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AIRBORNE PARTICULATE CONCENTRATIONS AND NUMBERS IN THE UNITED KINGDOM

Annual report 2018

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1 INTRODUCTION

The UK Airborne Particulate Concentrations and Numbers Network currently operates four air pollution monitoring sites. The sites are located 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 particle number concentrations (CPCs) and size distributions (SMPSs), and Organic and Elemental Carbon, anion and cation concentrations. One Black Carbon monitor is included in this Network, separate from the larger Black Carbon Network. An Aerosol Chemical Speciation Monitor (ACSM) is operated by King's College London as part of the Contract, but this is not reported here.

This report shows a summary of the 2018 data, 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 2018 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). NPL has continued its role of overall coordination and management, together with QA/QC activities, which included site audits, instrument calibrations, data ratification and reporting.

2.2 NETWORK STRUCTURE

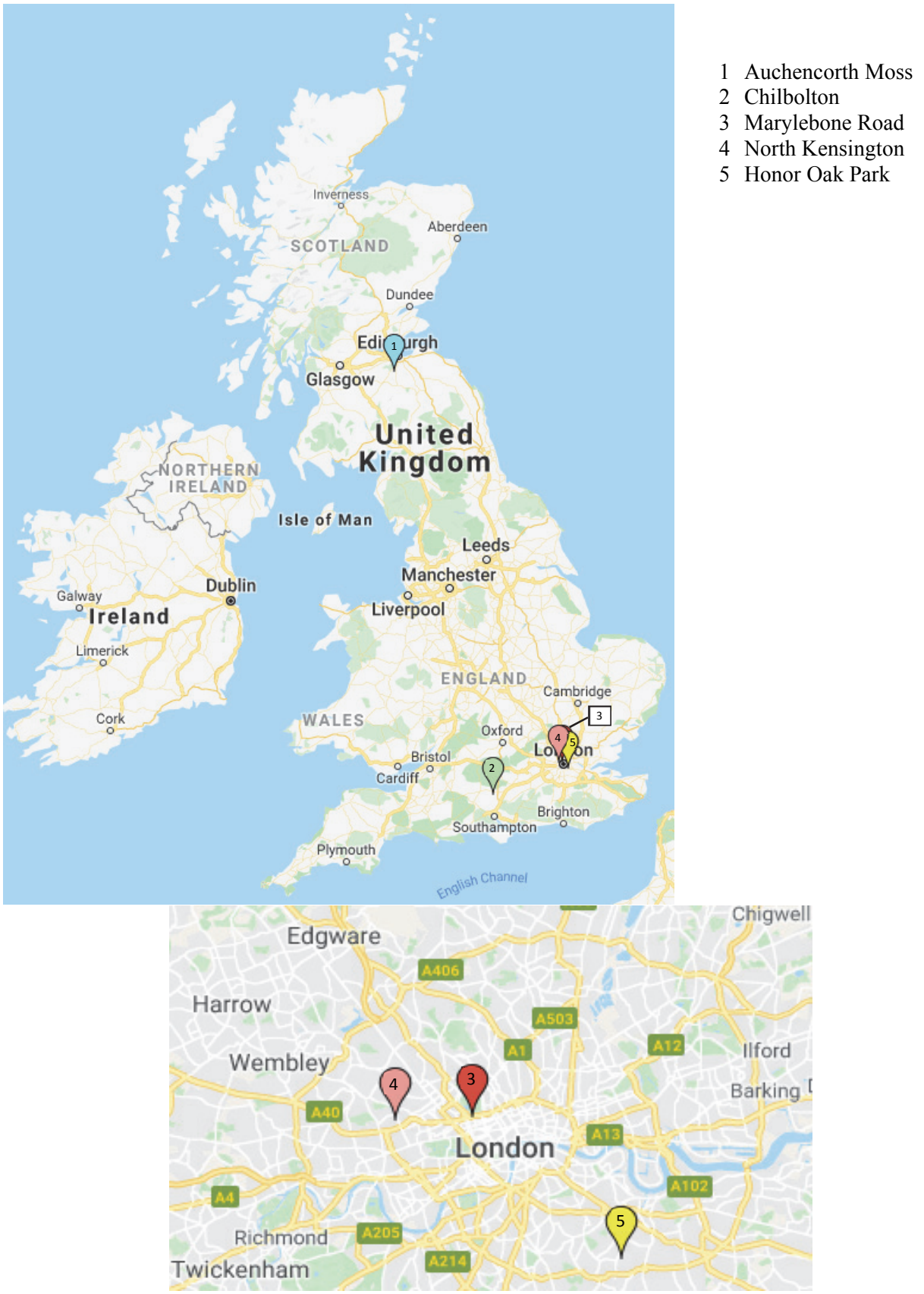
The measurement programme during 2018 is shown in Table 2-1. In November 2018, four of the samplers were relocated from North Kensington to the newly operational site, Honor Oak Park. *During this site change, the URG PM10 head was changed to a PM2.5 head.

Table 2-1 Network structure in 2018

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 background)		X	X	X	X	X
Auchencorth Moss (Rural background)			X			
London Marylebone Road (Urban Roadside)	X	X			X	X
London North Kensington (Urban background)	X	X			X	X
London Honor Oak Park (Urban background)	X*	X			X	X

Site locations are shown in Figure 2-1 and site details are available through

https://uk-air.defra.gov.uk/interactive-map .



1 Auchencorth Moss
2 Chilbolton
3 Marylebone Road
4 North Kensington
5 Honor Oak Park

Figure 2-1 Network sites in 2018

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 3772-CEN. The new 3772-CEN instruments were installed at the sites in June 2017, however, due to communication issues the Chilbolton CPC produced no data in 2017. A site move for the CPC and SMPS instruments from North Kensington to Honor Oak Park happened in mid-November 2018 with data capture up and running in December 2018.

The CPC instrument works by passing the continuous air 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. These CPCs are sensitive to particles from about 7 nm up to several μm in size, and have a concentration measurement range from zero to 50 000 cm^{-3}. The model has been developed to comply with the requirements of CEN/TS 16976:2016. At all concentrations each particle is counted individually.

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

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.

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 was originally controlled and monitored through drying units designed by NPL, which used Nafion driers. When the new Condensation Particle Counter (CPC) TSI model 3772-CEN instruments were installed, new drier systems manufactured by TSI were installed with them. After some initial teething problems, a solution of a TSI Nafion drier system for the stand-alone CPC and a separate NPL designed Nafion drier system for the SMPS was employed.

Figure 2-2 shows this equipment at a typical site.

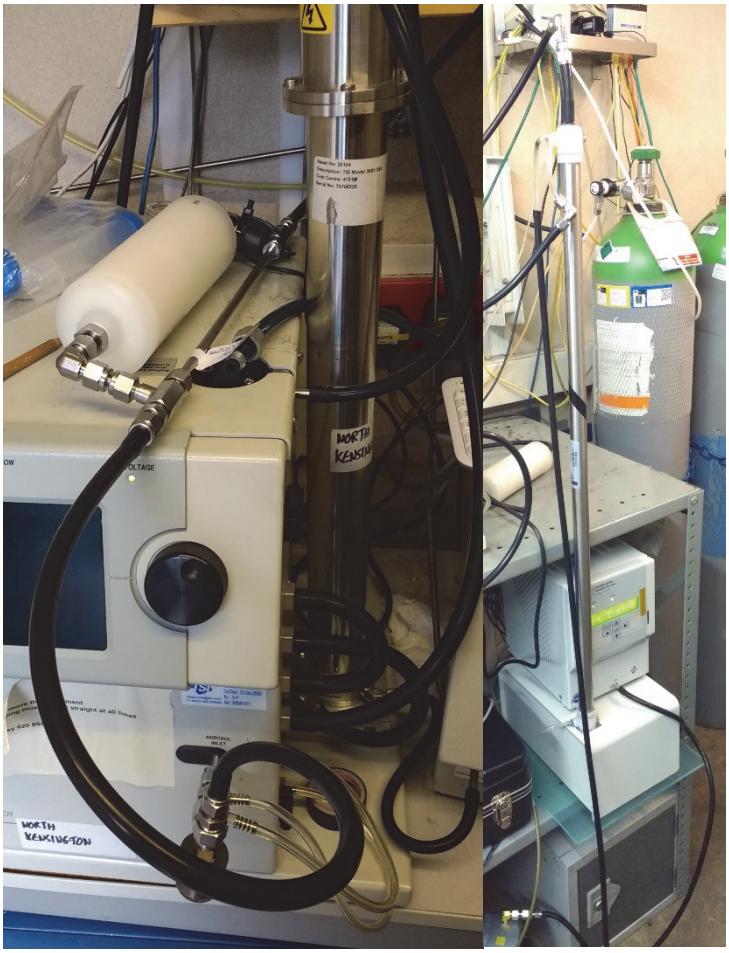


Figure 2-2 Typical configuration of CPC, SMPS and drying units at the Network sites

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

The analysis was carried out using the Sunset Laboratory Inc. thermal/optical carbon analyser (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, as specified in EN 16909:2017. The protocol also specifies that the transmittance correction must be used.

The temperatures are calibrated using the Sunset Laboratories calibration kit.

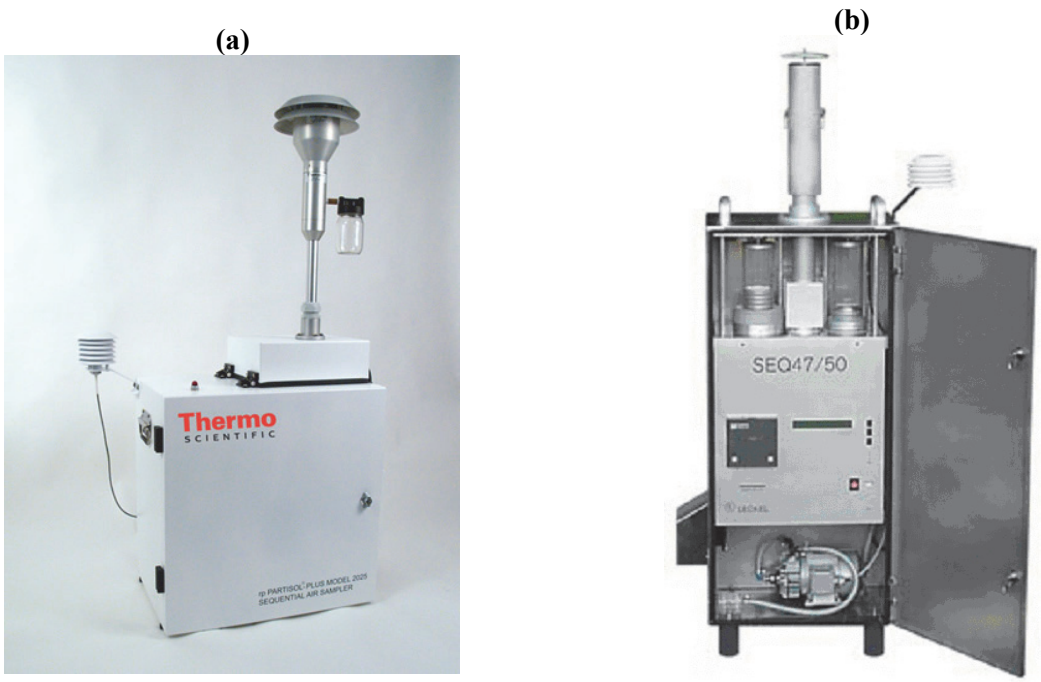


Figure 2-3 (a) Thermo Partisol 2025 sampler (b) Leckel SEQ47/50 sampler

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

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

Aethalometers quantify Black Carbon on filter samples based on the transmission of light through a sample. The sample is collected onto a quartz tape, and the change in 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 not presented in this report, but in the 2018 Black Carbon Network report alongside the aethalometers in that network.[2]

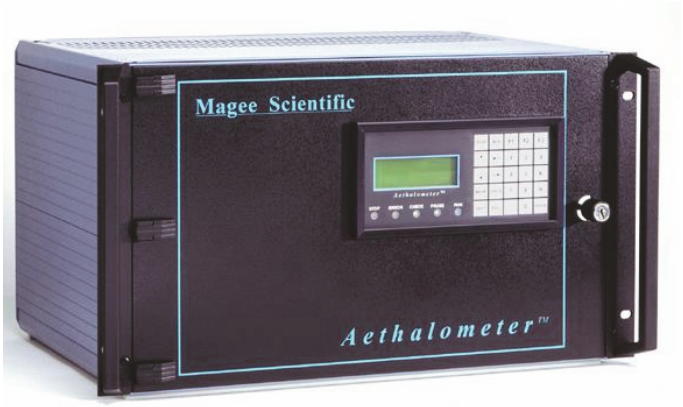


Figure 2-5 Magee Scientific aethalometer

2.3.5 URG – AIM 9000B (PM_{10} and $PM_{2.5}$ 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 used in the field includes two Thermo Fisher Scientific Dionex ICS-2100 Ion

chromatography systems (ICS), both of which has its own eluent generator to facilitate automated running. The eluent used for cation measurements is methanesulfonic acid (MSA) and the eluent used for anion measurement is potassium hydroxide. The 2000 series ICS also allows ramps in eluent concentration to speed up analysis for the longer retention time species.

The sampler draws air through a sharp cut cyclone inlet head designed to be size-selective. Dependent on the head used, either particulate matter with diameters less than 2.5 um (PM2.5) or 10 um (PM10) are drawn in. The sampler draws a volumetric flow by measuring the pressure drop across an orifice, along with the orifice temperature, ambient temperature and pressure. The ambient air sample is then 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 two Ion Chromatography Systems.

The instrument samples for 55 minutes during each hour then the two Ion Chromatography systems analyse 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 output. The two instruments in this Network were originally installed with a PM_{10} size selective monitoring head for consistency with the previous anions sampling equipment. When the sampler stationed at North Kensington was moved to Honor Oak Park and began sampling on 27 November 2018, and the size selective head was changed from PM_{10} to $PM_{2.5}$ (the change to $PM_{2.5}$ for Marylebone Road occurred later, on 9 January 2019).

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 an independent team from NPL.
- Regular calibrations are carried out automatically, or manually by the LSO or NPL, and calibration checks at are carried out at regular intervals throughout the year by the NPL site audit team, the Equipment Support Unit (ESU), and/or the LSO (instrument dependent). All this calibration data is used to produce an appropriate scaling factor to apply to the measurement data.
- For OCEC analysis, 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

Since January 2009, the network 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.

The 2025 Partisols at Chilbolton, North Kensington (Honor Oak Park after 30 November 2018), and Marylebone Road were serviced by the ESU, Air Monitors during 2018. The Leckel SEQ47/50s at Auchencorth Moss and Chilbolton were serviced by the ESU, Enviro Technology Services. These service procedures include replacing old or worn parts, temperature and flow calibrations, leak tests and pump refurbishment.

The Sunset Laboratory Inc. thermal/optical carbon analyser is serviced annually by a Sunset Laboratory Inc. employed engineer, as per the manufacturer’s guidelines. The service involves replacing worn parts and a full test and calibration. NPL run a daily calibration check using a lab blank filter and a filter spiked with a traceable standard solution.

The URG-AIMs at North Kensington (Honor Oak Park after 27 November 2018), and Marylebone Road were serviced by the ESU, Enviro Technology Services during 2018. NPL continue to make the ion chromatography system calibration standards from traceable stock standard solutions and carry out quarterly calibrations.

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 (rural background), London North Kensington (urban background) and London Marylebone Road (urban roadside). The last day of sampling at North Kensington was 12 November 2018; the Partisol was moved to the new urban background site at London Honor Oak Park, and began sampling on 30 November 2018.

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 2018 were 97%, 93% and 85% at Chilbolton, London North Kensington/Honor Oak Park combined, and London Marylebone Road, respectively. The time series of OC, EC and TC (Total Carbon – the sum of OC and EC) are displayed in Figure 4-1 and Figure 4-2 for all the sites. Concentrations for EC and OC are shown for thermal/optical transmission (TOT), as specified by EN 16909:2017. Data are reported as the mass of carbon atoms per unit volume of air.

Further information on London pollution episodes identified during 2018 is available at KCL's London air website http://www.londonair.org.uk.

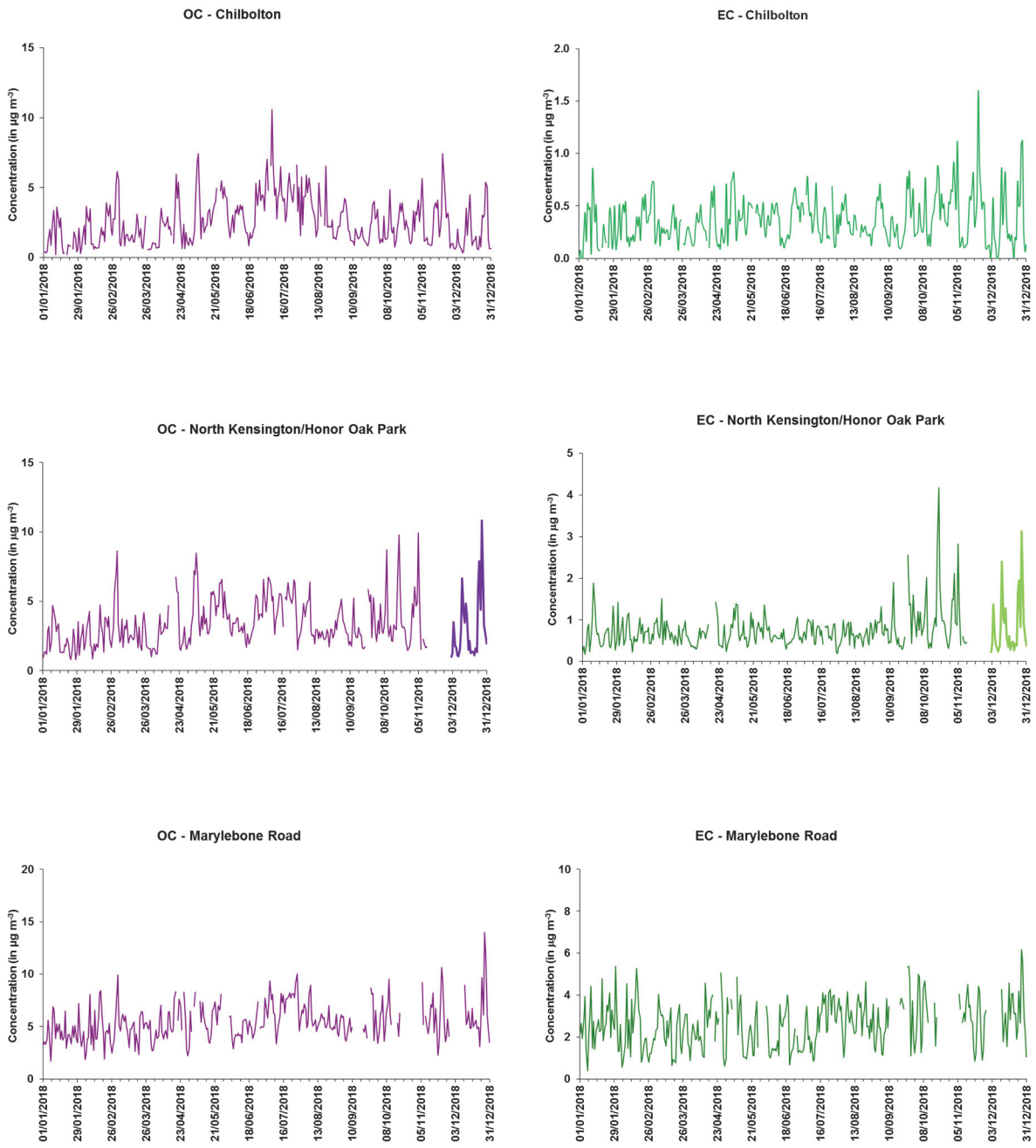


Figure 4-1 PM_{10} OC and EC concentrations at Chilbolton, *North Kensington/Honor Oak Park and Marylebone Road during 2018. The sampler at North Kensington was relocated to Honor Oak Park and began sampling on 30 November 2018. The data relating to Honor Oak Park are shown in bold.

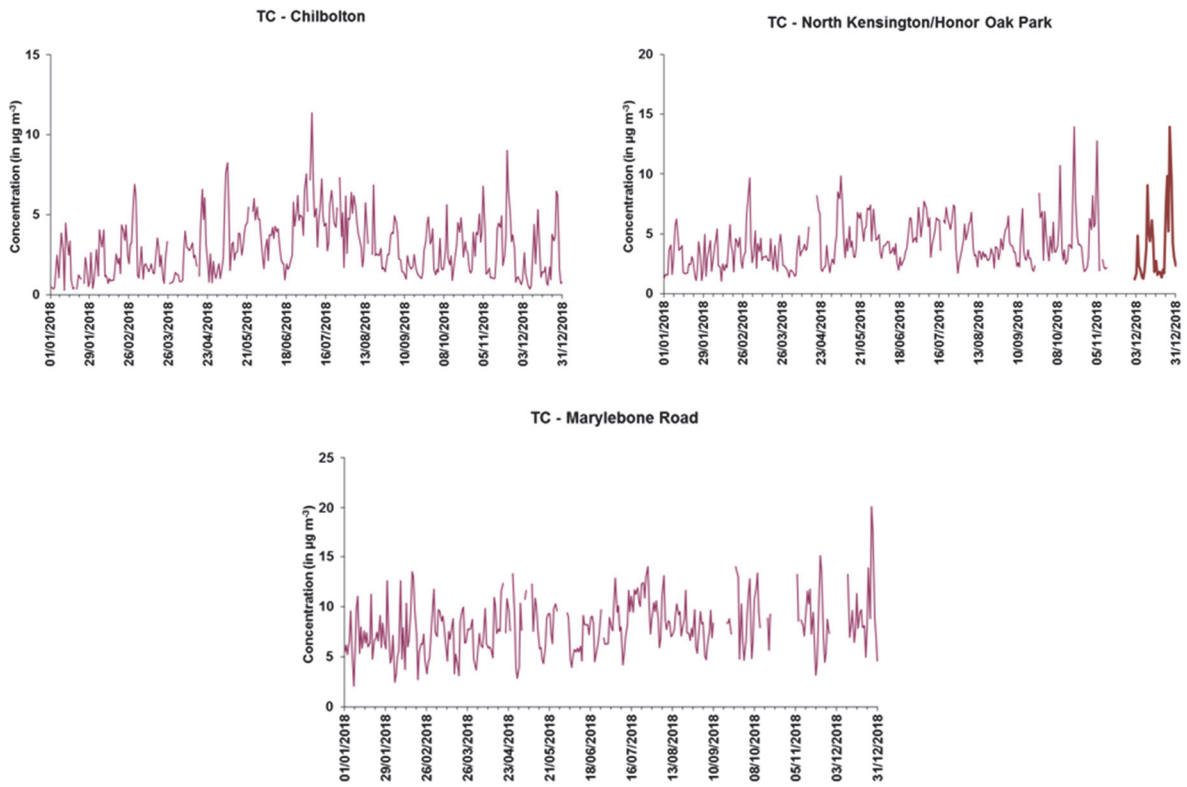


Figure 4-2 PM_{10} TC concentrations at Chilbolton, *North Kensington and Marylebone Road during 2018. The data relating to Honor Oak Park are shown in bold.

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 2.5µm 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 4-3. The regression is calculated according to the Reduced Major Axis (RMA) method.[3]

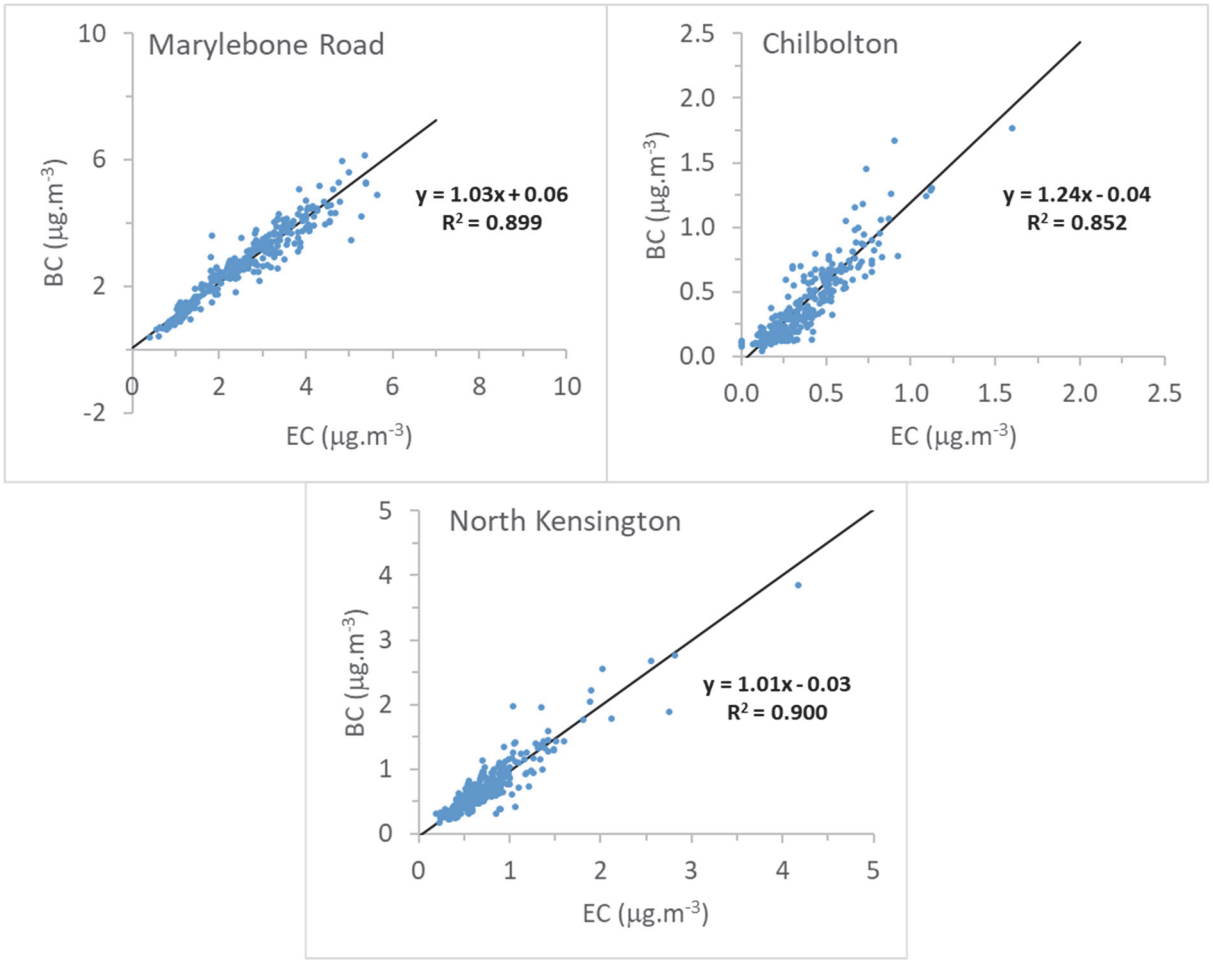


Figure 4-3 Comparison between $PM_{2.5}$ BC and PM_{10} EC at the 3 sites in 2018

It can be seen that there is a generally good linear relationship between the Elemental Carbon and Black Carbon concentrations ($R^2 > 0.85$ at all sites), and with comparable slopes. 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 have historically been higher than the EC measurements by about 25%.[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
2017	0.92 x + 0.02	0.827	1.04 x – 0.01	0.939	1.15 x + 0.02	0.902
2018	1.24 x – 0.04	0.852	1.01 x – 0.03	0.900	1.03 x + 0.06	0.899

*There was not enough BC data collected at Harwell in 2009 to form a reliable relationship as the Aethalometer was only installed in November 2009. 2016, 2017 and 2018 data are from Chilbolton and so may not be directly comparable to the Harwell data in 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 2018 was 100% for Chilbolton and 90% 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 former Harwell site.

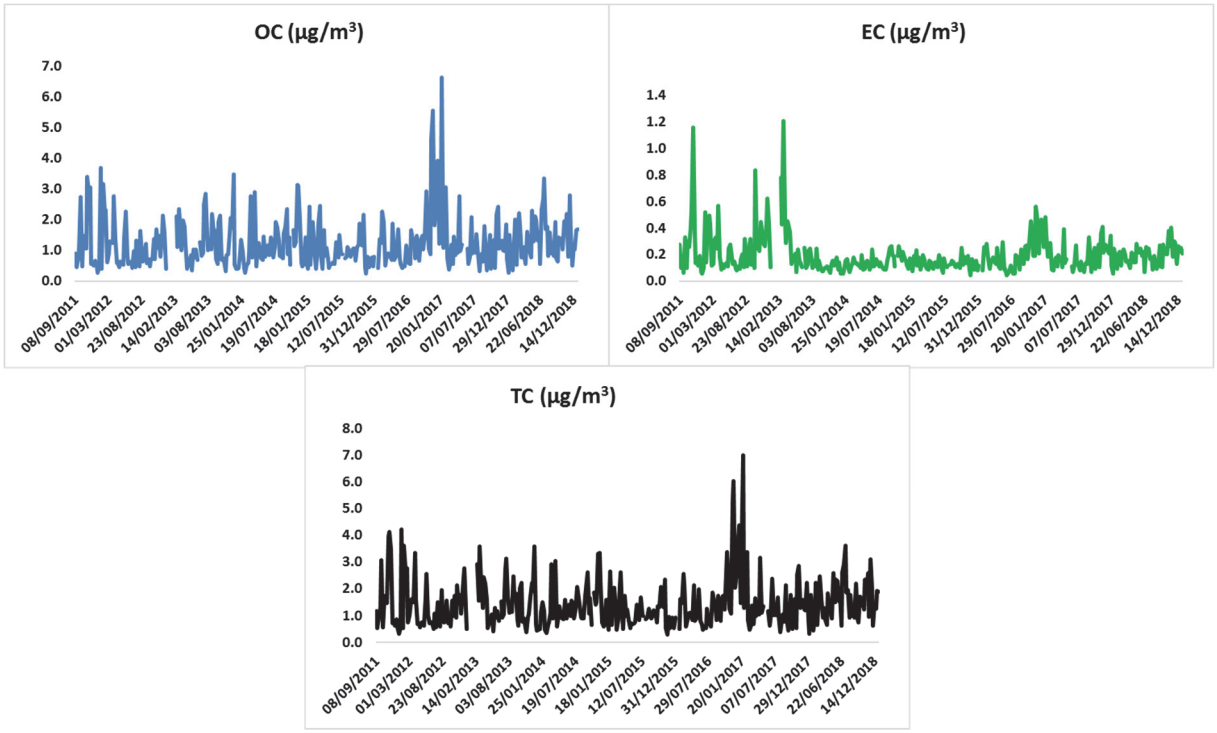


Figure 4-4 Time series of OC, EC and TC in the $PM_{2.5}$ fraction at Harwell/Chilbolton since the installation of the sampler up to the end of 2018 (weekly samples) (µg/m³). The sampler moved from Harwell to Chilbolton in February 2016.

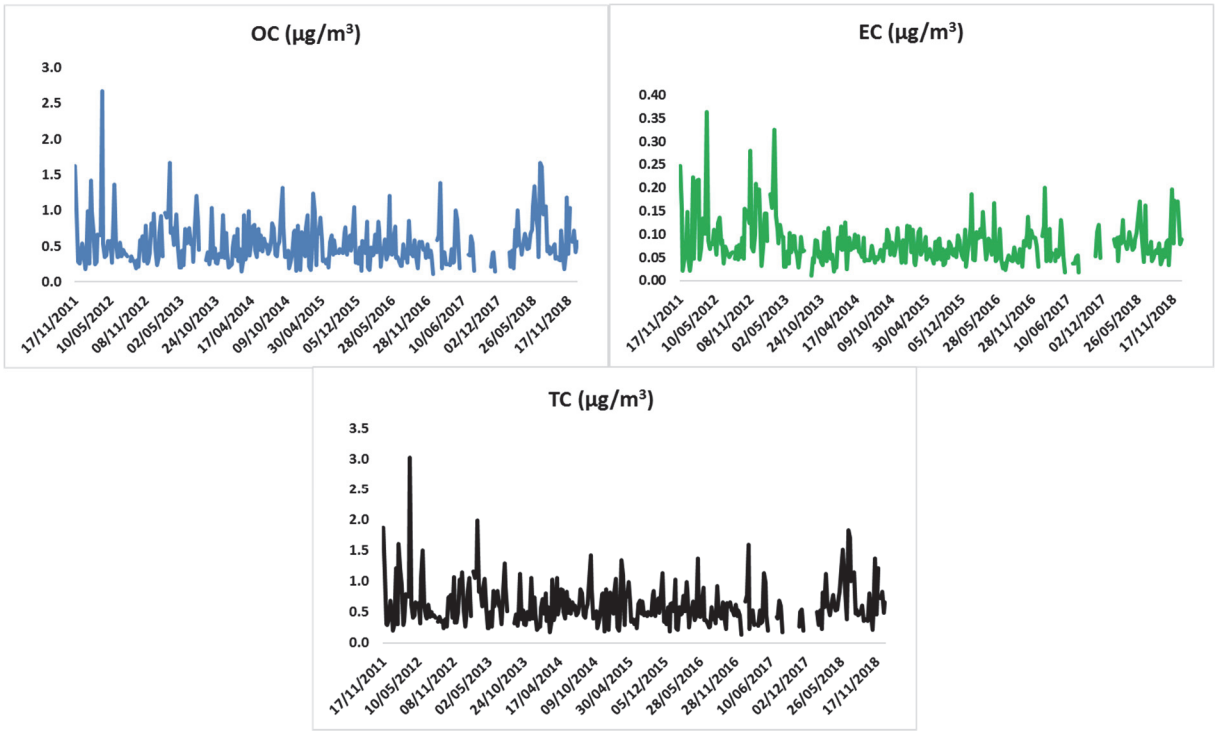


Figure 4-5 Time series of OC, EC and TC in the $PM_{2.5}$ fraction at Auchencorth Moss since the installation of the sampler up to the end of 2018 (weekly samples) (µg/m^3)

The $PM_{2.5}$ carbon concentrations at Chilbolton were compared with weekly averages of the daily measurements of the PM_{10} fraction from the Partisol (Figure 4-6).

As seen in previous years, 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.

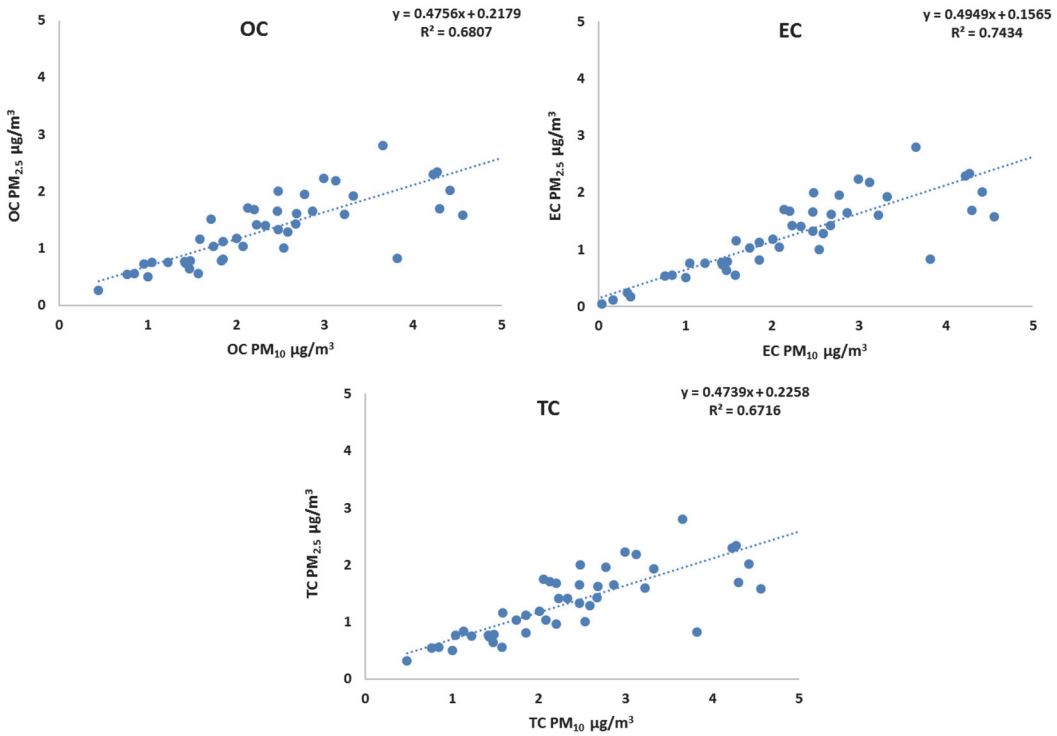


Figure 4-6 Comparison between PM_{10} OC/EC weekly averages and $PM_{2.5}$ OC/EC at Chilbolton in 2018

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 with PM10 size-selective heads. 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 PM10 anion measurements were made on this Network at Harwell, North Kensington and Marylebone Road using a manual, filter-based, method.

In 2011, this manual method was replaced by automatic URG-AIM instruments at, North Kensington and Marylebone Road, giving a higher time resolution measurement and adding information on cation content of PM_{10}. At Harwell another PM10 anion and cation measuring system, a MARGA instrument, was already in operation under a different Network. In January 2016, the MARGA at Harwell was moved to Chilbolton. In November 2018, the URG at North Kensington was moved to Honor Oak Park and the size selective monitoring head was changed from PM_{10} to $PM_{2.5}$.

The 2018 annual data capture (averaged using all of the eight ions) was 62% for Marylebone Road and 52% for North Kensington/Honor Oak Park combined.

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

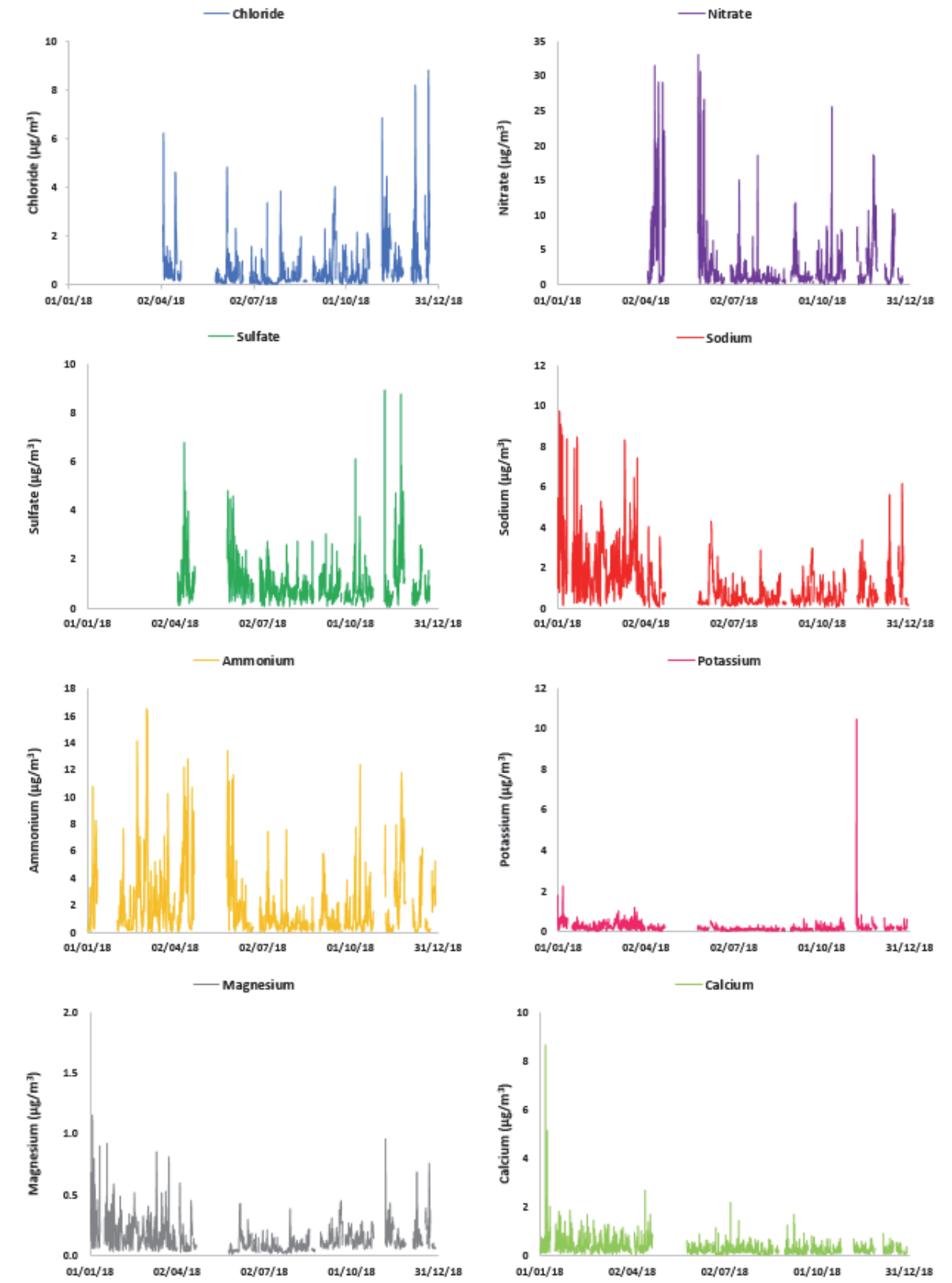


Figure 4-7 Time series for PM_{10} ion concentrations at Marylebone Road in 2018

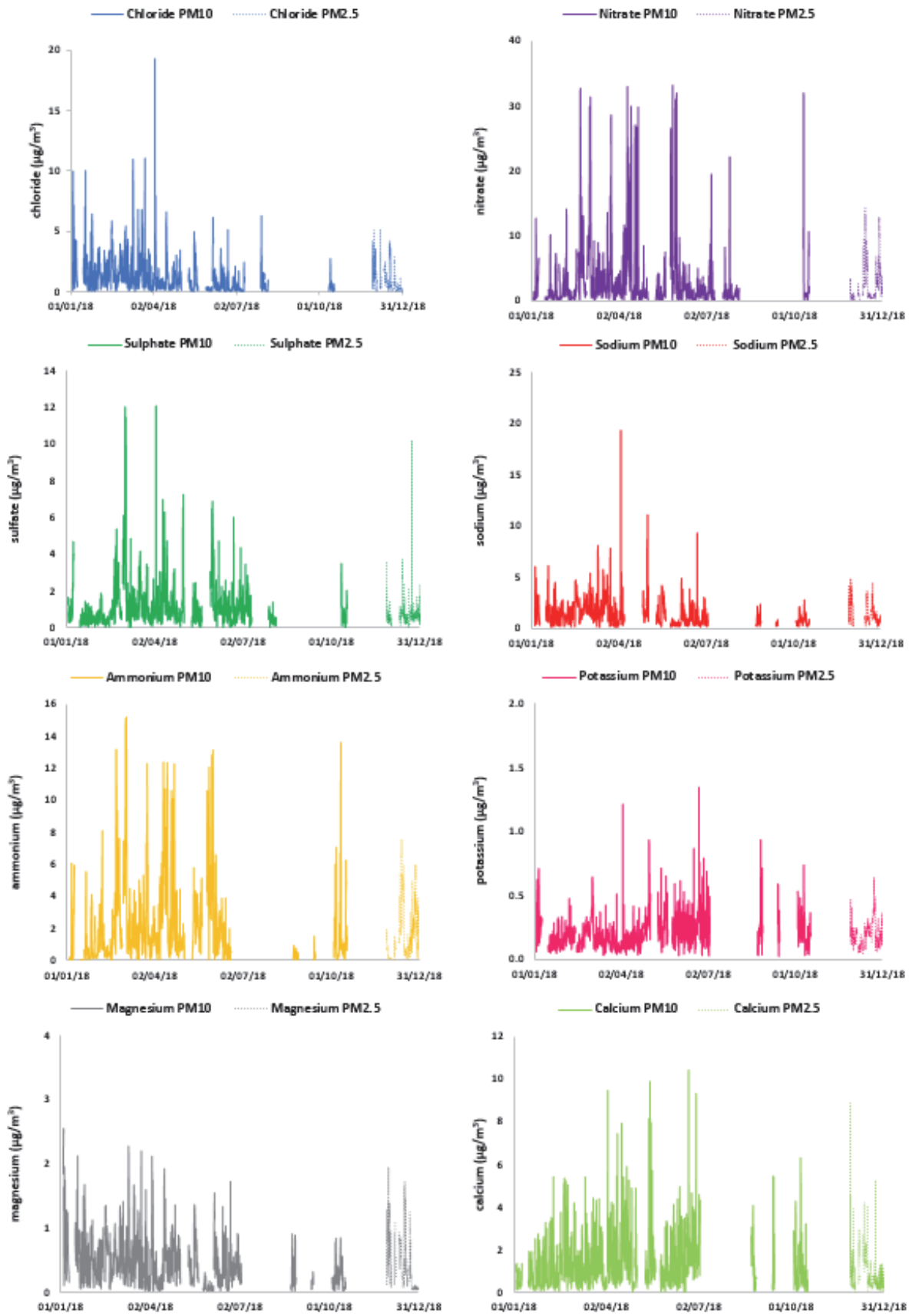


Figure 4-8 Time series for ion concentrations at North Kensington/Honor Oak Park in 2018

4.4 PARTICLE NUMBER CONCENTRATIONS AND SIZE DISTRIBUTIONS

4.4.1 Particle number concentrations (CPCs)

Time series of hourly particle number concentrations (between about 7nm and several micrometres in diameter) measured at network sites during 2018 are shown in Figure 4-9.

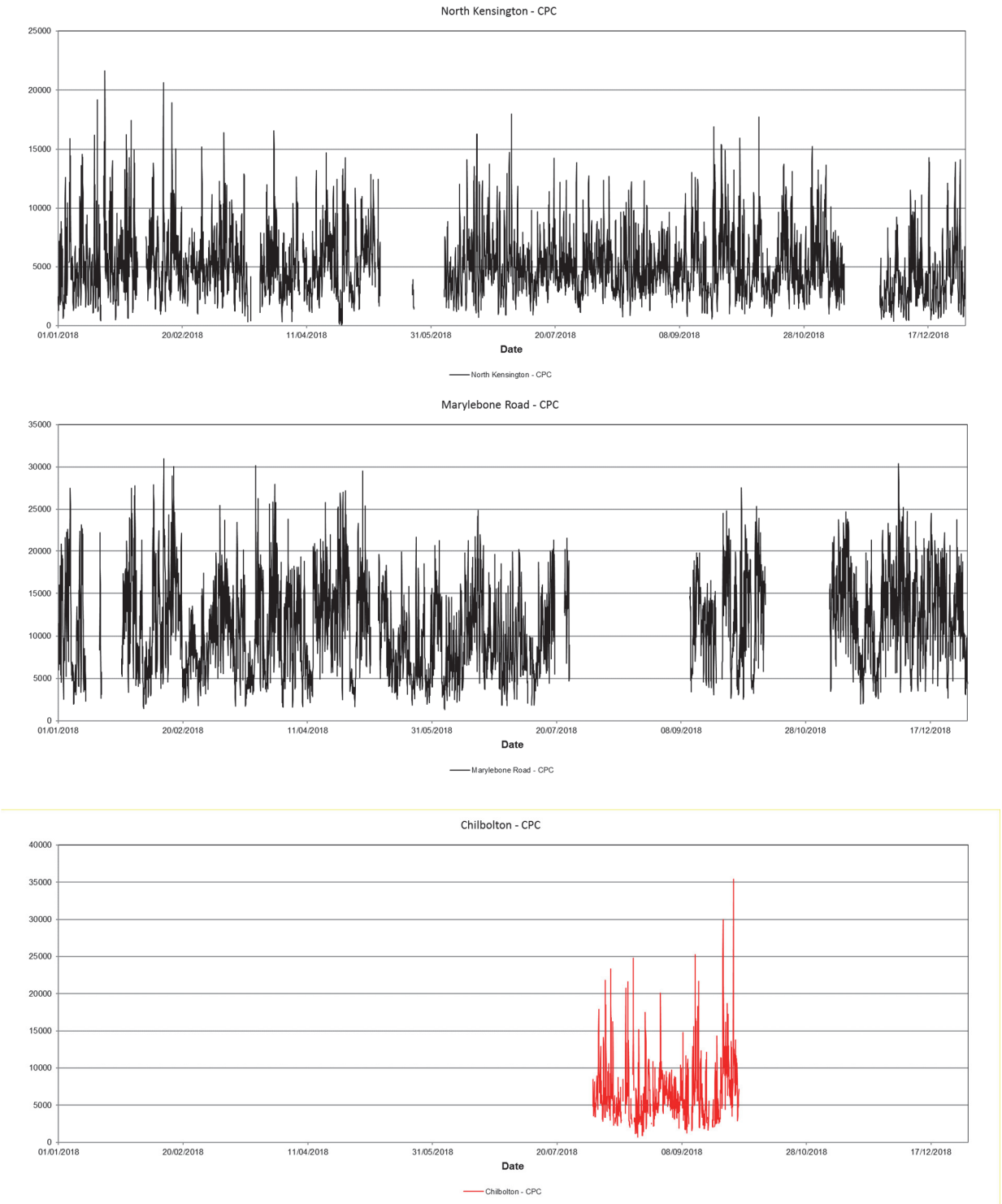


Figure 4-9 Hourly particle number concentrations at North Kensington (including Honor Oak Park from November), Marylebone Road and Chilbolton in 2018

The average data captures for the CPC instruments during 2018 were 87%, 73%, 14% and 100% respectively for North Kensington, Marylebone Road, Chilbolton and Honor Oak Park.

4.4.2 Particle size distributions

The average data captures for the SMPS instruments during 2018 were 68%, 29%, 44% and 100% respectively for North Kensington, Marylebone Road, Chilbolton and Honor Oak Park. This equates to 71% data coverage for North Kensington and Honor Oak Park combined as Urban Background sites in London.

The production of data from SMPS instruments is a complicated process, summarised schematically in Figure 4-10. 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.

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 4-11. The overall effect of the two corrections is to increase the particle number counts at smaller sizes and to increase the total particle count.

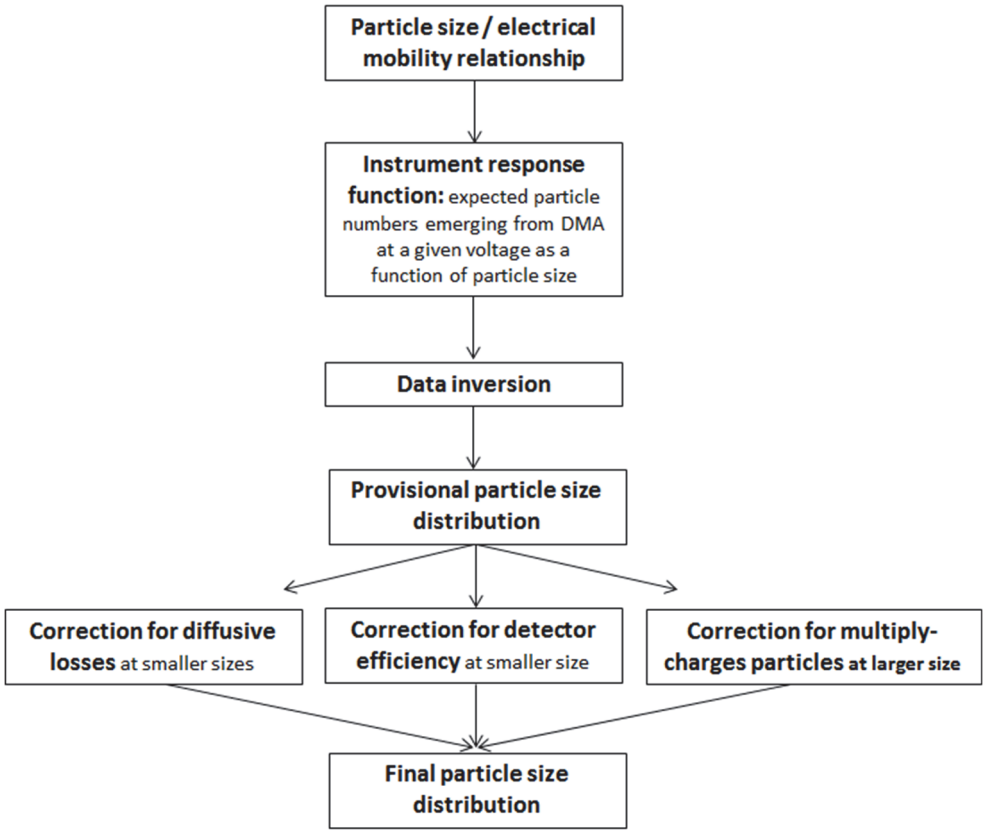


Figure 4-10 Schematic of the internal data processing of SMPS measurements in the Network

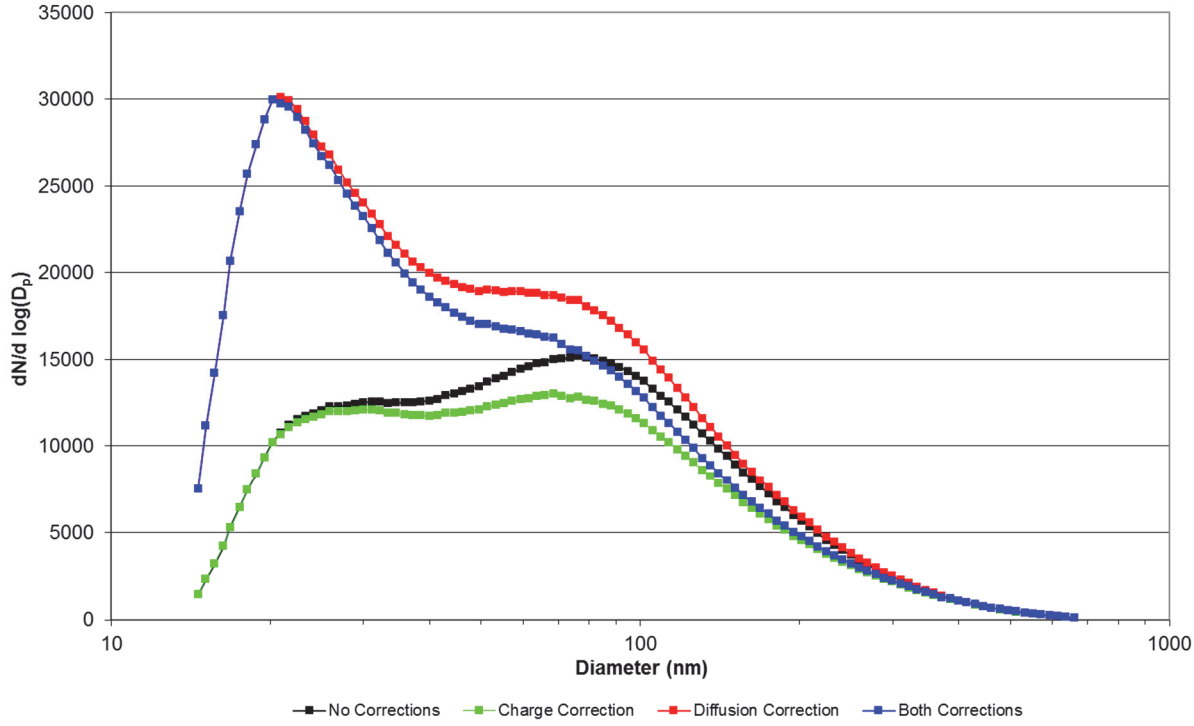
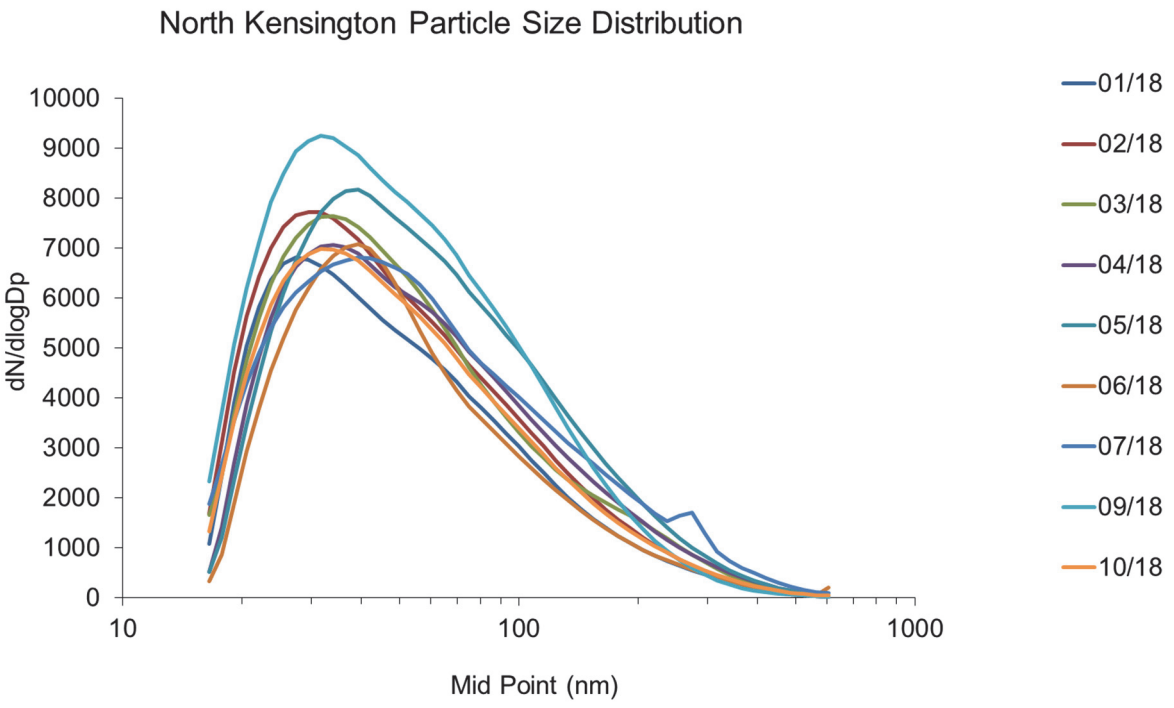
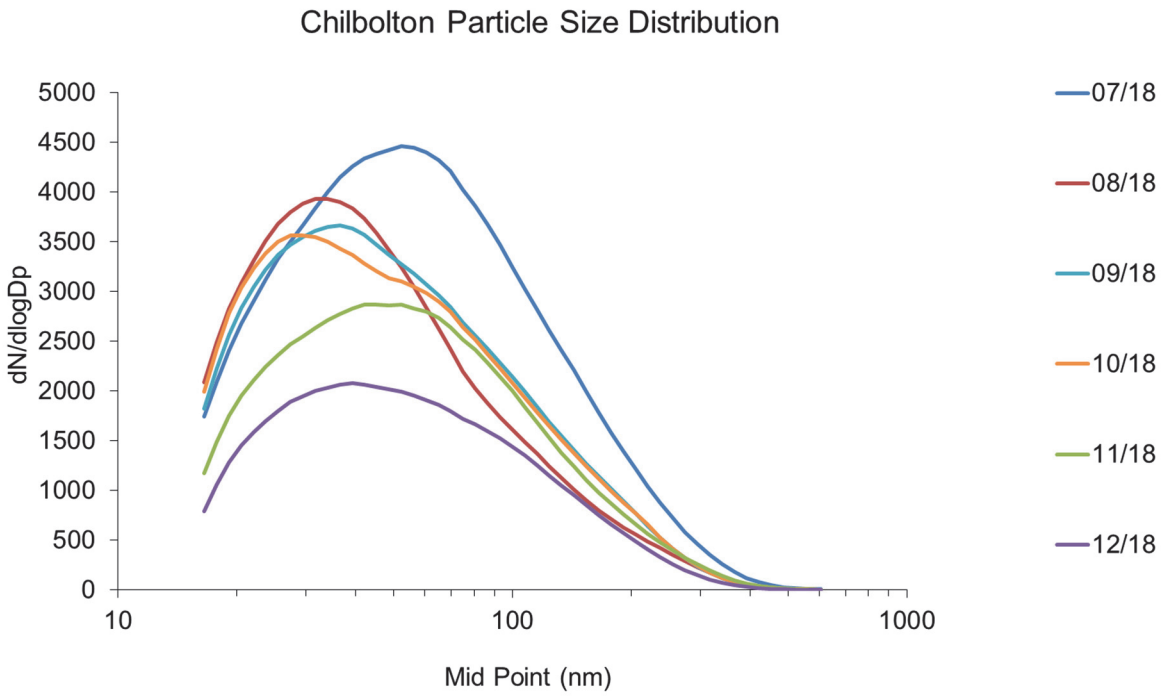
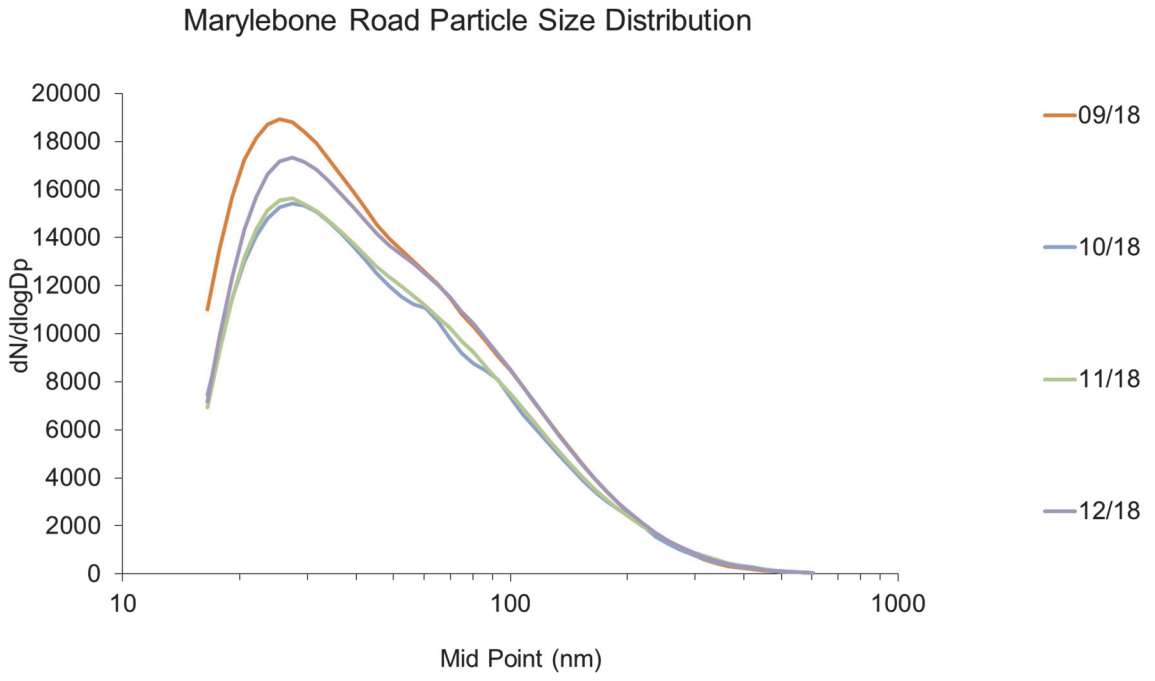


Figure 4-11 Effect of the multiple charge, the diffusion loss and their combined correction in the SMPS size spectrum

The counts in each particle size bin measured during 2018 are presented as monthly averages in Figure 4-12 and as annual averages in Figure 4-13.




Chilbolton Particle Size Distribution
dN/dlogDp
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10
100
1000
Mid Point (nm)
07/18
08/18
09/18
10/18
11/18
12/18


Marylebone Road Particle Size Distribution
dN/dlogDp
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
10
100
1000
Mid Point (nm)
09/18
10/18
11/18
12/18

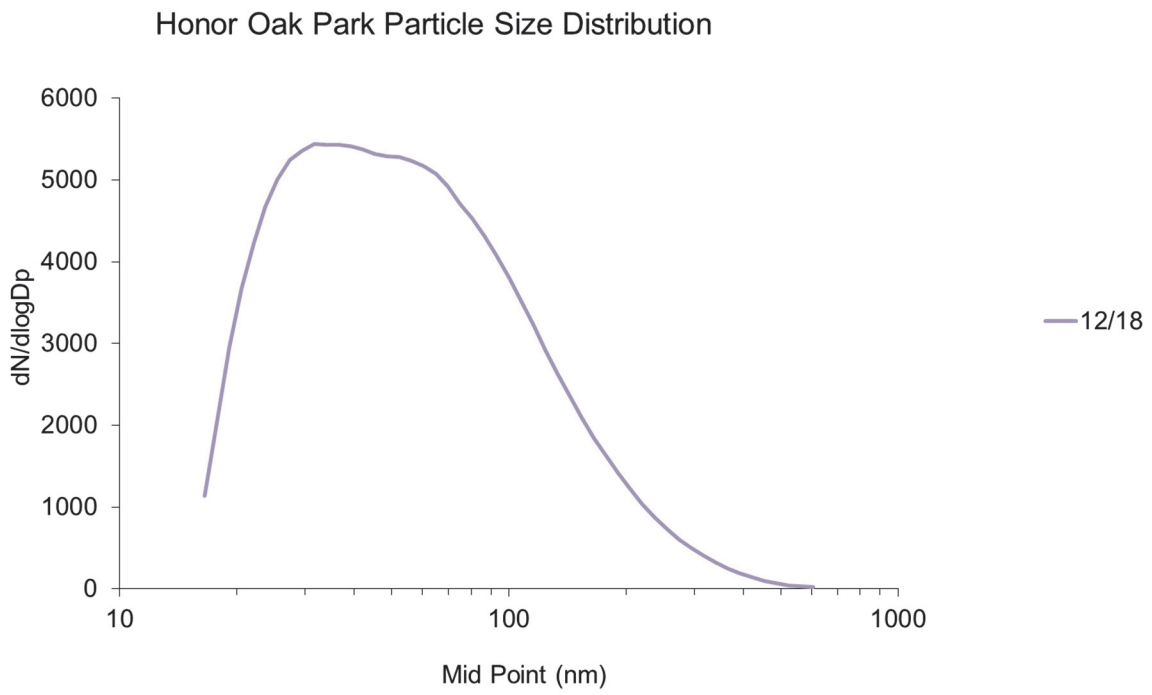
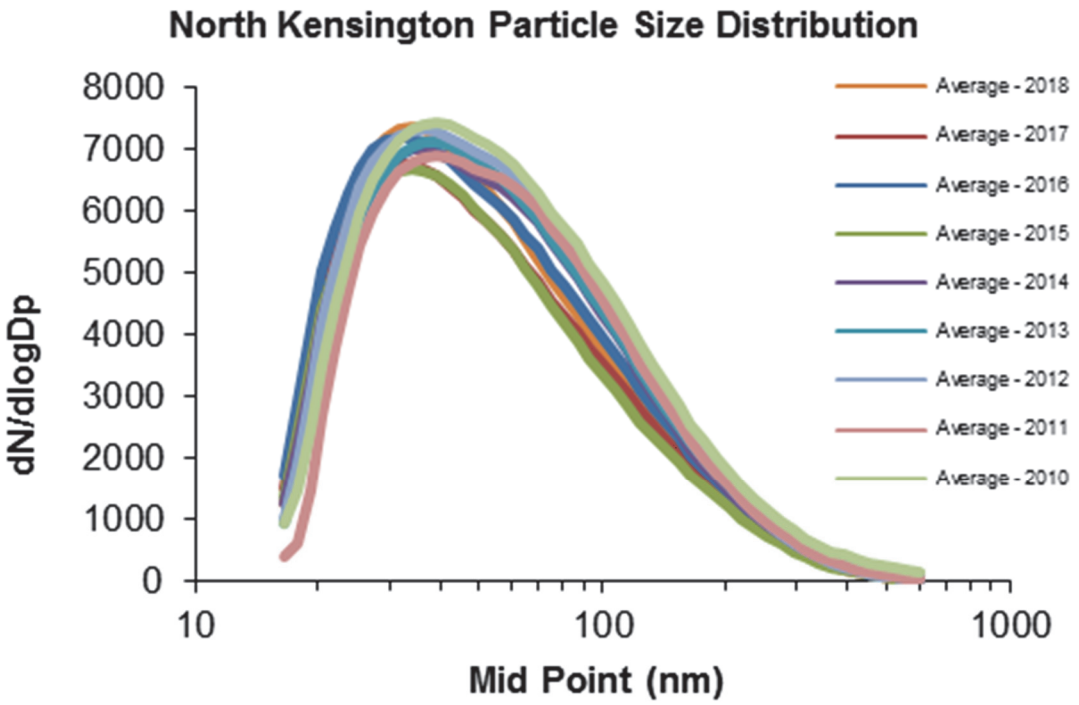


Figure 4-12 Monthly averaged particle size distributions at the Network sites during 2018



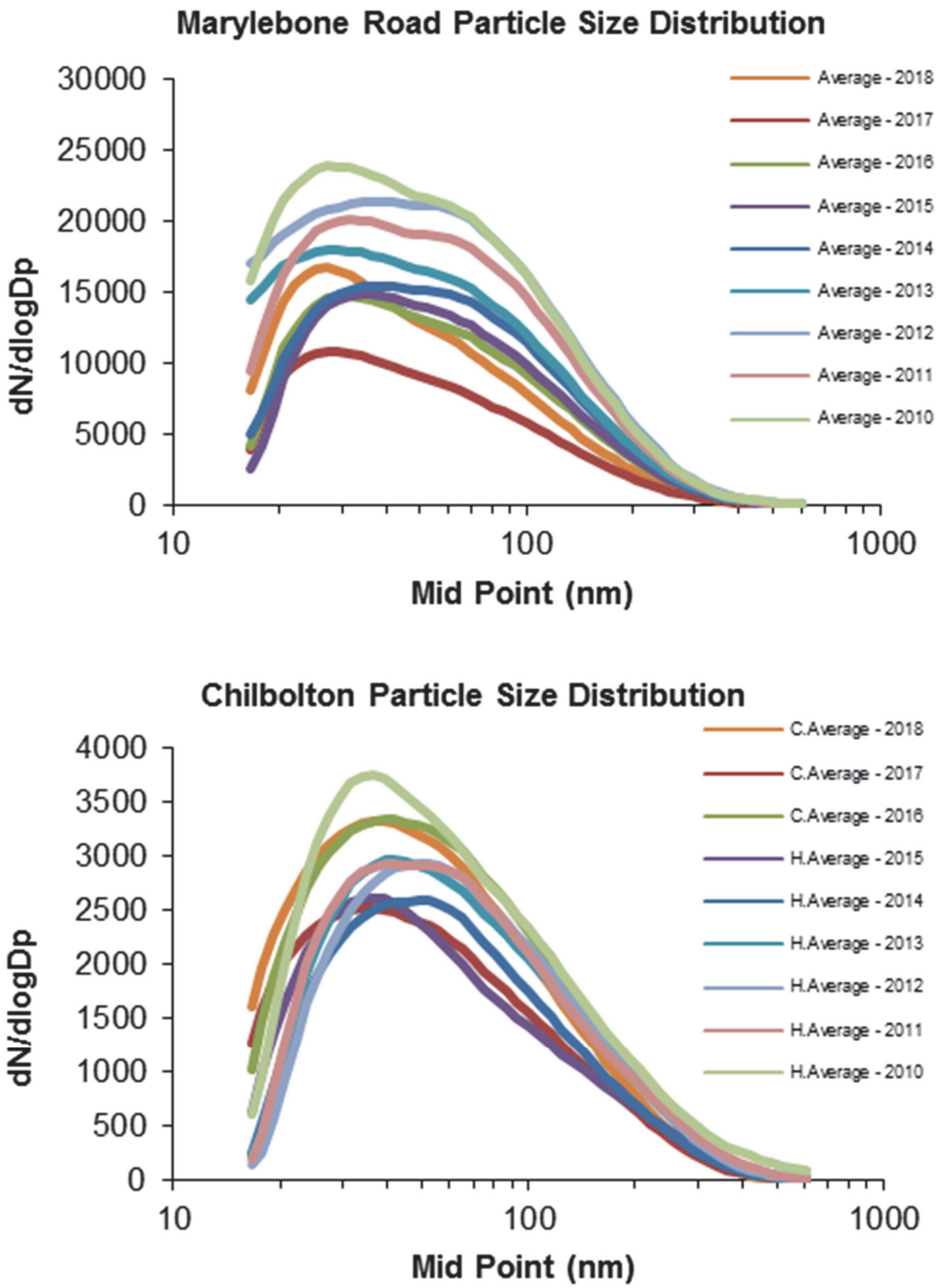


Figure 4-13 Comparison of the 2010 to 2018 annual-averaged size distributions

4.5 LONG TERM TRENDS

4.5.1 Carbon measurements

Figure 4-14 shows the long-term trends in annual averages for OC/EC/TC measurements. The Partisol instrument at North Kensington was sampling at site up until 12 November 2018 and then resumed sampling at Honor Oak Park on 30 November. The data from Honor Oak Park in 2018 is excluded from these charts.

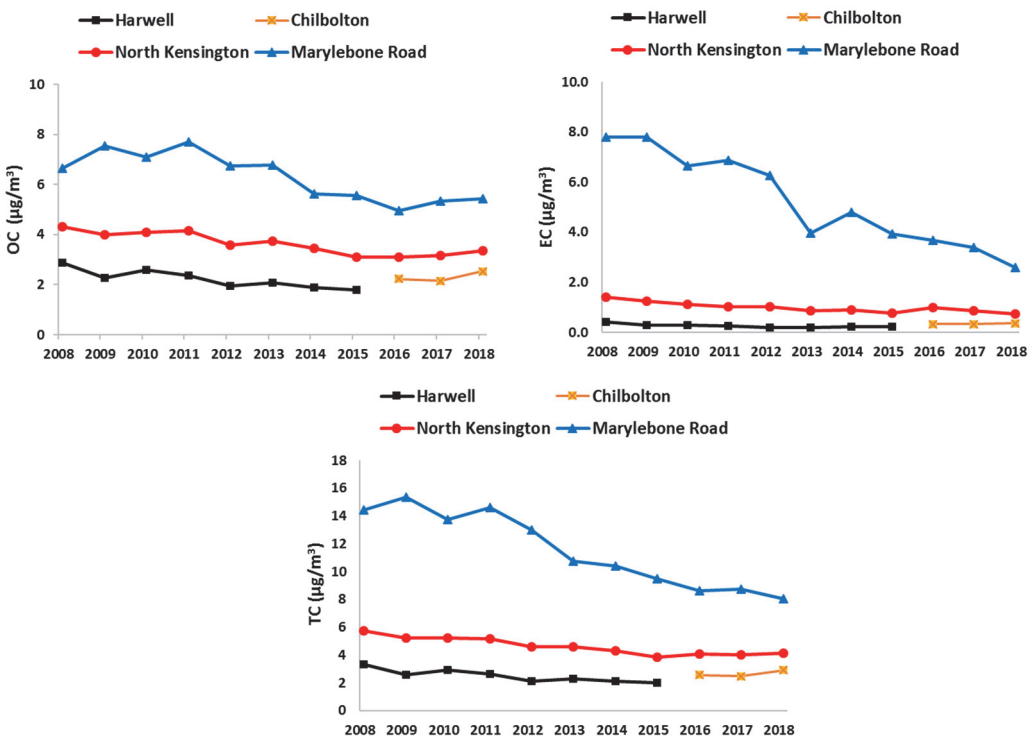


Figure 4-14 Annual trends for OC, EC and TC measurements.

Figure 4-1 shows the annual Black Carbon and Elemental Carbon concentrations along with the average daily traffic flow past the site at Marylebone Road.

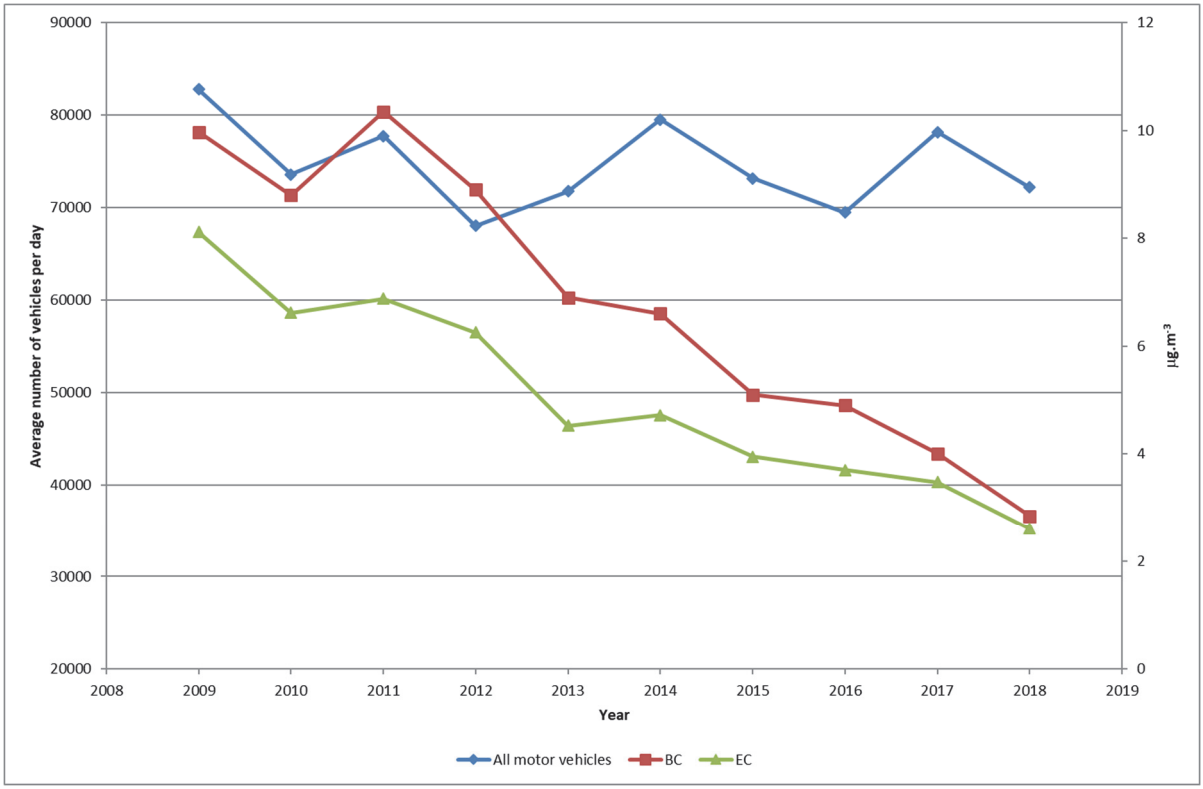


Figure 4-15 Annual Average Black Carbon, Elemental Carbon and Motor Vehicles per day at Marylebone Road for the period 2009 – 2018

It can be seen that the changes in Black Carbon and Elemental Carbon concentrations broadly followed 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 reduced over the last 7 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 2018. 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 4-16 is Figure 4-1 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 2018[6]

		Number of buses								
Bus Type	**Drive train type**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**
New Routemaster	Hybrid	0	0	5	8	168	432	736	953	1,000
Routemaster	Diesel	18	18	19	20	19	19	10	10	10
Artic	Diesel	320	260	0	0	0	0	0	0	0
Single deck	Diesel	2,676	2,670	2,661	2,608	2,606	2,662	2,617	2,612	2,587
	Fuel Cell/Hybrid	0	5	5	5	8	8	8	8	10
	Hybrid	27	27	33	28	23	23	18	18	13
	Electric	0	0	0	0	2	8	17	66	91
Double deck	Diesel	5,554	5,487	5,787	5,696	5,296	5,026	4,794	4,380	3,453
	Hybrid	29	79	233	352	643	799	981	1,564	2,227
	Electric	0	0	0	0	0	0	5	5	5
TOTAL		8,624	8,546	8,743	8,717	8,765	8,977	9,186	9,616	9,396
% low emission		0.65	1.30	3.16	4.51	9.63	14.15	19.21	27.18	35.61

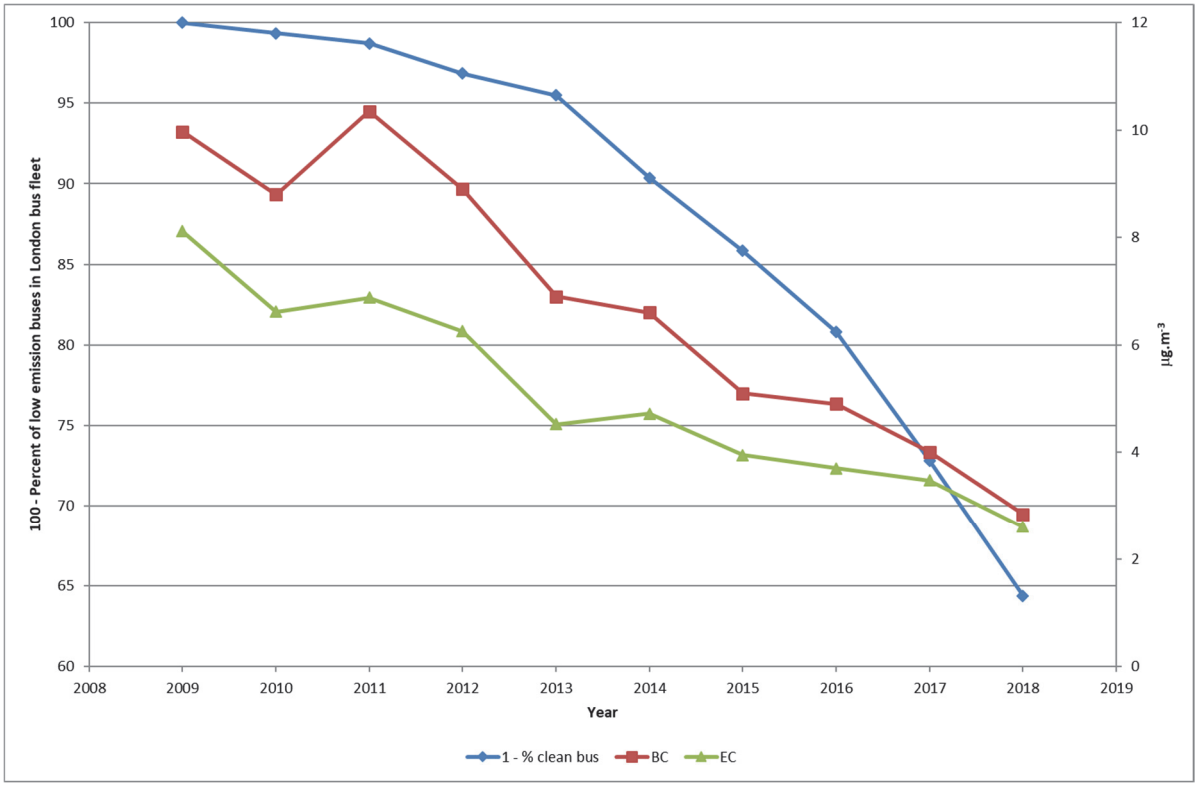


Figure 4-16 Annual Average Black Carbon, Elemental Carbon and [100 – percentage of low emission buses in the London bus fleet] for the period 2009 – 2018.

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. The fall from 2012 to 2015 appears to mirror the clean buses, but as the number of these continues to rise sharply the results on the BC and EC concentrations have tailed off. This suggests that there is another factor preventing concentrations continuing to fall and further increase in clean buses will not have a significant effect.

4.5.2 PM10 anion measurements

Figure 4-17 shows long-term trends for the anion species.

Between 2003 and 2010, the PM10 anion concentrations were measured using a manual, filter-based, method at Harwell, Marylebone and North Kensington. Ratified data were not available for the three sites in 2010 and two sites in 2011. In 2011, the method was changed to automatic URG-AIM instruments at North Kensington and Marylebone Road, and at Harwell the relevant data from the MARGA network instrument was used. In January 2016, the MARGA was moved to Chilbolton. In November 2018, the URG at North Kensington was moved to Honor Oak Park and the size selective head was changed from PM_{10} to $PM_{2.5}$, but this single month of data is not included in the graphs below.

After the change to automatic instruments in 2011, and the move from Harwell to Chilbolton in 2016, some discontinuity can be observed.

Overall, Chloride has been at a steady level apart from a spike in 2008, Nitrate has shown a slight downward trend, and Sulphate has shown a distinct downward trend but has levelled off over the last 3 years.

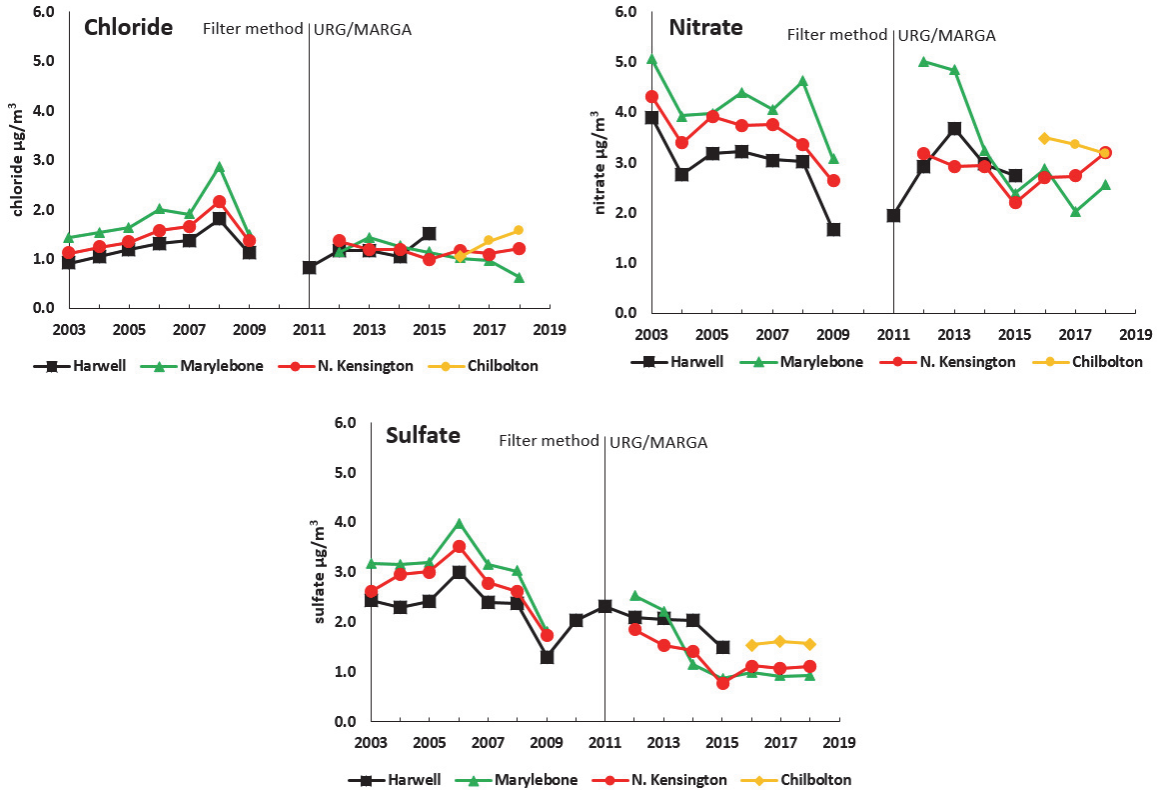


Figure 4-17 PM10 Anion long-term annual trends (clockwise chloride, nitrate and sulphate).

4.5.3 Particle number concentrations

Figure 4-18 shows long-term annual trends for CPC measurements at all sites. Due to the installation of the CPCs mid-way through 2017, the 2017 data is omitted. 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] It is not yet clear whether the increase in concentrations in 2018 relative to those in 2016 is significant.

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 had 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.

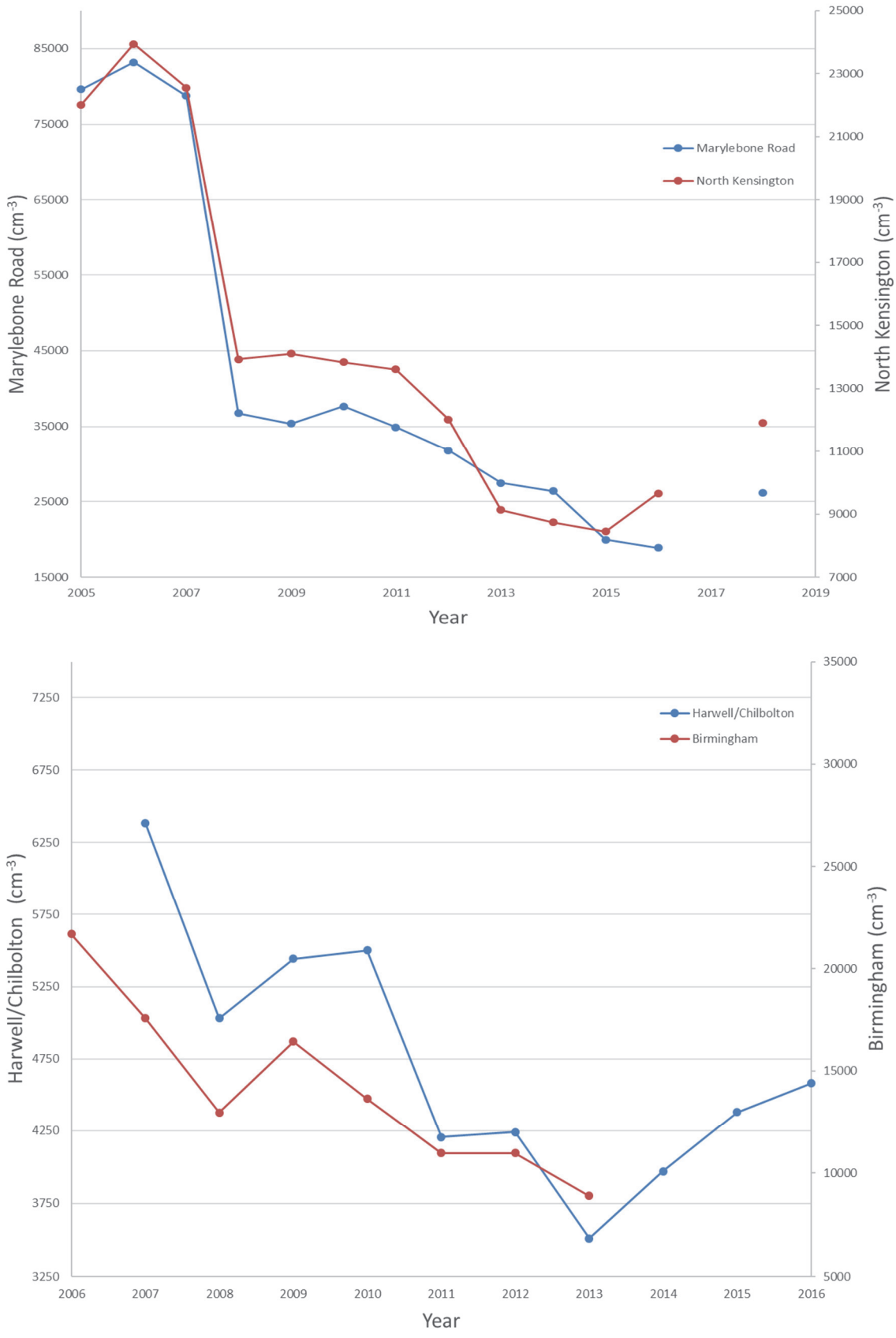


Figure 4-18 Historic CPC long-term annual trends at all sites. No data are available since 2014 for the Birmingham site. The Harwell site moved to Chilbolton in 2016. Insufficient data was available from Chilbolton for reliable averages in 2017 and 2018.

4.6 DIURNAL, WEEKLY AND MONTHLY PROFILES

Diurnal, weekly and monthly profiles have been plotted in Figures 4-19, 4-20, and 4-21 for the hourly concentrations, using the Openair tools.[11, 12, 13]

4.6.1 Profiles for anion and cation species

The correlation between NH_4^+, NO_3^- and SO_4^{2-} in Figure 4-19 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 4-2 shows the profiles for Cl^-, Mg^{2+} and Na^+ 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, most likely sea salt.

Ca^{2+} profiles at both sites in Figure 4-21 show values characteristic of traffic contribution, possibly re-suspension of crustal material from road surfaces.

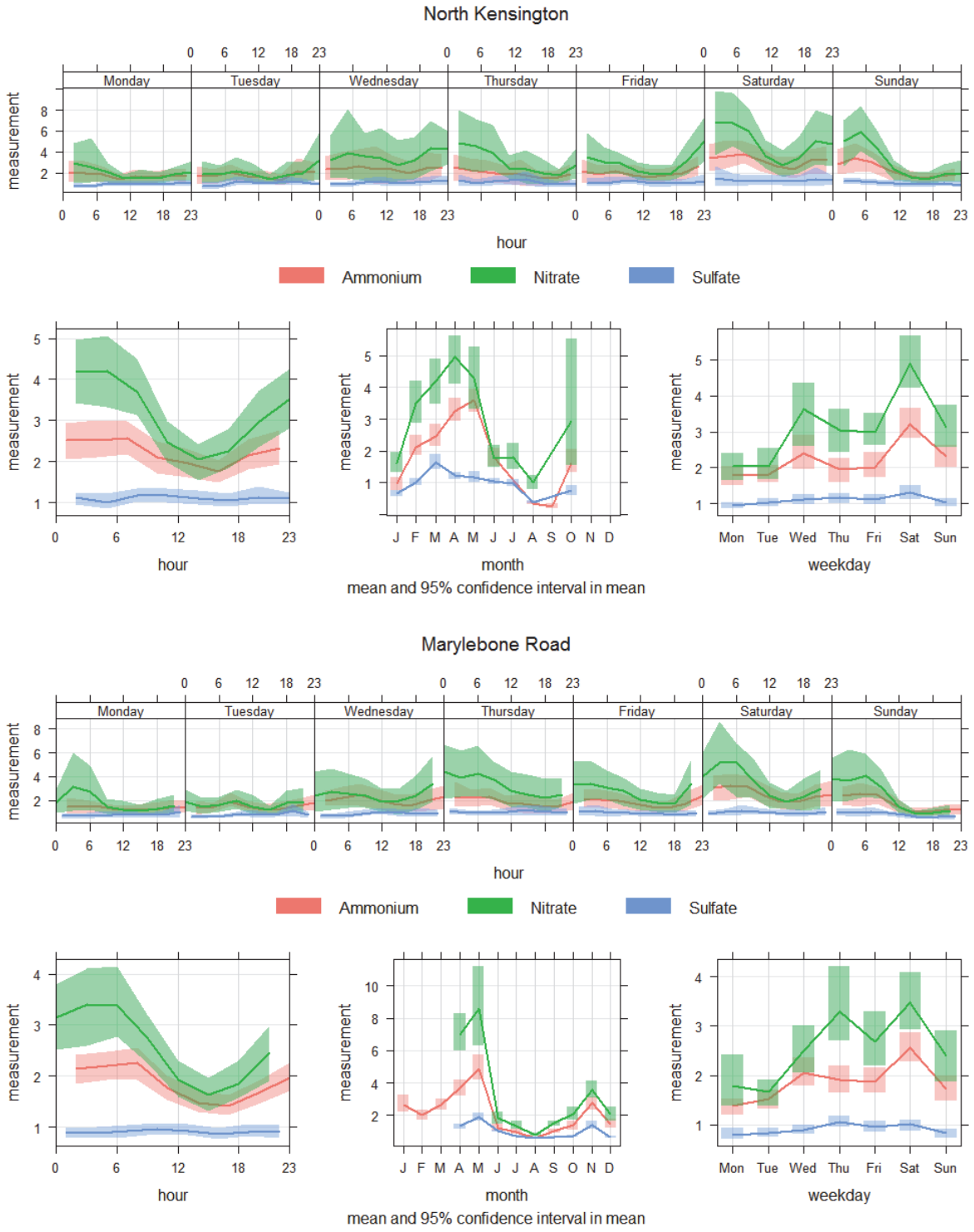


Figure 4-19 Diurnal, weekly and monthly profiles for and NH_4^+, NO_3^- and SO_4^{2-} during 2018 at North Kensington (top) and Marylebone Road (bottom).

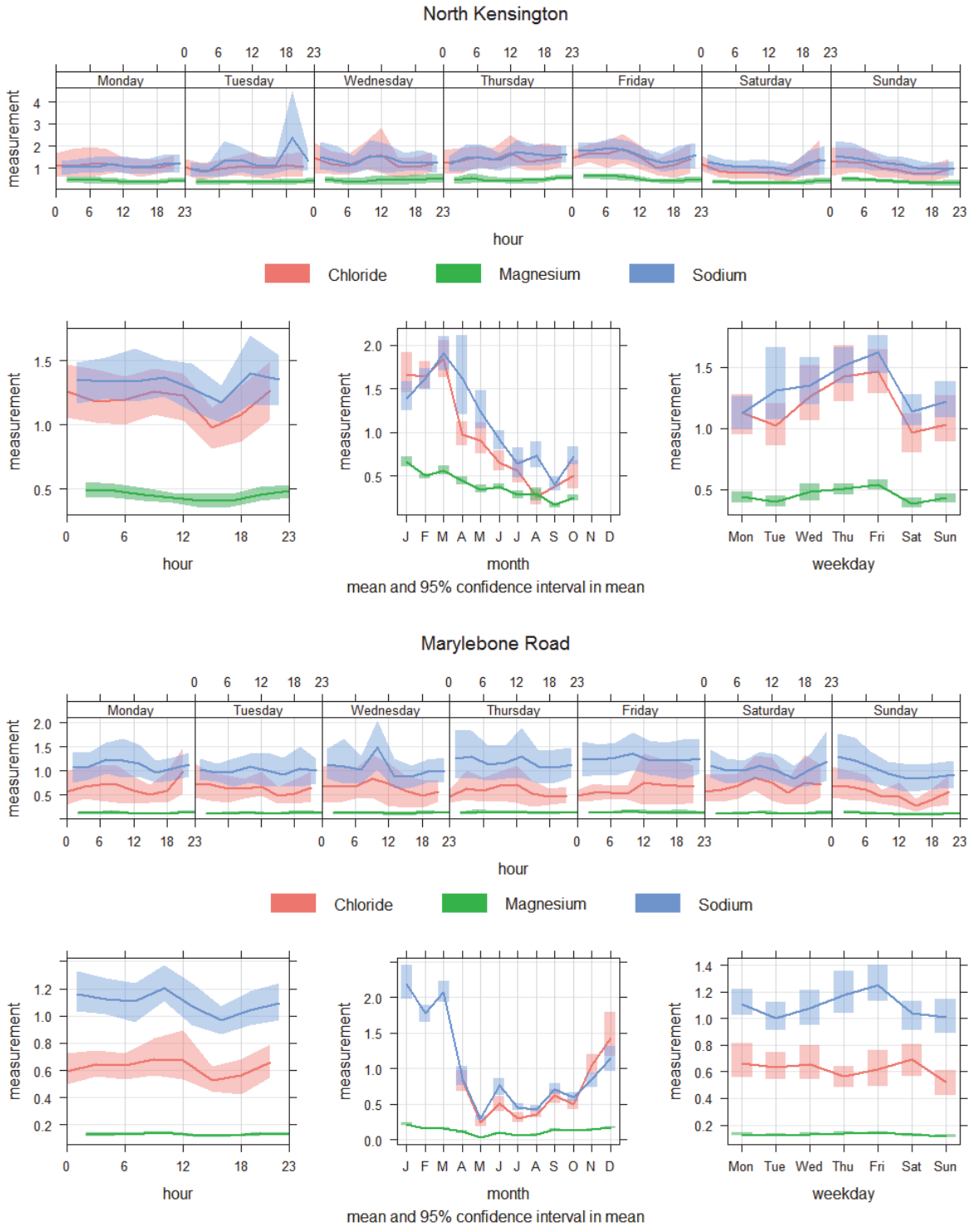


Figure 4-20 Diurnal, weekly and monthly profiles for Cl^-, Mg^{2+} and Na^+ concentrations during 2018 at North Kensington (top) and Marylebone Road (bottom).

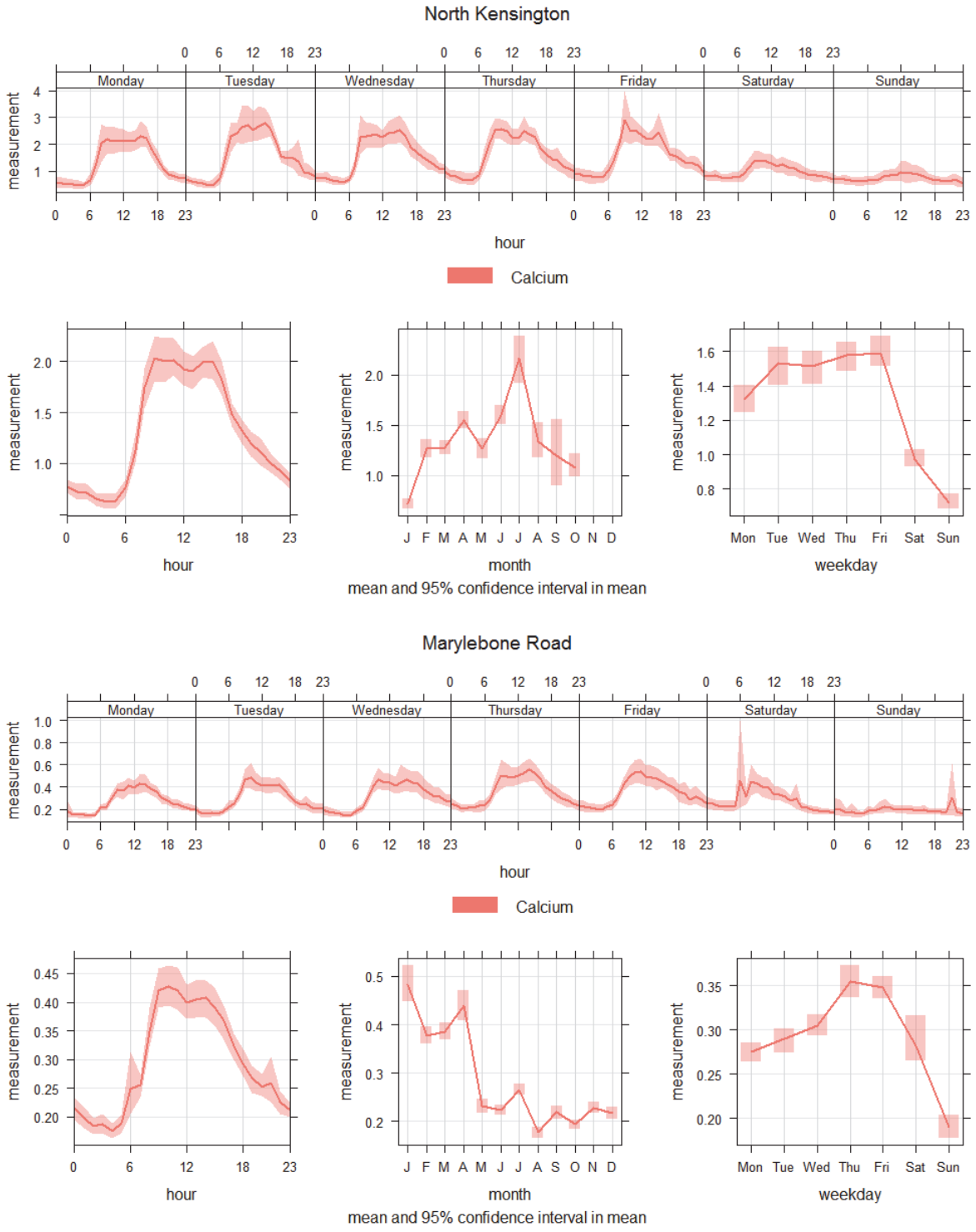


Figure 4-21 Diurnal, weekly and monthly profiles for Ca^{2+} during 2018 at North Kensington (top) and Marylebone Road (bottom).

4.6.2 Profiles for particle number concentrations

The diurnal, weekly and monthly profiles for number concentrations in 2018 are shown for the North Kensington and Marylebone Road sites in Figures 4-22 and 4-23 respectively. At these urban sites they show a strong correlation with human activity, with lower concentrations on Sundays.

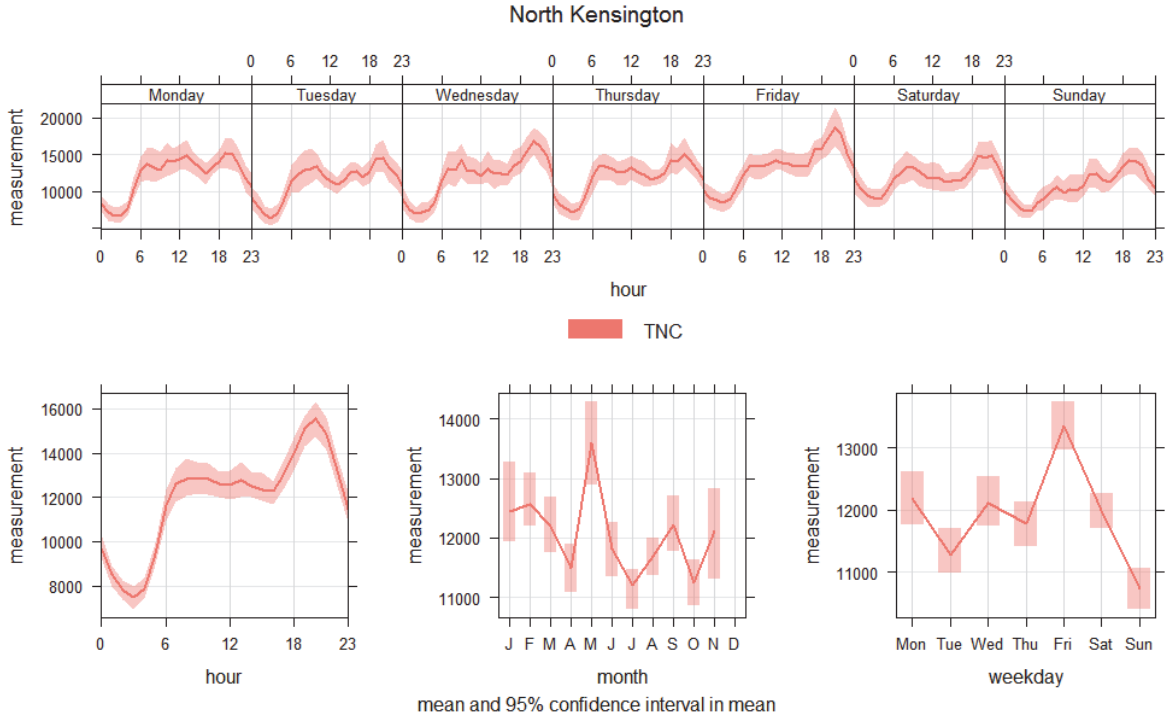


Figure 4-22 Temporal variations of number concentrations in 2018 at North Kensington

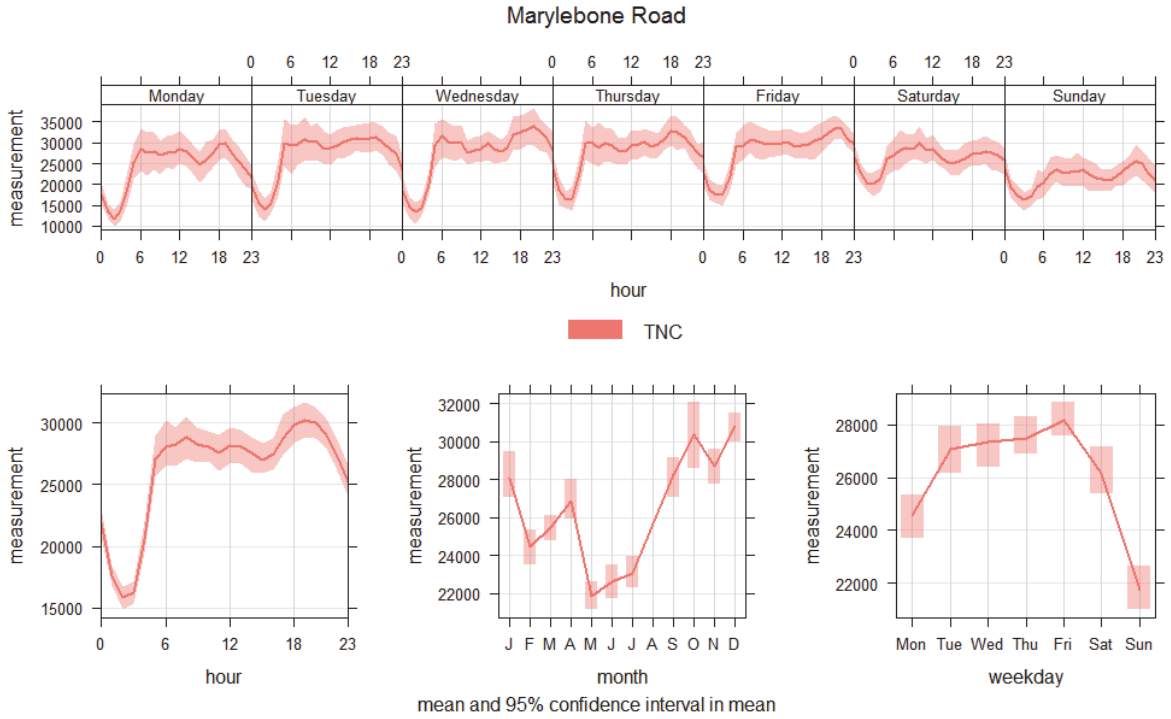


Figure 4-23 Temporal variations of number concentrations in 2018 at Marylebone Road

5 UPDATE ON WIDER POLICY AND RESEARCH CONTEXT

5.1 UPDATE ON RELATED UK ACTIVITIES

5.1.1 Defra and other National Monitoring activities

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, as described in 2.3.4. The infrared wavelength metric is designed to give concentrations that approximate to Elemental Carbon. There are strong links to this Network through NPL and KCL's involvement in both, and the Black Carbon data from the Chilbolton site have been incorporated in the Black Carbon Network Report.

Rural Monitoring

As part of the UK implementation of the EMEP monitoring strategy, two rural sites, Auchencorth Moss and Chilbolton, have been established to monitor, *inter alia*, particulate matter. 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.

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 were 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, and is expected to be submitted as a Technical Specification in 2019.

CEN TC 264 WG 35 covers Elemental Carbon and Organic Carbon and, up until May 2018, **CEN TC 264 WG 34** covered anions and cations, both for laboratory analysis of samples collected on filters.

Activities in 2018 were as follows:

WG 34:

The UK relies on automated instrumentation, instead of a filter-based method, to report ion concentrations to Europe. During the last held WG 34 meeting in March 2017, it was decided by members that further work was required to bring automatic instrumentation into the standardisation process. The UK drafted a new work item proposal for submission to CEN/ TC 264 and was circulated to WG members for comments before submission.

In 2017, funding had been requested in order to enable a study of existing data on the collocation of filter based and automatic instruments for measurement of anions and cations in $PM_{2.5}$, with the aim of testing possible equivalence and the requirement for future studies. However, this funding was not granted.

During a CEN/TC 264 meeting in May 2018, it was decided to put WG 34 "on hold".

WG 35:

Two new work items are in progress; "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.

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.

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