leading to poor dispersal of local pollutants, including wood burning and fireworks, along with some pollution imported from continental Europe.

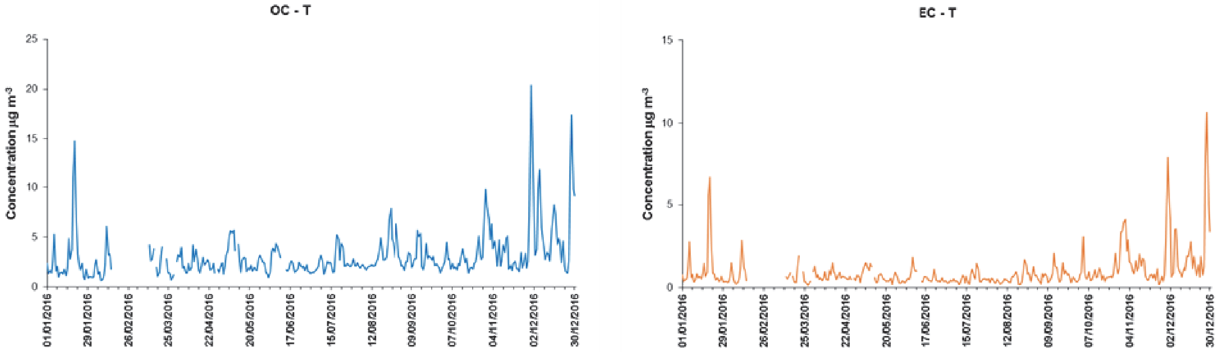
5. **End November:**
   Elevated pollution on 29 November was due to an area of high pressure over the UK causing cold, calm and settled conditions leading to poor dispersal of pollutants. London experienced a prolonged winter smog episode between 29 November and 6 December 2016 giving 'very high' PM_{10} and 'high' $PM_{2.5}$. On 1 December a continued north-west airflow with a slight increase in wind speed helped reduce pollution levels but was not enough to completely disperse local emissions. Easterly breeze arriving from the North Sea on 3 December brought relatively clean air and increased wind speeds on 4 December helped to disperse reduced local emissions.

6. **Late December:**
   This episode resulted from the cold, foggy, calm and settled conditions with poor dispersion of local emissions including those from traffic and wood burning. On the 28 and 29 December an import of particulate from the near continent also added to the local emissions.

Chilbolton



North Kensington



Marylebone Road

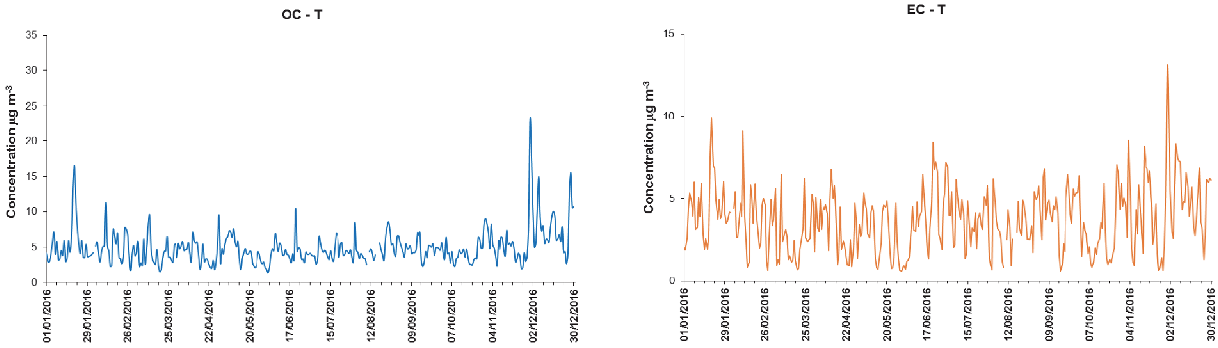


Figure 4-1 PM$_{10}$ OC and EC concentrations at Chilbolton, North Kensington and Marylebone Road during 2016.

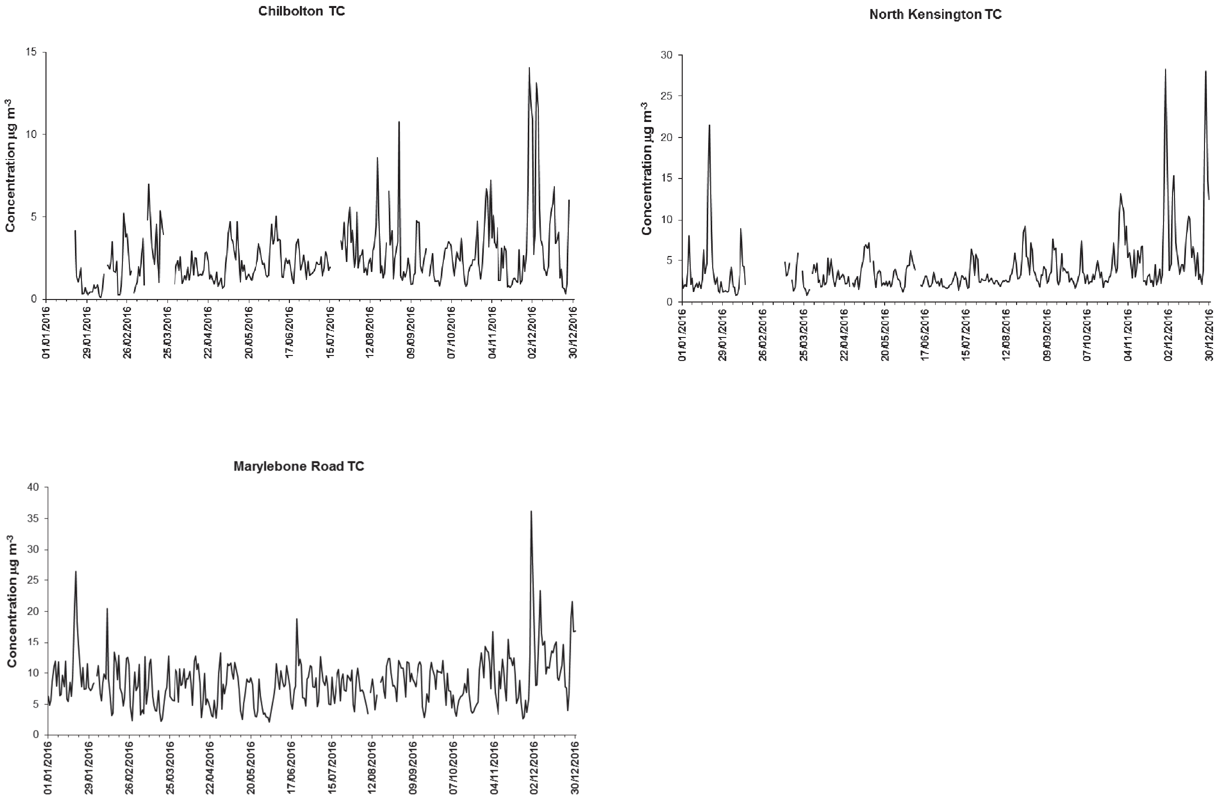


Figure 4-2 PM_{10} TC concentrations at Chilbolton, North Kensington and Marylebone Road during 2016

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 Chilbolton 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 the EUSAAR2 method, and black carbon (BC) measurements, from aethalometers, have been compared, and scatter plots are shown in Figure 4-2. The regression is calculated according to the Reduced Major Axis (RMA) method.[3]

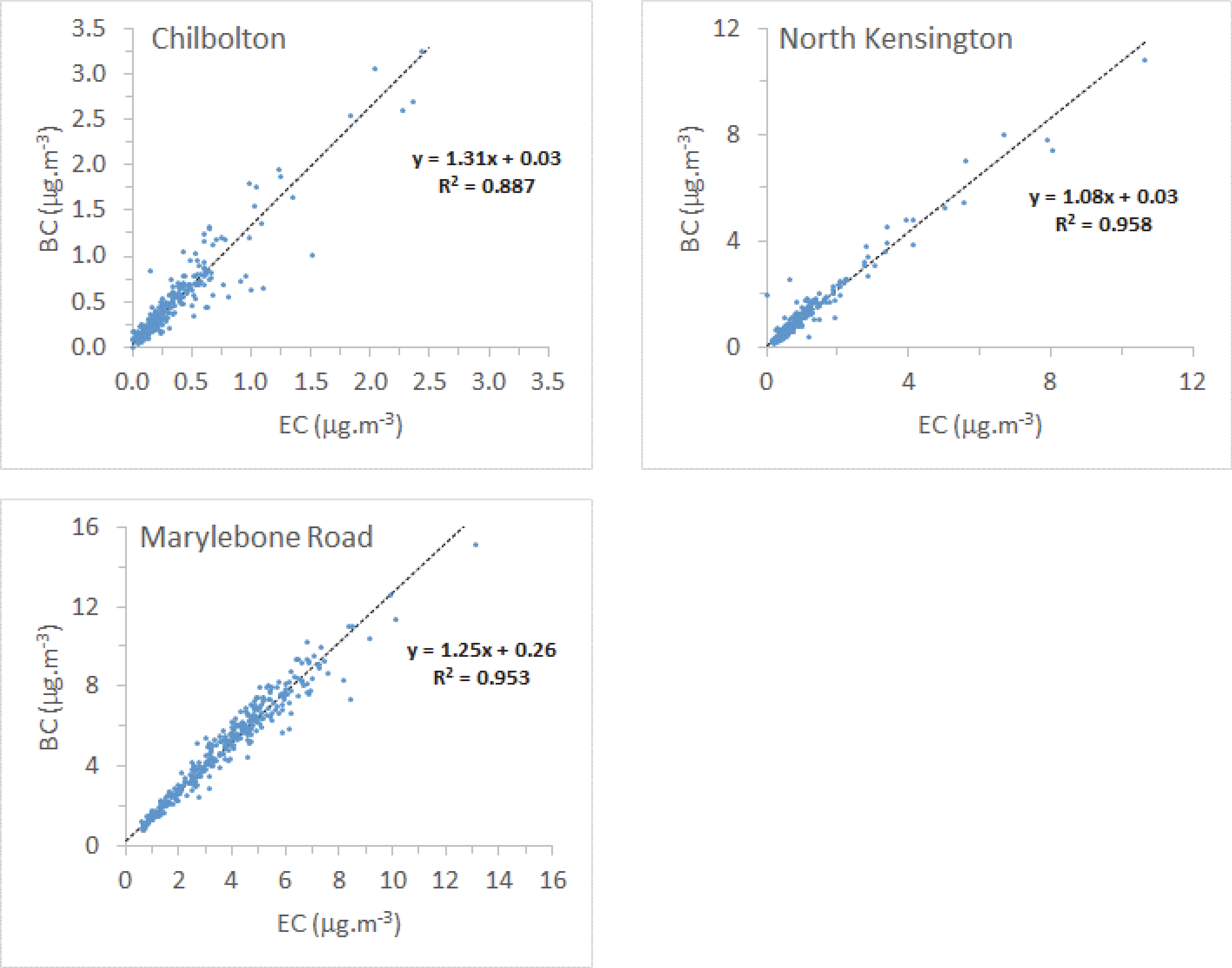


Figure 4-2 Comparison between PM$_{2.5}$ BC and PM$_{10}$ EC at the 3 sites in 2016

It can be seen that there is a generally good linear relationship between the Elemental Carbon and Black Carbon concentrations ($R^2 > 0.88$ at all sites), but with a variable slope. The relationship between Black Carbon and Elemental Carbon has been quite variable year on year, as shown in Table 4-1, although this will be partly due to the relatively narrow range of concentrations at Harwell, Chilbolton, and North Kensington.

The BC measurements are generally higher than the EC measurements by about 25%. This is consistent with published work.[4]

Table 4-1 Relationship between Black Carbon ($PM_{2.5}$) and Elemental Carbon (PM_{10}) and the three Network sites

	Harwell/Chilbolton		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 + 0.01	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
2016	1.31 x + 0.03	0.887	1.08 x + 0.03	0.958	1.25 x + 0.26	0.953

*There was not enough BC data collected at Harwell in 2009 to form a reliable relationship as the Aethelometer was only installed in November 2009. 2016 data is from Chilbolton and so may not be directly comparable to previous years.

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

$PM_{2.5}$ weekly sampling at Chilbolton and Auchencorth Moss is done to comply with a statutory requirement under the European Directive 2008/50/EC,[5] which requires measurements of OC and EC in the $PM_{2.5}$ fraction in rural background areas.

The sampler previously stationed at Harwell (since 1 September 2011) was moved to Chilbolton and operated there from 4 February 2016. The sampler at Auchencorth Moss has been operational since 17 November 2011. Data capture for 2016 was 91% for Chilbolton and 88% for Auchencorth Moss. Figure 4-4 and Figure 4-5 show the time series for these measurements since the installation of the samplers. The data from Chilbolton is plotted continuously with the data from the Harwell site.

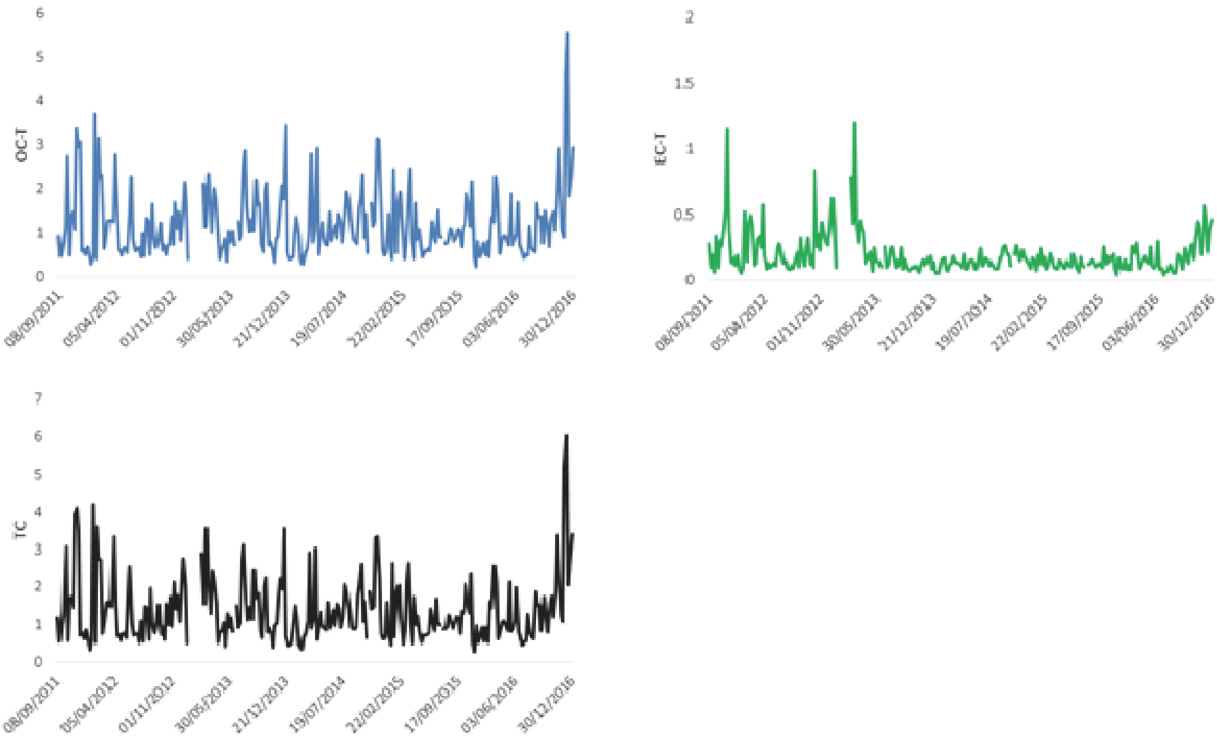


Figure 4-4 Time series of OC, EC and TC in the $PM_{2.5}$ fraction at Harwell/Chilbolton since the installation of the sampler (weekly samples) ($\mu g/m^3$)

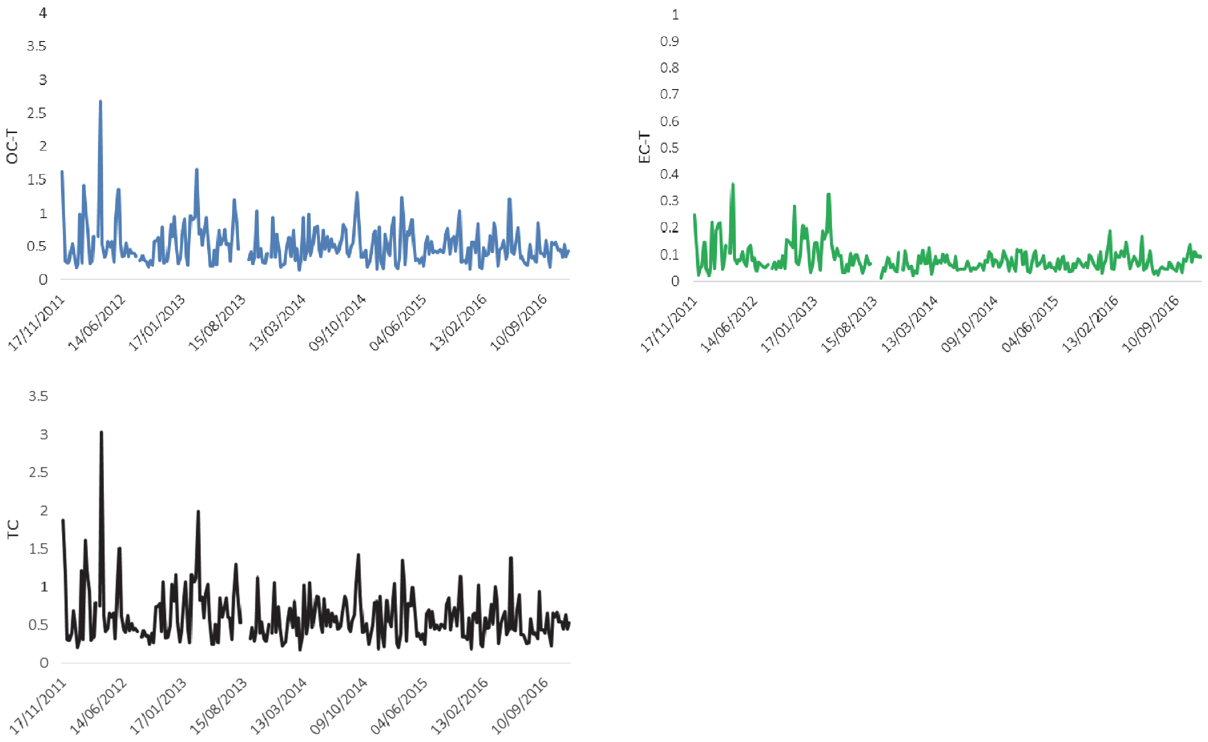
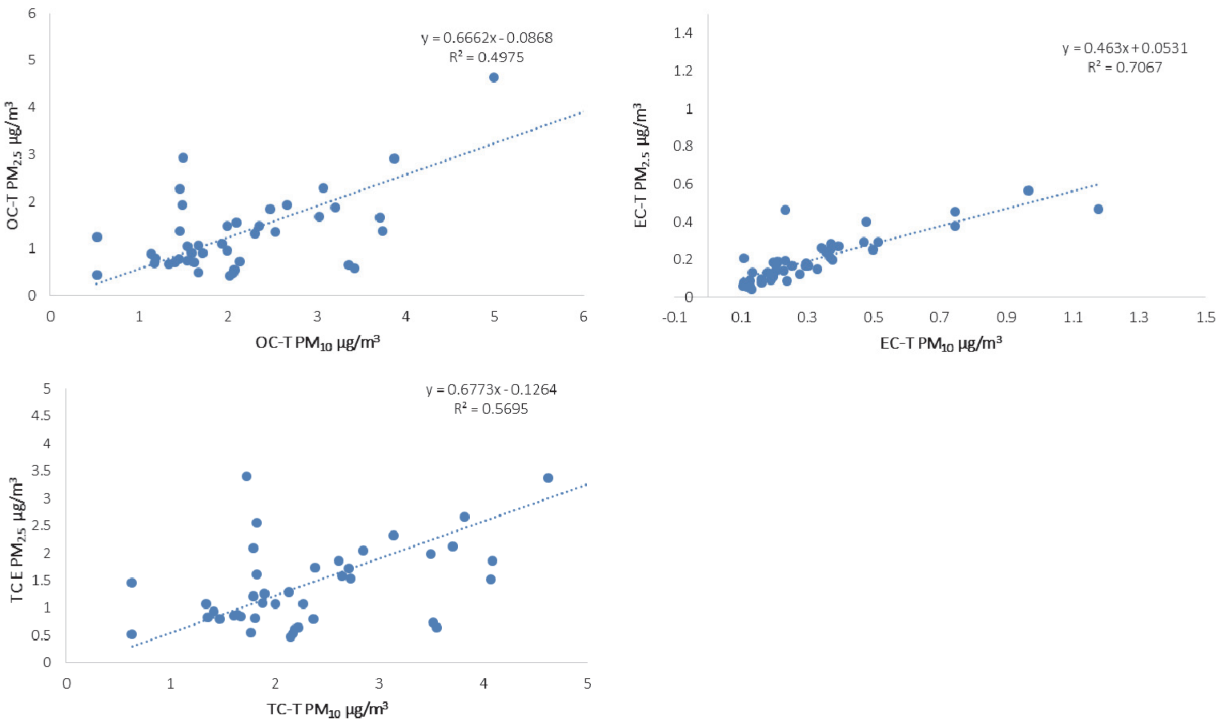


Figure 4-5 Time series of OC, EC and TC in the $PM_{2.5}$ fraction at Auchencorth Moss since the installation of the sampler (weekly samples) (µg/m^3)

The $PM_{2.5}$ carbon concentrations at Chilbolton were compared with weekly averages from the PM_{10} filters from the Partisol. The $PM_{2.5}$ data is generally lower than the PM_{10} data, implying the presence of OC and EC in the coarse size fraction. However, concentrations are low, with associated high scatter, and the difference 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.



Error! Reference source not found. Comparison between PM_{10} OC/EC weekly averages and $PM_{2.5}$ OC/EC at Chilbolton

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 76% for Marylebone Road and 68% for North Kensington.

Figure 4-7 and Figure 4-8 show the times series for all the ion concentrations at the two sites.

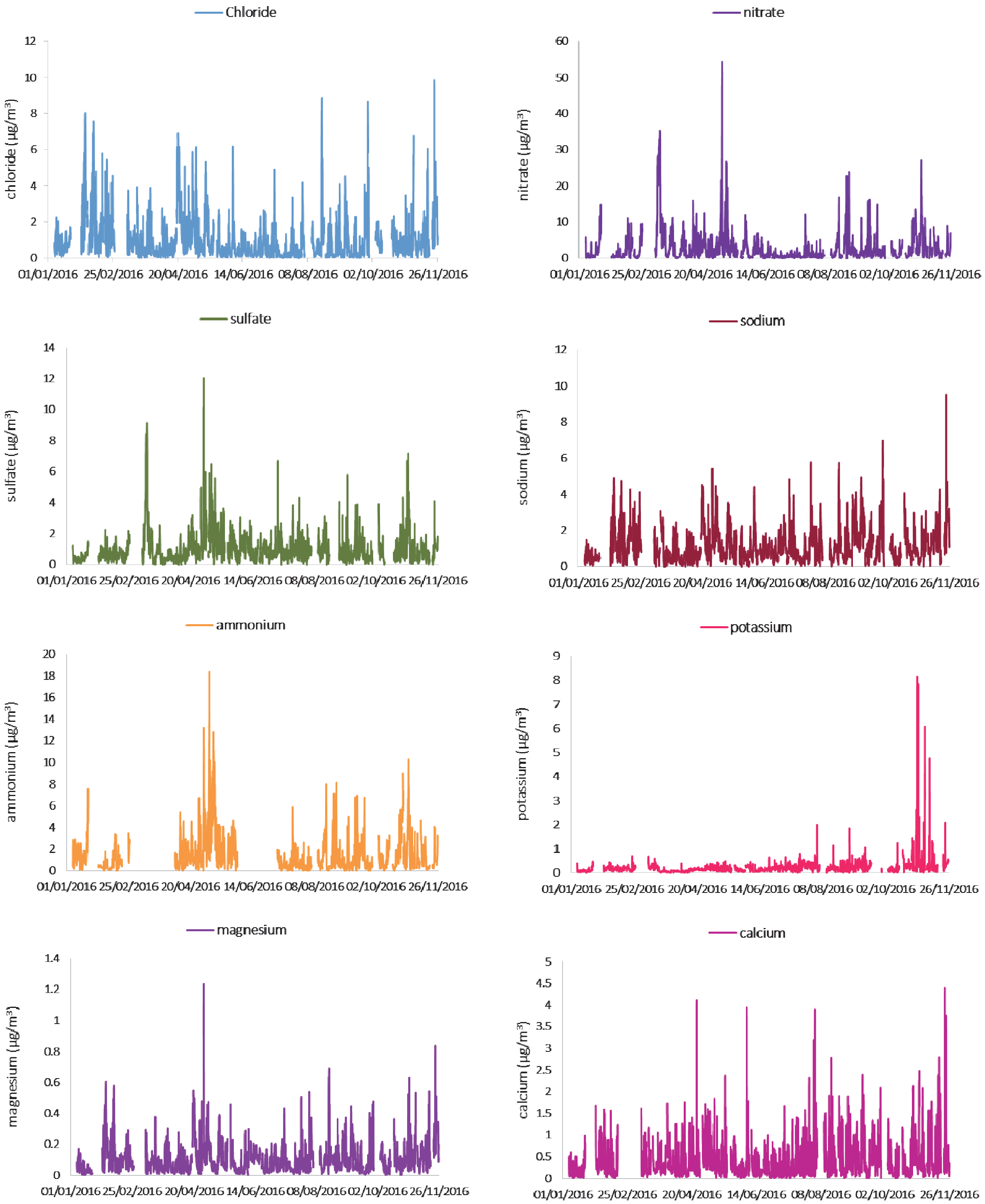


Figure 4-7 Time series for ion concentrations at Marylebone Road in 2016

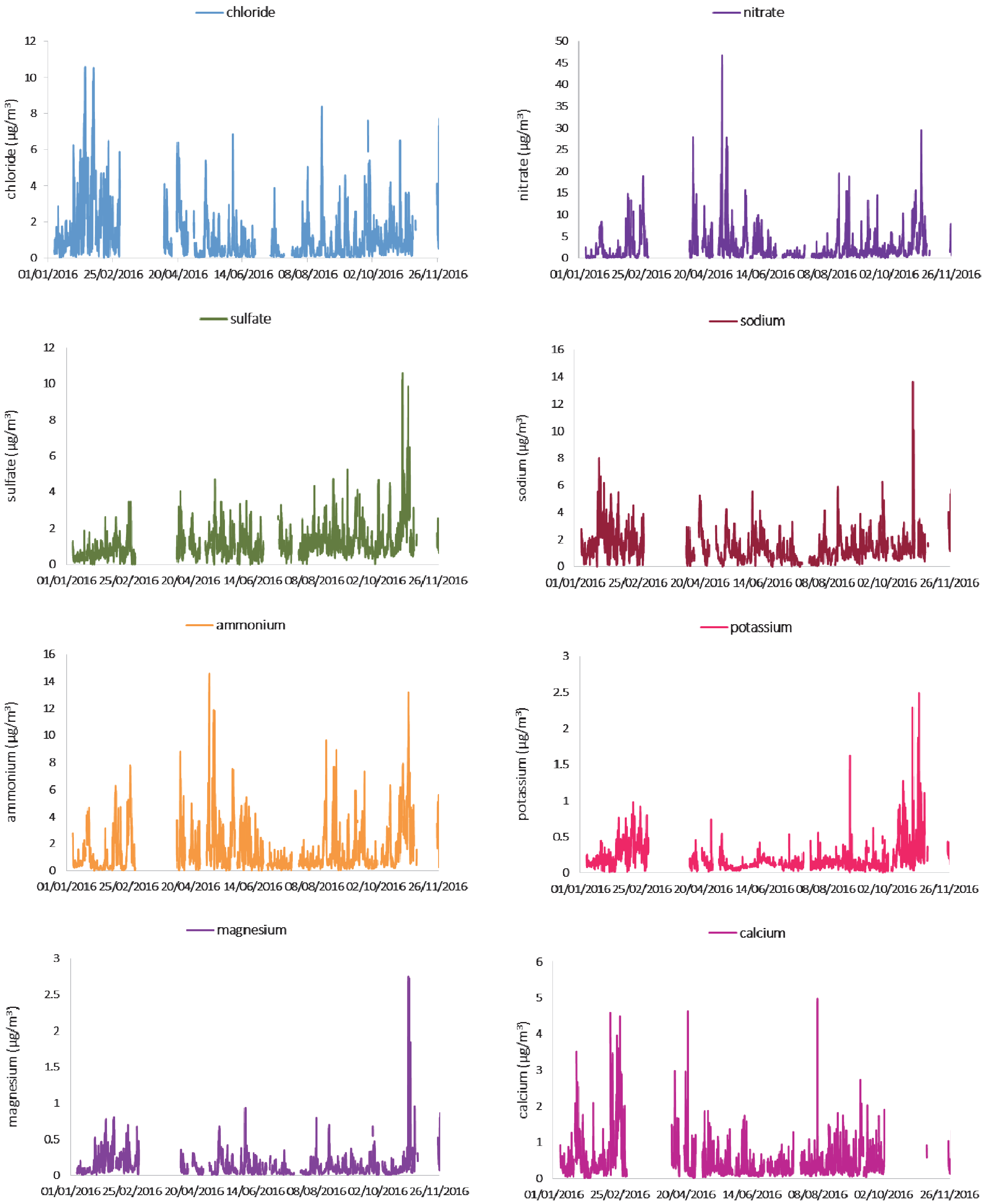


Figure 4-8 Time series for ion concentrations at North Kensington in 2016

Figure 4-9 shows the pollution episode on 19 – 21 January described in Section 4.1.1. The increase of NH_4NO_3 on 20 January coincided with low wind speeds and air circulating over the south-east that had travelled through industrialised areas of the continent.

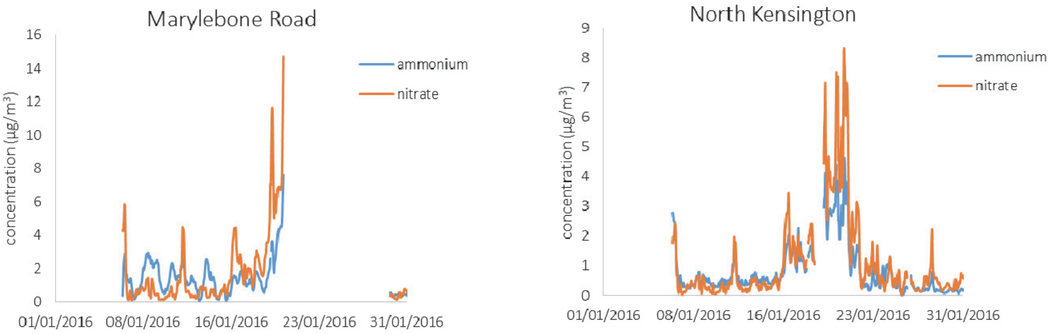


Figure 4-9 Pollution episode on 19 – 21 January 2016 at the two sites in London. Poor chromatography at Marylebone Road led to an incomplete profile for the time period.

Two more pollution episodes affected London in March; however, both sets of instruments experienced various problems resulting in only data for NO_3^- at Marylebone Road being useable.

Figure 4-10 shows the concentration of NO_3^-, SO_4^{2-} and NH_4^+ at both sites during the 6 May episode. The high nitrate concentrations are 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.

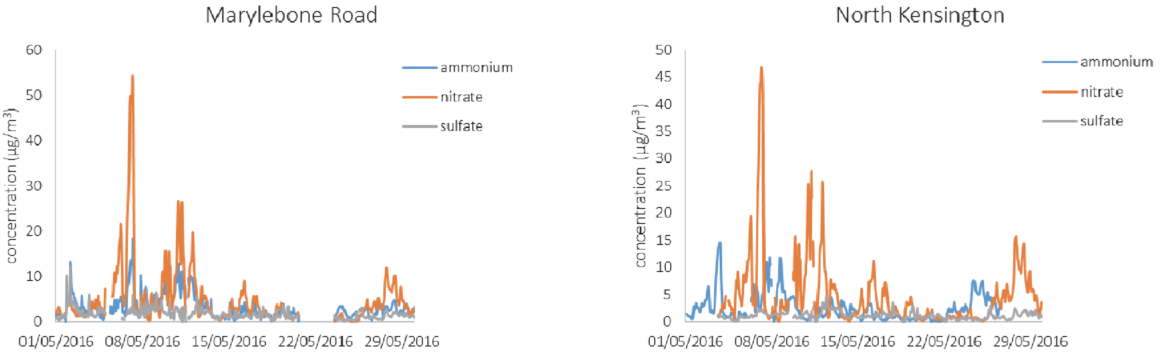


Figure 4-10 6 May 2016 pollution episode at the two sites in London.

Figure 4-11 shows the pollution episodes in October at both sites. The episode on 25 October was dominated by a combination of imported particulates and poor dispersal of local emissions resulting in a build-up of PM10 particulate. 'Moderate' PM_{10}' and $PM_{2.5}$ were also measured in London during the weekend of 29 and 30 October. This was due to a combination of calm settled conditions leading to poor dispersal of local pollutants, including wood burning and fireworks, along with some pollution imported from continental Europe. Continentally driven particulate episodes are marked by an influx of very fine particles in the $PM_{2.5}$ fraction which can travel long 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.

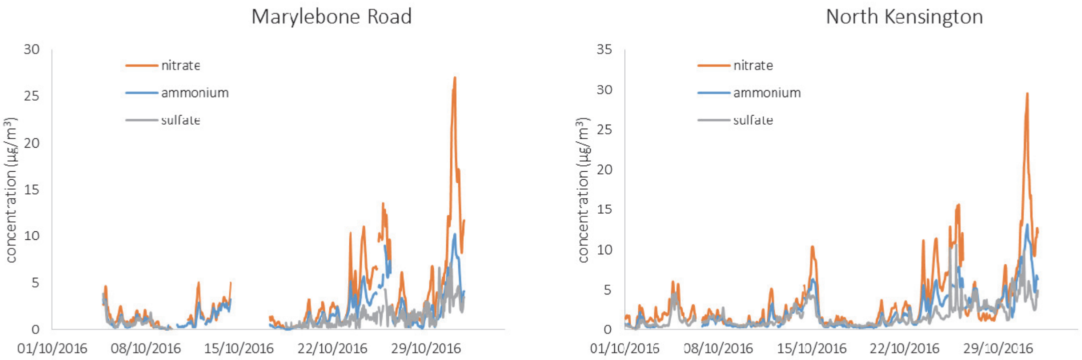


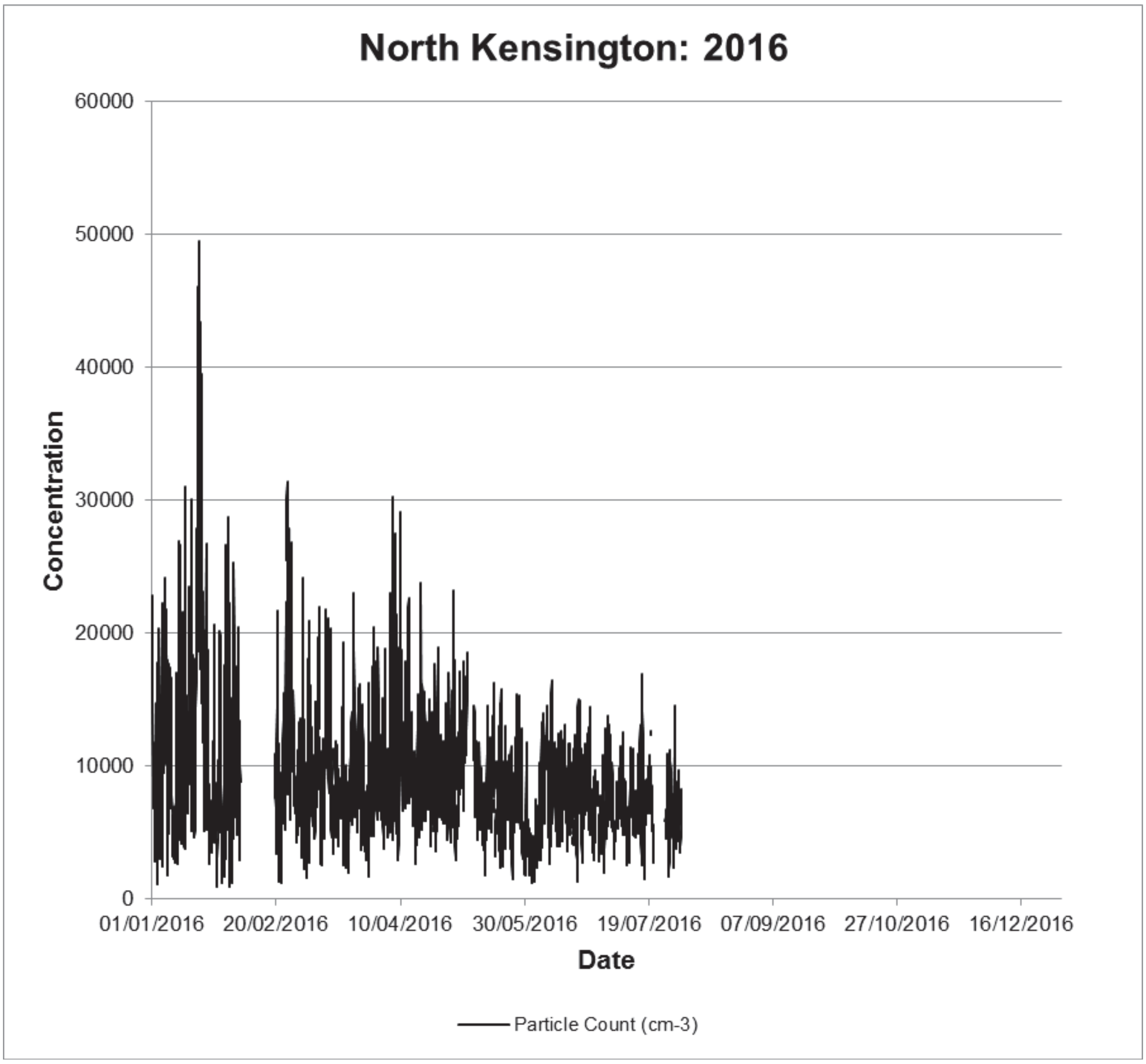
Figure 4-11 October pollution episodes at the two sites in London.

Higher K^+ concentrations on the evening of 5 November at Marylebone Road are also noteworthy; these are due to fireworks and bonfires on Bonfire Night on 5 November. The instrument at North Kensington was not operational on 5 November, but it would be expected to show a similar trend.

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 2016 are shown in **Error! Reference source not found.**. There is no data for the Harwell/Chilbolton site as there was no CPC present.


North Kensington: 2016
Concentration
60000
50000
40000
30000
20000
10000
0
01/01/2016
20/02/2016
10/04/2016
30/05/2016
19/07/2016
07/09/2016
27/10/2016
16/12/2016
Date
Particle Count (cm-3)

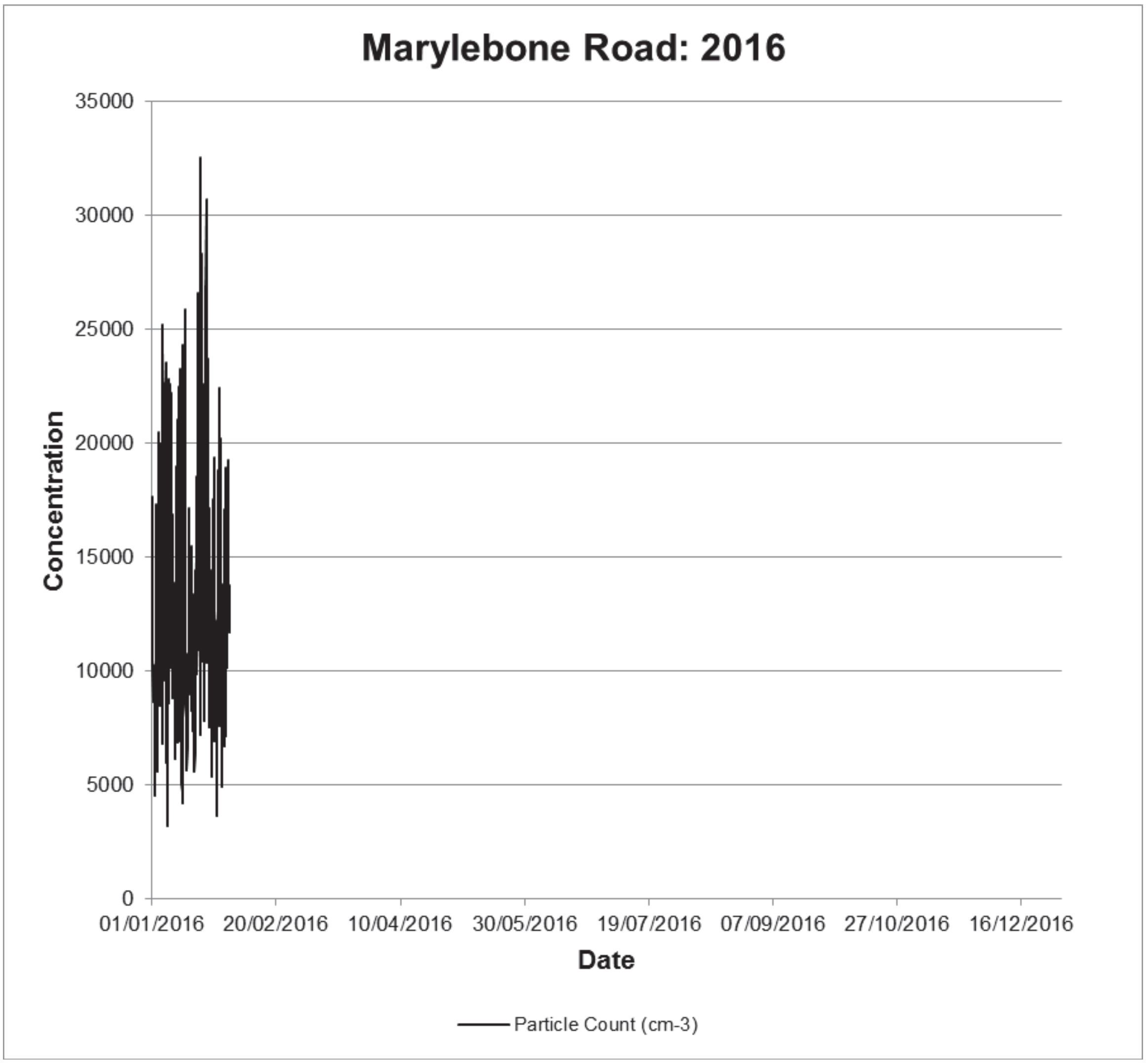


Figure 4-12 Hourly particle number concentrations at network sites

As described below, during 2016 the CPCs were due to be replaced, as they had been operated beyond their useful life. No working instrument was available for the Chilbolton site. The instruments at North Kensington and Marylebone Road permanently broke down in August 2016 and February 2016 respectively.

The average annual data captures for the CPC instruments during 2016 were 87% and 100% respectively for North Kensington (up to the end of July 2016) and Marylebone Road (up to the end of January 2016).

For the purposes of this report, the long-term ratio between integrated number concentrations from the SMPS data and CPC data was used for the Chilbolton, North Kensington and Marylebone Road datasets to estimate long term trends in the next section. The uncertainty for these extra data, however, cannot be accurately estimated, and they have not been included in the datasets submitted to the UK-Air website.

The TSI 3022A is an old model that has been discontinued by TSI. A Technical Specification has been produced by CEN TC 264 WG 32 for CPC instruments to be used for reporting data (see Section 5.2.1 for details). Four new CPC CEN compliant instruments (TSI 3772-CEN) have been purchased in early 2017. Three of the CPCs have been installed in 2017 so far, one each at the Marylebone Road, North Kensington and Chilbolton sites. New drier systems have also been purchased for use with the CPCs but these are currently undergoing laboratory testing before they are installed in the field sites. Once testing on the drier systems is complete (using the 4th CPC in the Nanoparticles laboratory at NPL) the four drier systems will be installed at Marylebone Road, North Kensington and Chilbolton. The fourth CPC and drier system will then be installed at the Birmingham monitoring site (this has been delayed due to the Birmingham site being due to be moved during 2017).

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 2016 were 89%, 92% and 92% respectively for Chilbolton, North Kensington and Marylebone Road.

The reasons for the main data gaps were:

- **Chilbolton: Problems with the CPC in the SMPS system and the SMPS calibration at NPL**
- **North Kensington: the SMPS calibration at NPL**
- **Marylebone Road: the SMPS calibration at NPL**

The production of data from SMPS instruments is a complicated process, summarised schematically in Figure 4-13. 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. 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 4-14. The overall effect of the two corrections is to increase the particle number counts at smaller sizes and to increase the total particle count.

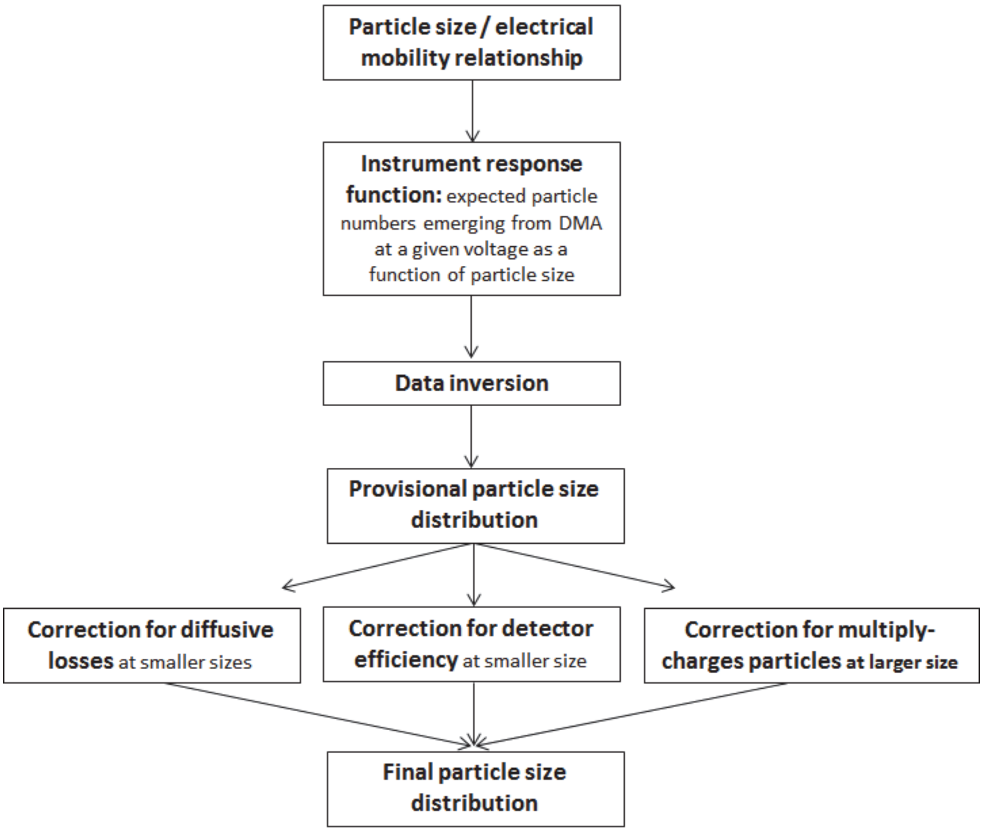


Figure 4-13 Schematic of the internal data processing of SMPS instrument in the Network

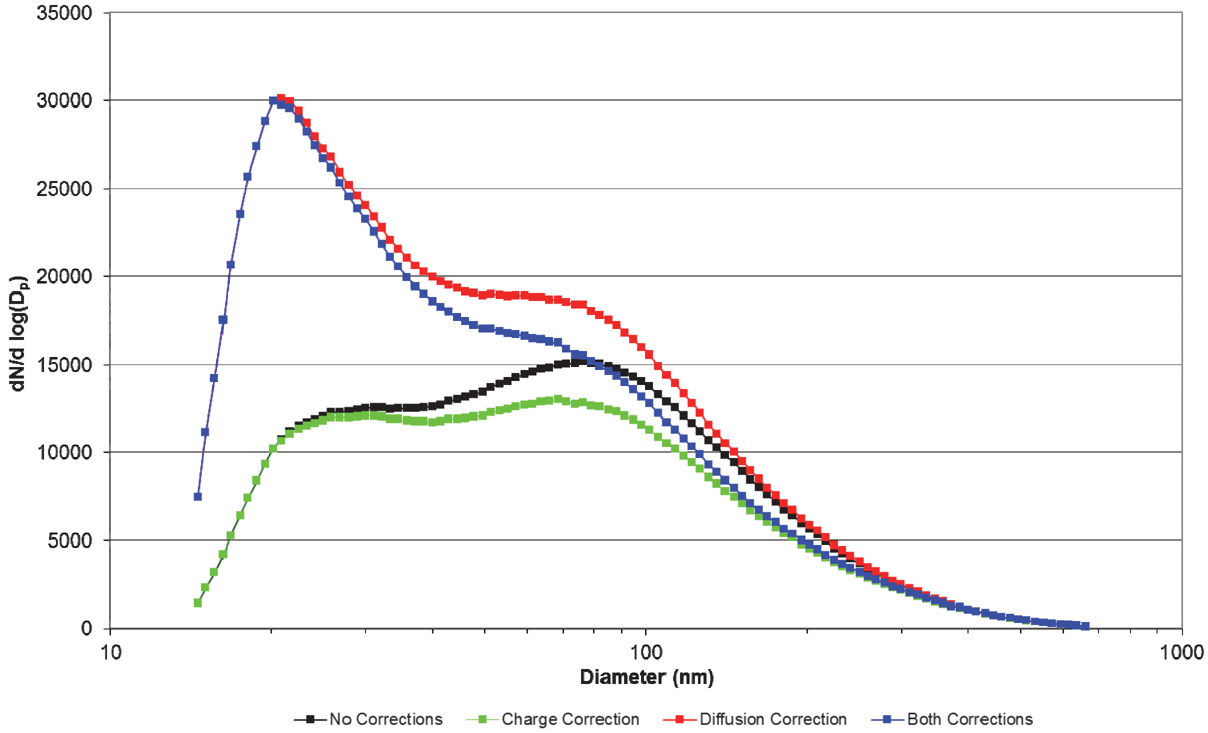
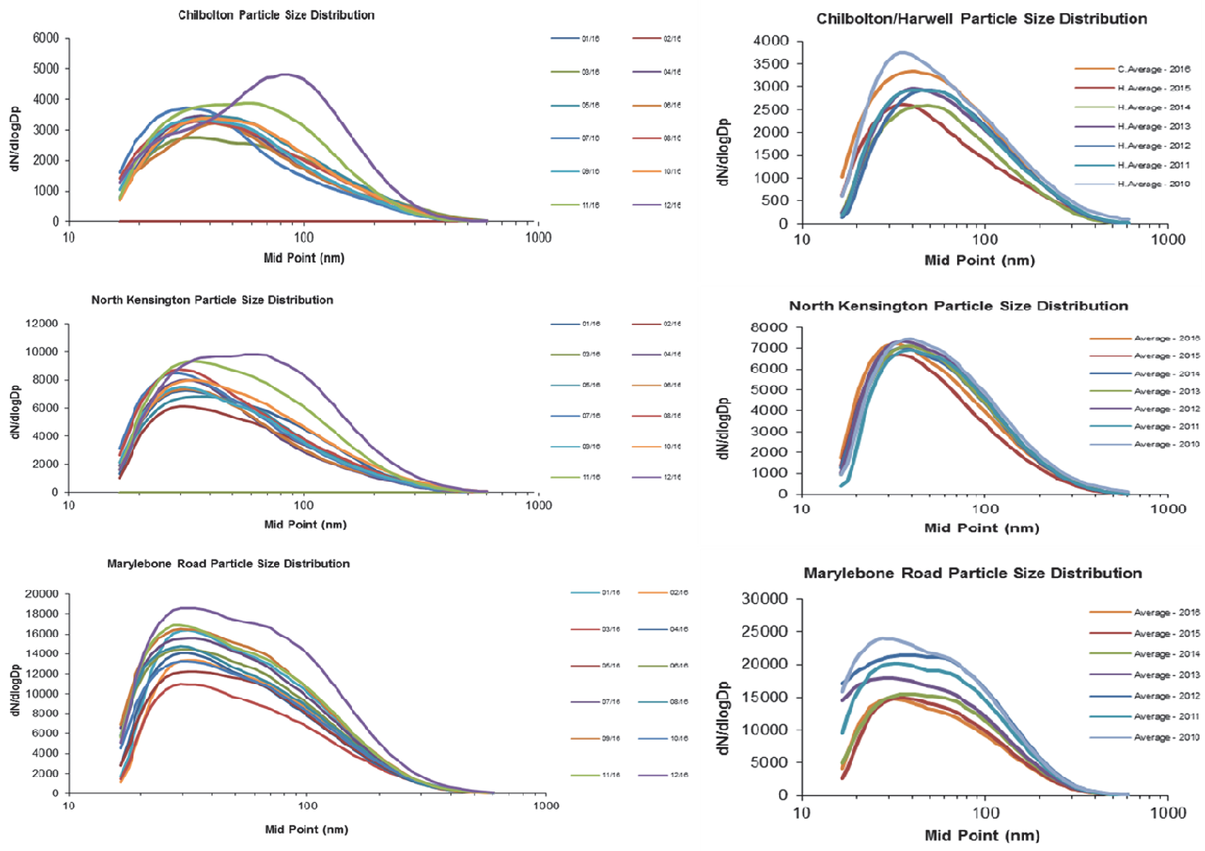


Figure 4-14 Effect of the multiple charge, the diffusion loss and their combined correction in the SMPS size spectrum

The counts in each particle size bin measured during 2016 are presented as monthly averages in the left-hand panels of Figure 4-15 and as annual averages in the right-hand panels.


Chilbolton Particle Size Distribution

Chilbolton/Harwell Particle Size Distribution

North Kensington Particle Size Distribution

North Kensington Particle Size Distribution

Marylebone Road Particle Size Distribution

Marylebone Road Particle Size Distribution

Figure 4-15 Monthly averaged particle size distributions at the Network sites during 2016 [left-hand panels] and comparison of the 2010, 2011, 2012, 2013, 2014, 2015 and 2016 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 in February 2016. The Marylebone (Mar), Chilbolton (Chl) and North Kensington (NK) SMPSs were tested in parallel (along with an NPL-based SMPS), under controlled lab conditions. Certified latex spheres were used as test 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 4-16. 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.

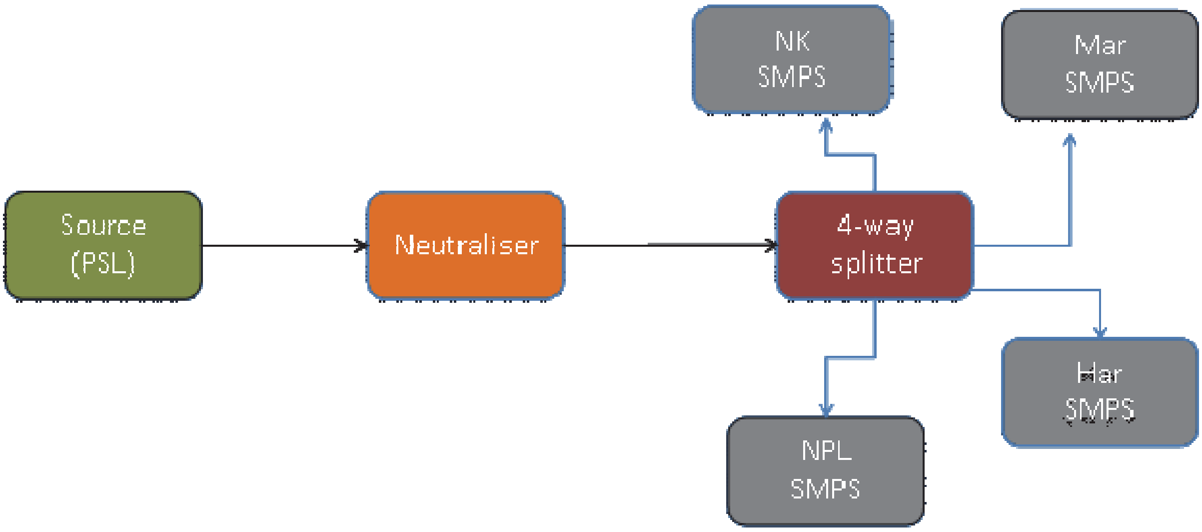


Figure 4-16 Schematic showing the parallel sampling of the four SMPS when connected to a flow splitter and fed with a single particle source (PSL) conditioned with a single neutraliser.

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.

Conclusions

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

				PSL		
		41	**60**	**92**	**125**	**203**
		± 4	± 4	± 3	± 3	± 5
Site		nm	nm	nm	nm	nm
Mar	Geometric mean	**41.7**	**64.6**	**90.8**	**124.4**	**199.4**
	Geometric st. dev.	1.09	1.09	1.07	1.06	1.06
Chl	Geometric mean	**42.2**	**64.6**	**90.7**	**124.1**	**198.0**
	Geometric st. dev.	1.10	1.09	1.07	1.06	1.06
NK	Geometric mean	**42.7**	**65.8**	**92.0**	**125.9**	**200.7**
	Geometric st. dev.	1.10	1.10	1.08	1.07	1.06
Mean 2016		**42.2**	**65.0**	**91.2**	**124.8**	**199.4**
Mean 2015		41.9	64.3	90.2	124.8	198.7

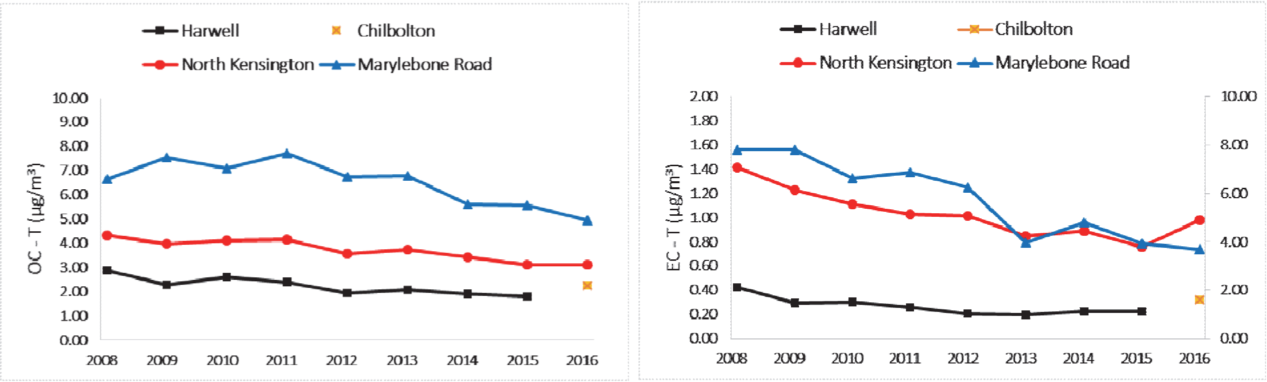
Table 4-2 Comparison of SMPS measured distributions with polystyrene latex (PSL) certified values.

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 concentrations of all components at all sites.



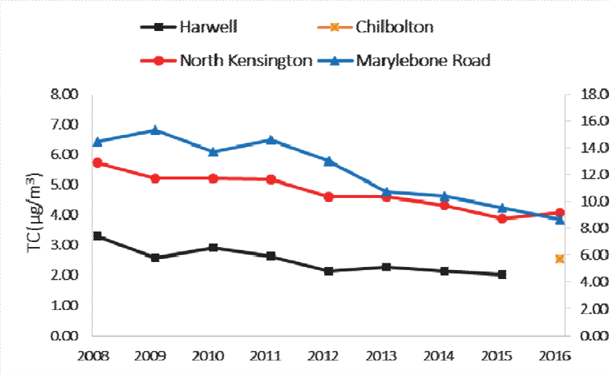


Figure 4-18 Annual trends for OC/EC/TC measurements. EC and TC values for Marylebone Road are shown on the right-hand axis

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

Figure 4-19 Annual Average Black Carbon, Elemental Carbon and Motor Vehicles per day at Marylebone Road for the period 2009 – 2016

It can be seen that the changes in Black Carbon and Elemental Carbon concentrations broadly follow changes in the total traffic flow for the years 2009 to 2012, but they do not correlate well from 2013 onwards. This would indicate that Black Carbon and Elemental Carbon emissions per vehicle have changed over the last 4 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.[6] Table 4-3 shows the composition of the London bus fleet over the period 2010 to 2016. The bottom row of the table shows the percentage of low emission buses, which is a combination of the hybrid, electric 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 and Elemental Carbon emissions.

In 2012 the vehicle types affected by the London Low Emission Zone (LEZ) were 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- 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 4-3 Composition of London bus fleet, 2010 to 2016[6]

		Number of buses						
Bus Type	**Drive train type**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**
New Routemaster	Hybrid	0	0	5	8	168	432	736
Routemaster	Diesel	18	18	19	20	19	19	10
Artic	Diesel	320	260	0	0	0	0	0
Single deck	Diesel	2,676	2,670	2,661	2,608	2,606	2,662	2,617
	Fuel Cell/Hybrid	0	5	5	5	8	8	8
	Hybrid	27	27	33	28	23	23	18
	Electric	0	0	0	0	2	8	17
Double deck	Diesel	5,554	5,487	5,787	5,696	5,296	5,026	4,794
	Hybrid	29	79	233	352	643	799	981
TOTAL		8,624	8,546	8,743	8,717	8,765	8977	9186
% low emission		0.65	1.30	3.16	4.51	9.63	14.15	19.16

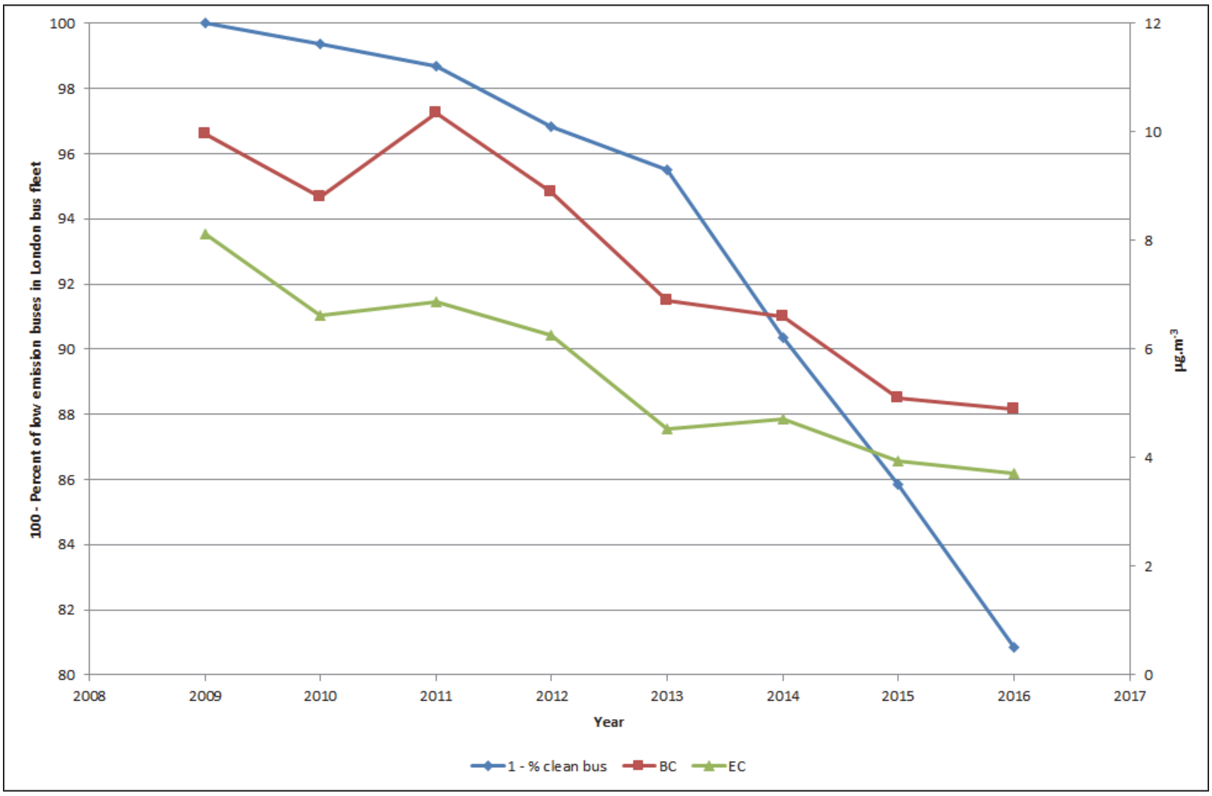


Figure 4-3 Annual Average Black Carbon, Elemental Carbon and [100 – percentage of low emission buses in the London bus fleet] for the period 2009 – 2016.

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 has led to reduced Black Carbon and Elemental Carbon concentrations.

4.5.2 Ion measurements

Figure 4-21 shows long-term trends for the anion species. Ratified data were not available for the three sites in 2010 or 2011 so are not included. 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. Since 2012, a general decrease in sulphate is observed at all sites.

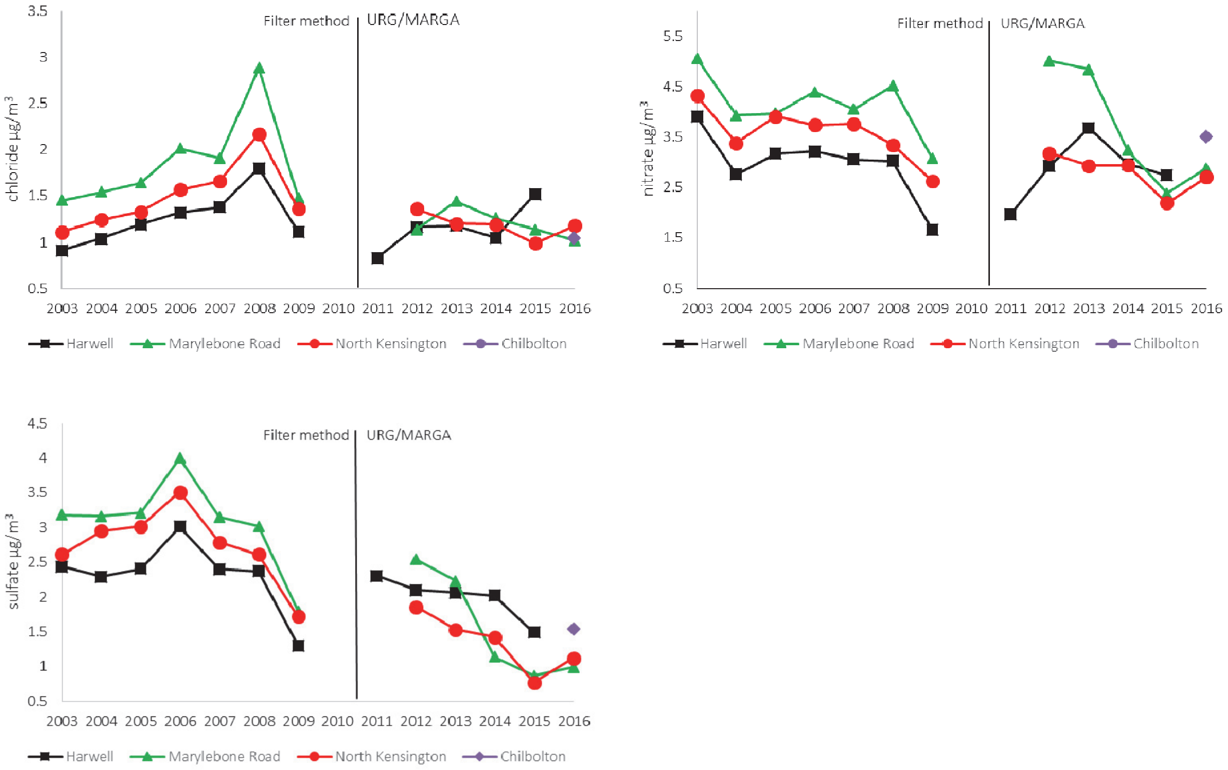


Figure 4-4 Anion long-term annual trends (clockwise chloride, nitrate and sulphate). The 2012 - 2016 data for Harwell have been derived from the MARGA measurements.

4.5.2 Particle number concentrations

Figure 4- shows long-term annual trends for CPC measurements at all sites. The particle number concentrations have continued to decrease more gradually 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).[7]

Legislation enacted in June 2007[8] 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)[9] 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[10] 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 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.

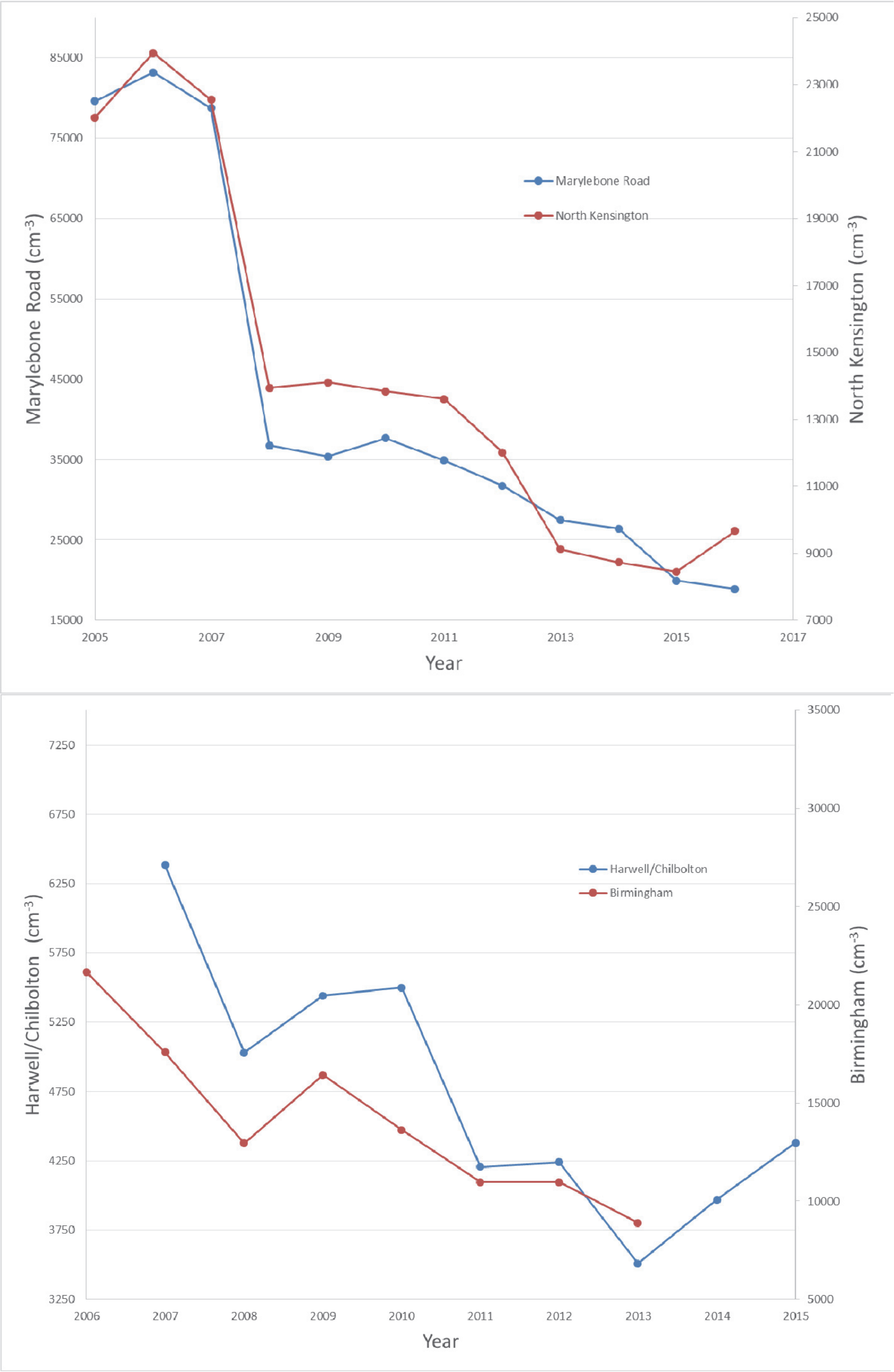


Figure 4-5 CPC long-term annual trends at all sites. No data are available from 2014 for the Birmingham site. The Harwell site moved to Chilbolton in 2016.

4.6 DIURNAL, WEEKLY AND MONTHLY PROFILES

Diurnal, weekly and monthly profiles have been plotted for the hourly concentrations using the Openair tools.[11, 12, 13]

4.6.1 Profiles for anion and cation species

The 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.

Figure 4-24 shows the profiles for Cl^- , Na^+ and Mg^+ concentrations at North Kensington and Marylebone Road. There is some correlation between Cl^- and Na^+, consistent with them having been derived from the same source, identifiable with sea salt.

Ca^{2+} profiles at both sites in Figure 4-25 show values characteristic of traffic contribution, possibly re-suspension of crustal material from road surfaces

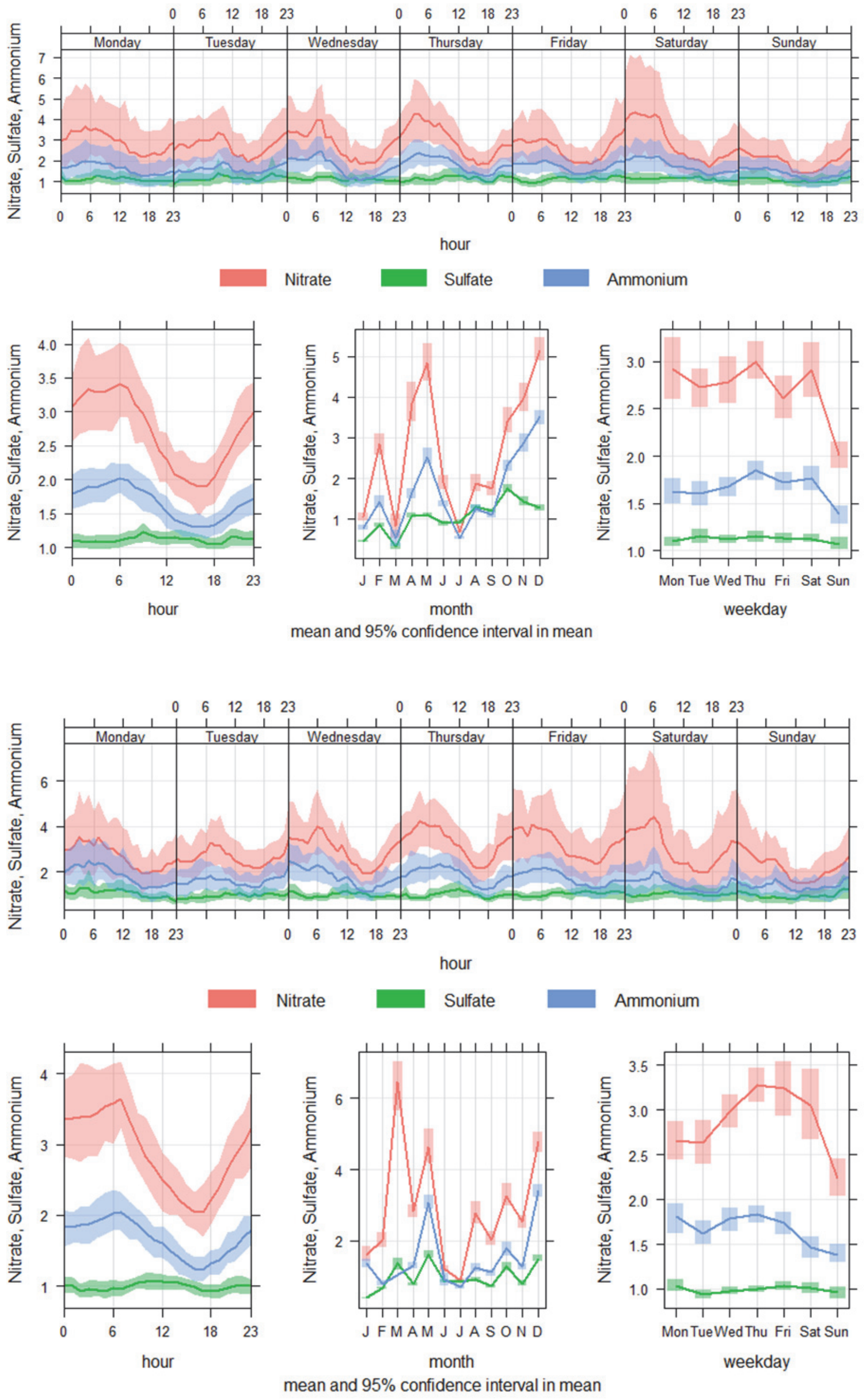


Figure 4-23 Diurnal, weekly and monthly profiles for NO_3^-, SO_4^{2-} and NH_4^+ during 2016 at North Kensington (top) and Marylebone Road (bottom)

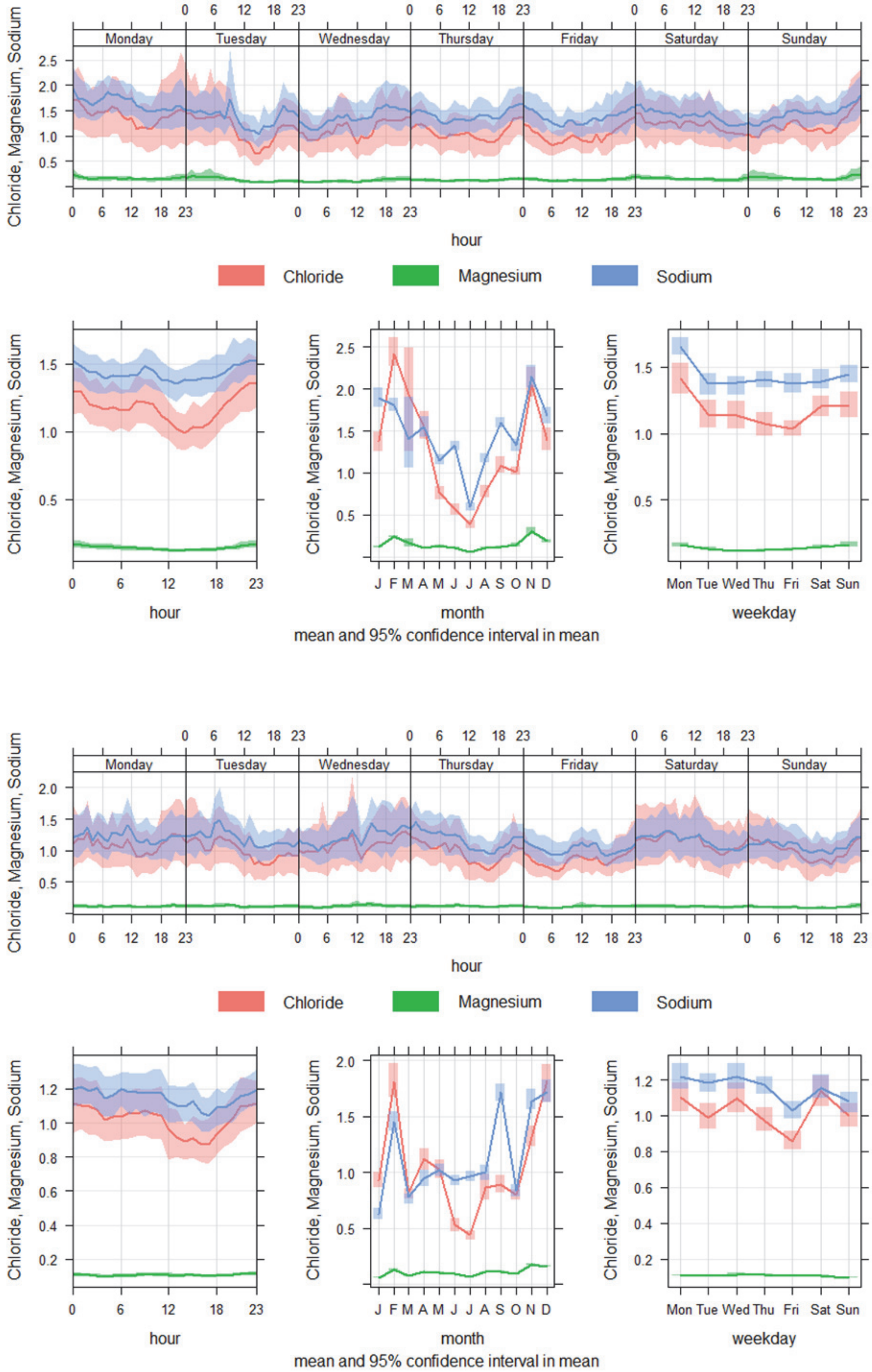


Figure 4-24 Diurnal, weekly and monthly profiles for Cl^-, Na^+ and Mg^{2+} concentrations during 2016 at North Kensington (top) and Marylebone Road (bottom).

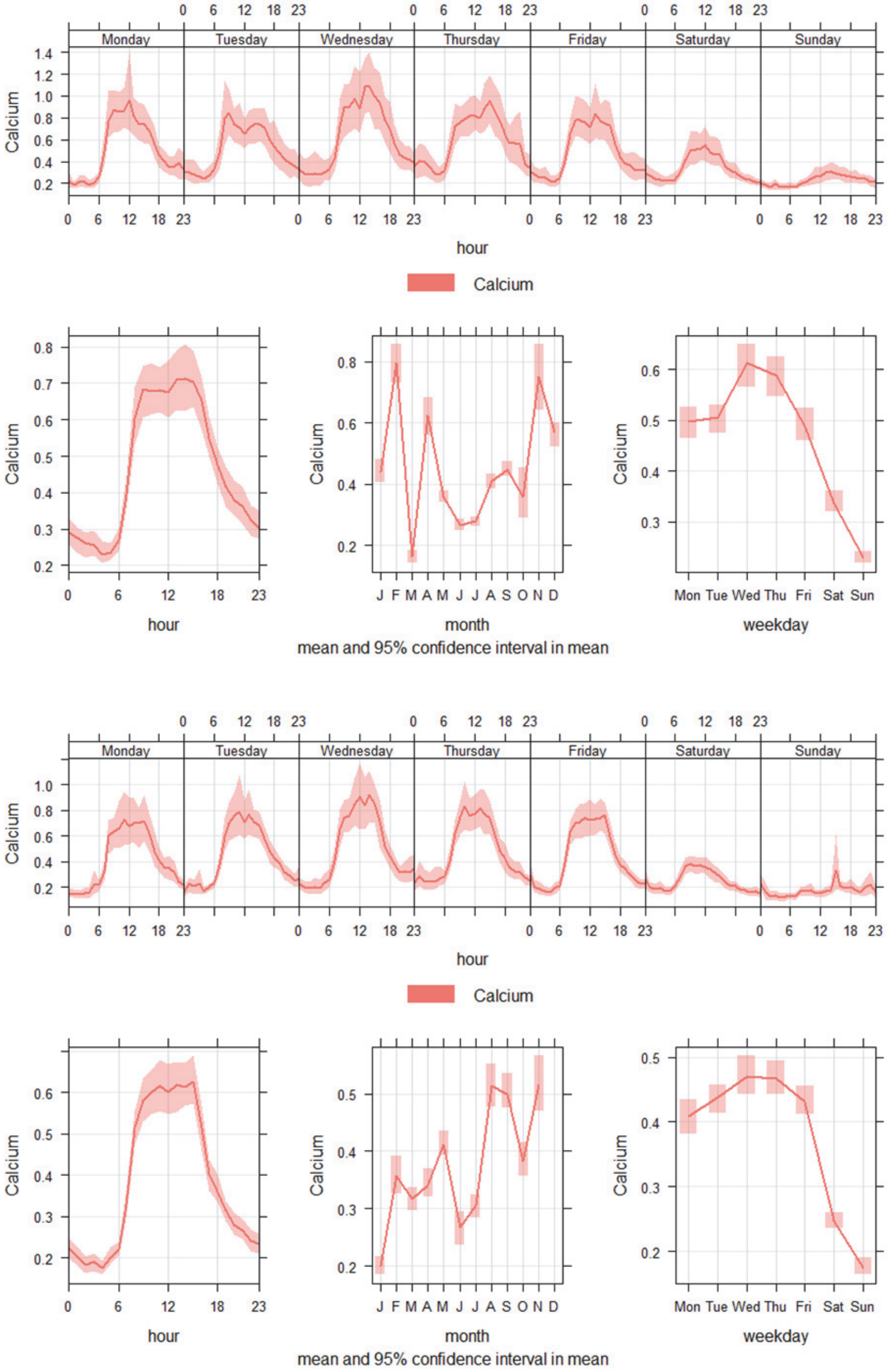


Figure 4-25 Diurnal, weekly and monthly profiles for Ca^{2+} during 2016 at North Kensington (top) and Marylebone Road (bottom).

4.6.2 Profile for number concentrations

The data for the diurnal, weekly and monthly profiles for number concentrations in 2016 are limited because there is only data for seven months from North Kensington and a single month for Marylebone Road. However, at these urban sites, the trends show a strong correlation with anthropogenic sources, with lower concentrations during the weekend, reflecting the traffic profile. In urban conditions (North Kensington), 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.

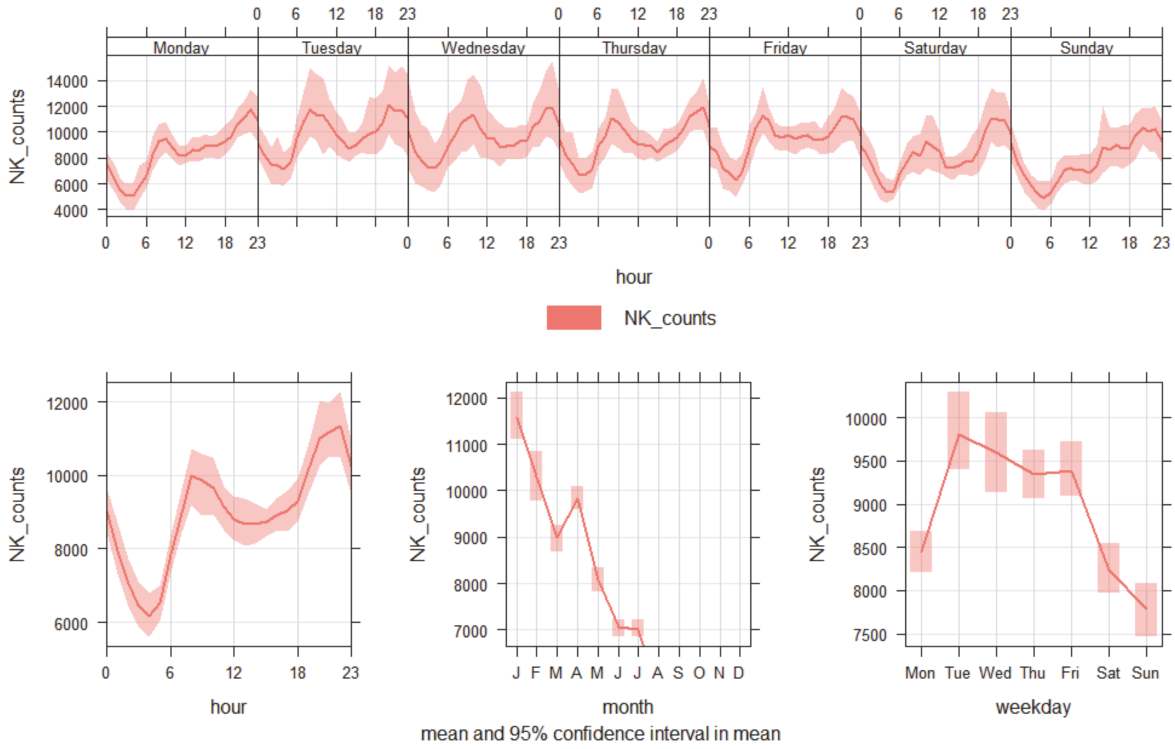


Figure 4-6 Diurnal, weekly and monthly profiles for number concentrations in 2016 at North Kensington

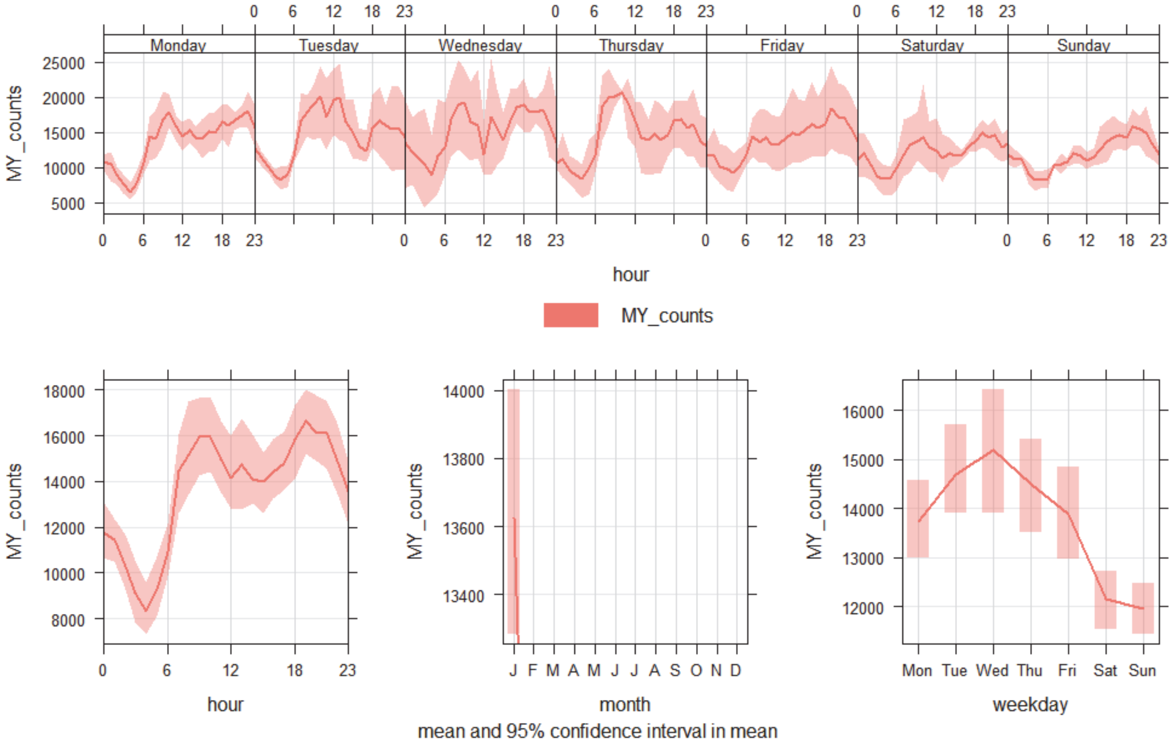


Figure 4-7 Diurnal, weekly and monthly profiles for number concentrations in 2016 at Marylebone Road

5 UPDATE ON WIDER POLICY AND RESEARCH CONTEXT

5.1 UPDATE ON RELATED UK ACTIVITIES

5.1.1 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 (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 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 STANDARDISATION ACTIVITIES

5.2.1 CEN standards

In March 2017, CEN TC 264 WG 15 published EN 16450:2017 for automatic PM measurement, which incorporates type approval of PM instruments, equivalence testing against the reference methods, ongoing QA/QC, and ongoing determination of equivalence. This accompanies EN 12341:2014, which sets out gravimetric reference methods for PM10 and PM2.5 (updating and combining EN 12341:1998 and EN 14907:2005). The latter standard is directly relevant to this network as it specifies how to sample PM10 and PM2.5 material onto filters for subsequent analysis.

The WG is next planning to update EN 12341:2014. Some key aspects to this are improved specification of the dimensions and tolerances of the reference inlets, an improved leak test, and a new procedure for demonstrating that samplers built to the reference specifications deliver adequate performance. There may also be reconsideration of the allowed filter material. Currently 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. Brian Stacey from Ricardo became convenor of the WG during 2016.

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):

1) In August 2016 the 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, was published. This provides a “standard” low size cut-off (7 nm, as determined with silver nanoparticles), sampling, operating, QA/QC and calibration procedures. It will be readily adoptable as a reference method.

The main impact of this Technical Specification on the Network has been the set of specifications for compliant CPCs. These were not met by any commercially available CPCs until 2016, and this delayed the purchase of overdue replacement stand-alone CPCs on the Network. Compliant CPCs have been purchased and installed in 2017.

Sampling systems have also been specified, and new systems have also been purchased. These will be tested and installed in 2017.

Requirements for calibrating CPCs within the TS simply refer to ISO 27891, as described below.

2) A Technical Specification covering 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.

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. They will include an assessment of the whole size spectrum against the output of a reference instrument. NPL will make arrangements for such a test after the installation of the new sampling systems.

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).

Activities in 2016 were as follows:

WG 34:

The revised version of the standard prEN 16913, “Ambient air — Standard method for measurement of NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+} in $PM_{2,5}$ as deposited on filters” was circulated to the WG members and sent to CEN for a formal vote. The document was circulated for approval in December.

It was also decided that further work was required to bring automatic instrumentation into the standardisation process. The UK was chosen to draft a new work item proposal for submission to CEN/ TC 264 and was circulated to WG members for comments before submission. The UK relies on automated instrumentation, instead of a filter based method, to report ion concentrations to Europe.

A paper, “Standardisation of a European measurement method for the determination of anions and cations in $PM_{2,5}$: results of the field trial campaign and the determination of a measurement uncertainty and working range” was completed and published in March 2017.

WG 35:

The final draft of the revised standard prEN 16909, “Ambient air - Measurement of elemental carbon (EC) and organic carbon (OC) collected on filters” was circulated to the WG members and sent to CEN for a formal vote in May. The document was circulated for approval in October and was published in March 2017.

Two new work items were discussed and finalised; "Measurement of elemental carbon (EC) and organic carbon (OC) in PM10 and PMcoarse" and "Equivalence of automatic measurements of elemental carbon (EC) and organic carbon (OC) in PM". The first covering the description of procedures including examination of previous data and literature search and the second covering practical testing when funding is available. The revised NWI proposal was approved by TC 264 in May 2017.

5.2.2 ISO Standards

ISO TC 24 SC4 WG 12

This group has published ISO 15900:2009, describing the general operation of SMPSs (i.e. not specifically aimed at monitoring ambient air), and ISO 27891:2015 describing the calibration of CPCs (again, not specifically for ambient air).
It is currently revising ISO 15900, to include a method for assessing the whole size spectrum, which will be similar to that in the second CEN TS, and also address measurements below 10 nm.

It is also writing a new standard, ISO 19996, which will describe how charge conditioners can be determined to be operating appropriately for their application. The charge conditioner (in the case of the network the 85Kr radioactive source) is assumed to bring the aerosol to a known charge distribution, i.e. a known probability of each particle size being zero-, singly-, or multiply-charged, as this distribution is assumed in the processing of the data to form a size distribution.

These standards will not lead directly to requirements for changes to network operations, but will help to improve various aspects of it.

6 REFERENCES

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

[2] NPL report "2016 Annual Report for the UK Black Carbon Network" 2017

[3] G.P. Ayers, Comment on regression analysis of air quality data, Technical Note, *Atmospheric Environment, 35 (2001) 2423 – 2425*

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

[5] Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe

[6] Number of Buses by Type of Bus in London, tfl-buses-type.xls, London Datastore, https://londondatastore-upload.s3.amazonaws.com/tfl-buses-type.xls

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

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

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

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

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

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

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