

**AIRBORNE PARTICULATE CONCENTRATIONS AND NUMBERS IN
THE UNITED KINGDOM**

Annual report 2017

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Airborne Particulate Concentrations and Numbers in the United Kingdom
Annual report 2017

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Approved on behalf of NPLML by
Richard Brown, Head of Metrology

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GLOSSARY/ABBREVIATIONS

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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 2017 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 2017 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

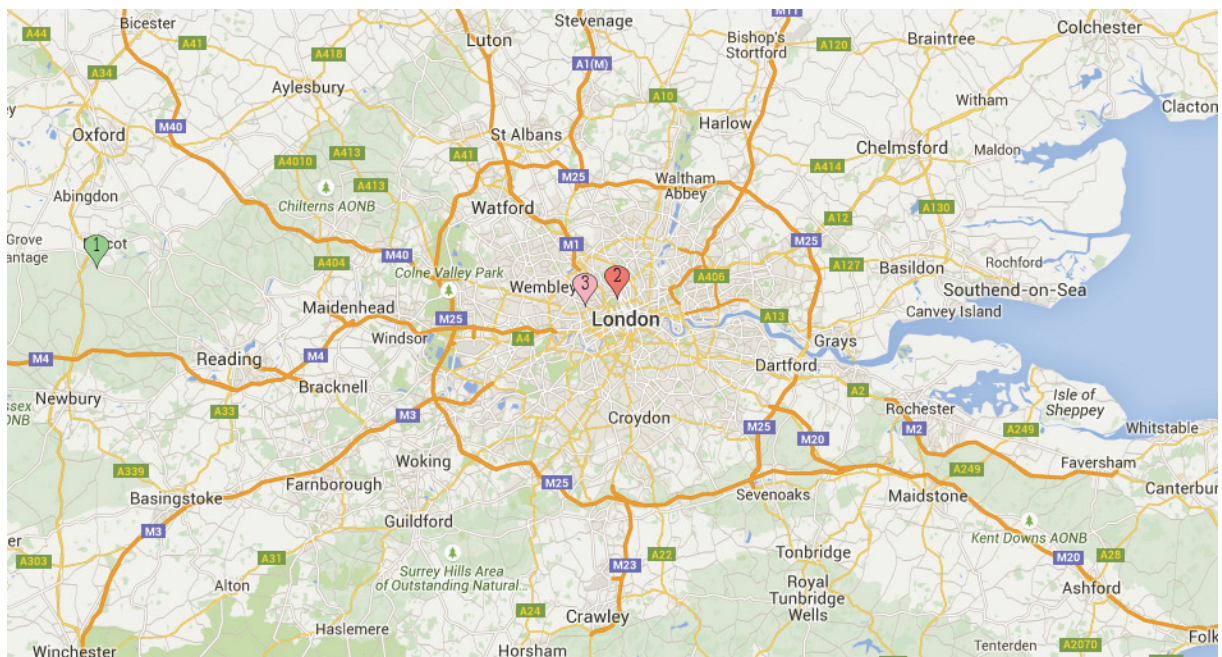
The measurement programme during 2017 is shown in Table 2-1.

Table 2-1 Network structure in 2017

SITE	Hourly PM₁₀ Anions/cations	Daily PM₁₀ 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 2017

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 old 3022a instruments at North Kensington and Marylebone Road permanently broke down in August 2016 and February 2016 respectively. There was never a 3022a CPC installed at Chilbolton as it had permanently broken down in 2015 before the site was commissioned. 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. The CPC instrument 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. 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 individually counted.

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_{10} size selective cyclones were installed for the SMPS and CPC at Harwell and the other Network sites in late 2009 to meet these recommendations. The humidity of the sample air going to both the CPC and SMPS instruments 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 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 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 (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 pyrolytically converted to elemental carbon. Measuring the transmission and reflection of a laser beam through the filter continuously monitors this pyrolytic conversion and allows a correction to be made for it. Elemental carbon is detected in the same way after heating to 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.

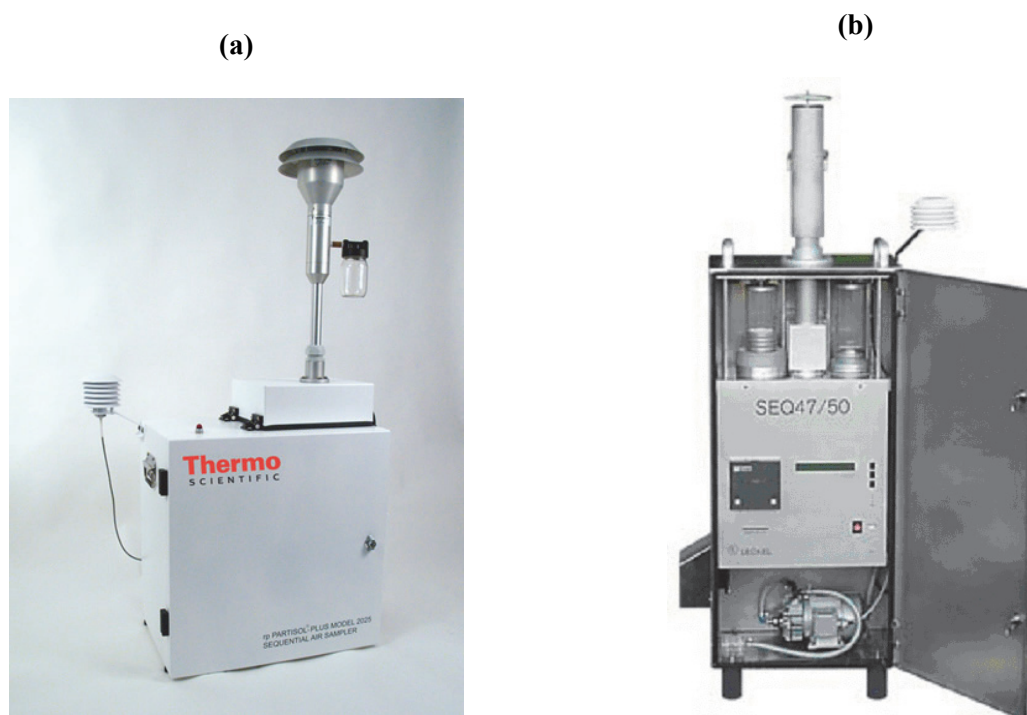


Figure 2-3 (a) Thermo Partisol 2025 sampler (b) Leckel SEQ47/50 sampler



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 ‘UVP’ is expressed in units of ‘BC Equivalent’.

It is well known that the assumption of constant mass extinction coefficient does not hold as the filter spot darkens, leading to nonlinearity in the Aethalometer response. The effect of this nonlinearity is that the Aethalometer under-reads at high filter tape loadings. To correct for this nonlinearity, the model developed by A Virkkula¹ 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 2017 Black Carbon Network report alongside the aethalometers in that network.²

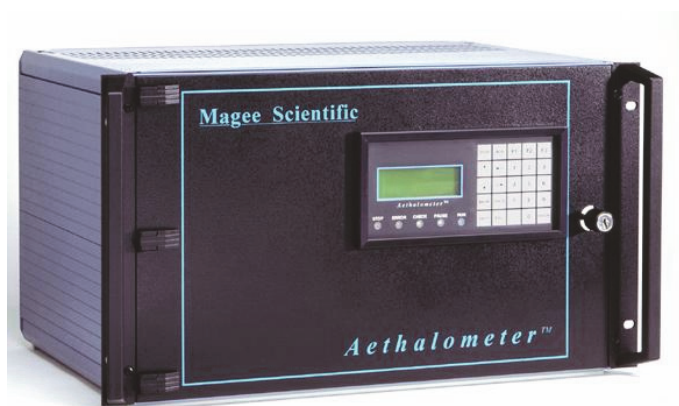


Figure 2-5 Magee Scientific aethalometer

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

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

The sampler draws a volumetric flow by measuring the pressure drop across an orifice, along with the orifice temperature, ambient temperature and pressure. The sample is drawn through a Liquid Diffusion Denuder where interfering acidic and basic gases are removed. In order to achieve high collection efficiencies, the particle-laden air stream next enters the Aerosol Super Saturation Chamber to enhance particle growth. An Inertial Particle Separator collects these enlarged particles, which it then stores in an Aerosol Sample Collector until the particles can be injected into the Ion Chromatograph.

The instrument samples for 55 minutes during each hour then analyses the collected sample. The analysis takes 15 minutes. It is a two-stage instrument, analysing the previous sample while it is collecting the current sample. Hence the instrument allows the production of hourly averages for all relevant anions and cations, dramatically improving the science outputs. The two instruments in this Network are supplied with a size selective PM₁₀ monitoring head for consistency with the previous anions sampling equipment.

The sampler is used in the field together with the 2100 Thermo Fisher Ion chromatograph (IC), which has its own eluent generator and makes automated running simpler. The eluent used for cation measurements is methanesulfonic 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 2017. The service procedure includes replacing old or worn parts, temperature and flow calibrations, leak tests and pump refurbishment.

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.

4 NETWORK DATA

4.1 OC/EC MEASUREMENTS (PM₁₀)

4.1.1 OC/EC/TC time trends

Daily measurements of OC (Organic Carbon) and EC (Elemental Carbon) in the PM₁₀ fraction collected on filters are provided in this Network at three sites: 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 2017 were 96%, 99% and 94% 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 and Figure 4-2 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 2017, as described by KCL's London air website <http://www.londonair.org.uk/>, can be identified in the graphs:

1. End January:

Cold, calm and settled weather conditions resulting from a high pressure system contributed to a widespread particulate pollution episode with levels reaching 'very high' between 20-26 January. On 22 January, an import of pollution from the continent during the afternoon was followed in the evening by cold foggy conditions with almost no dispersion. The rapid rise in pollution was caused by a combination of traffic pollution and also air pollution from wood burning. Weekday emissions then added to the already elevated pollution levels. Continuing very light winds causing poor pollution dispersion resulting in 'very high' particulate pollution at over twenty sites in both roadside and background locations across the Greater London area. On 24 January, a combination of higher ambient temperatures and a gentle westerly breeze for a few hours in the afternoon helped disperse some of the locally emitted pollution which had accumulated over the past week in calm conditions. Eventually, a change in weather conditions resulted in a breezier south westerly wind aiding in the dispersion of local emissions and an end to the pollution episode.

2. Middle of February:

On 10 February, across London and a small number of sites in Sussex, 'Moderate' PM₁₀ and PM_{2.5} particulate pollution was measured at several sites. Further 'moderate' PM_{2.5} was measured on 11 February and a smaller number of sites recorded 'moderate' PM₁₀. 'Moderate' PM₁₀ and PM_{2.5} were measured again on 12 February, with 'moderate' PM_{2.5} recorded at all sites in the Greater London area that measure this pollutant.

The 'moderate' particulate concentrations occurred at both roadside and background sites throughout the weekend. Air mass back trajectories indicate air being brought in from the northern part of Continental Europe, having travelled across areas such as Poland, Czech Republic, Germany and Holland. This, combined with elevated volatile particulate concentrations, suggests that the episode had a fairly large contribution from long range transport.

3. End of March:

'Moderate' PM₁₀ and PM_{2.5} particulate pollution was measured at several sites on 27 and 28 March across London and a small number of sites in Hampshire. These particulate concentrations were mainly due to a large import of pollution from Europe, adding to London's emissions. Air mass back trajectories showed air being brought in from the northern part of Continental Europe, having travelled across areas such as Czech Republic, Germany, Belgium and Holland. A large rise in volatile particulate concentrations throughout the day on 27 March and into the morning of 28 March indicated the main period of pollution import. Particulate concentrations fell during the afternoon of 28 March as winds veered south-westerly, bringing cleaner air.

4. April

'Moderate' PM₁₀ and PM_{2.5} particulate pollution was measured at several sites on 8 April across London which were due to a slowly swirling air mass reaching as far south as Paris. This air mass brought an import of pollution and gave poor dispersal of London's own emissions until winds veered the following day, bringing cleaner air.

[Furthermore in April, a notable isolated spike in OC/EC PM₁₀, was seen at Chilbolton on 27 April. The spike was also seen, to a lesser extent, in the weekly PM_{2.5} data. The on-line aethalometer at Chilbolton also measured very high concentrations of black carbon in the IR and UV channels at the early hours of the 27 April. It was suggested by the LSO that this was due to some local burning, but this cannot be confirmed].

5. June

On 21 June polluted air drifted over the southern part of the UK from the near continent which moved northwards and affected London during the late afternoon and early evening. Moderate PM₁₀ was measured at several locations in London but fresher conditions resulted in the polluted air moving eastwards.

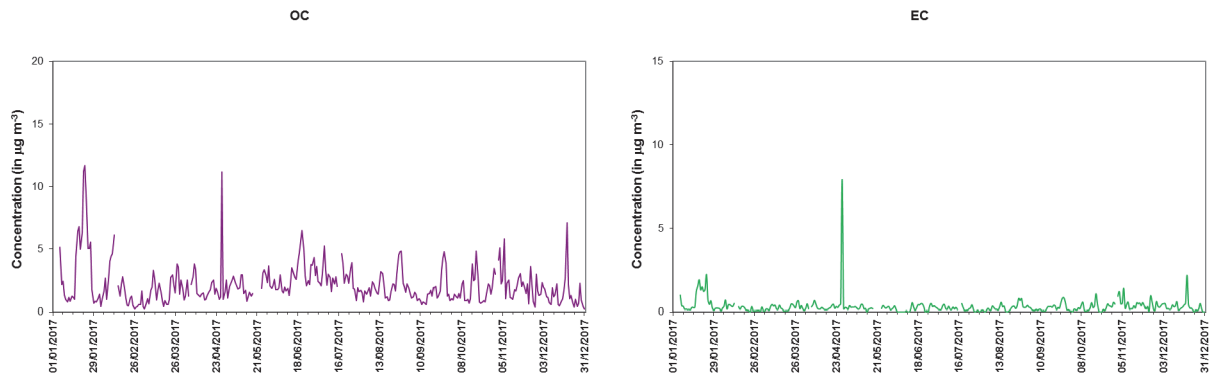
6. End of September

An import of polluted air from the continent added to our own emissions resulting in 'moderate' particulate levels between 25 and 27 of September. The air path started just south of the Baltic and moved further south during the three days picking up pollutants from urban, industrial and agricultural sources. The composition of the particulate pollution changed during the course of this three day episode with a bigger contribution from urban, traffic and agricultural sources as the episode progressed and the air path moved south. Levels dropped following a change in weather and the arrival of heavy rain.

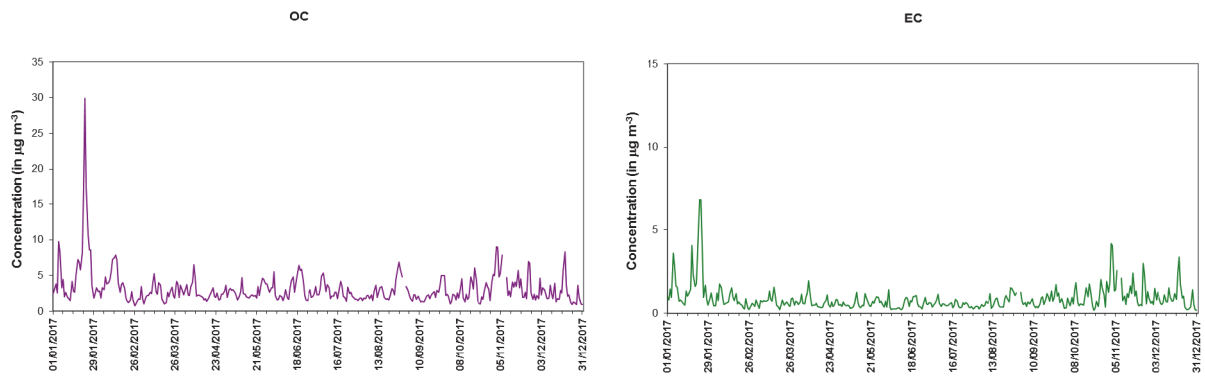
7. Early November

Foggy conditions and low wind speeds early on 3 November allowed a build-up of traffic emissions in the London area which continued throughout the day. Later in the evening an influx of air from the Paris region coupled with emissions from bonfires and fireworks, combined with the un-dispersed traffic emissions resulted in 'moderate' PM₁₀ and PM_{2.5} particulate. An increase in wind speed and temperature on 4 November and a change in the path of incoming air to a north-westerly direction resulted in particulate levels dropping overnight and returning to 'Low' for the rest of the weekend.

Chilbolton



North Kensington



Marylebone Road

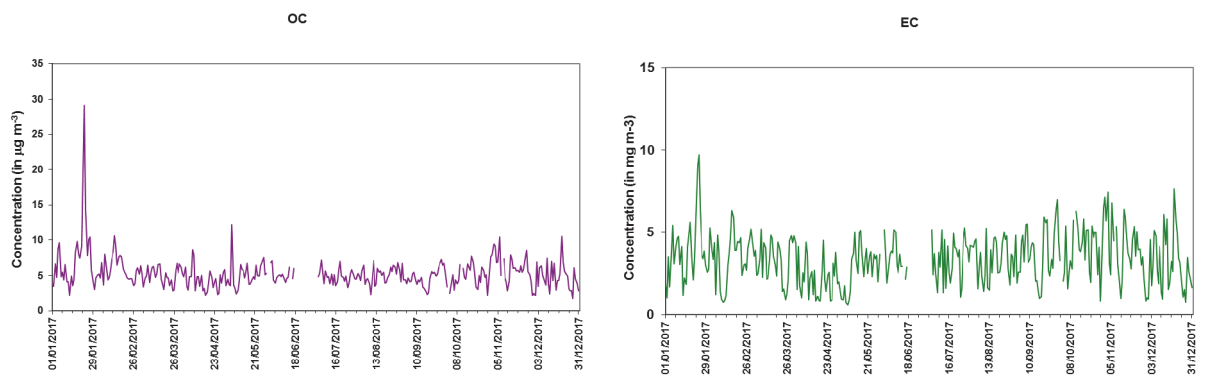


Figure 4-1 PM₁₀ OC and EC concentrations at Chilbolton, North Kensington and Marylebone Road during 2017.

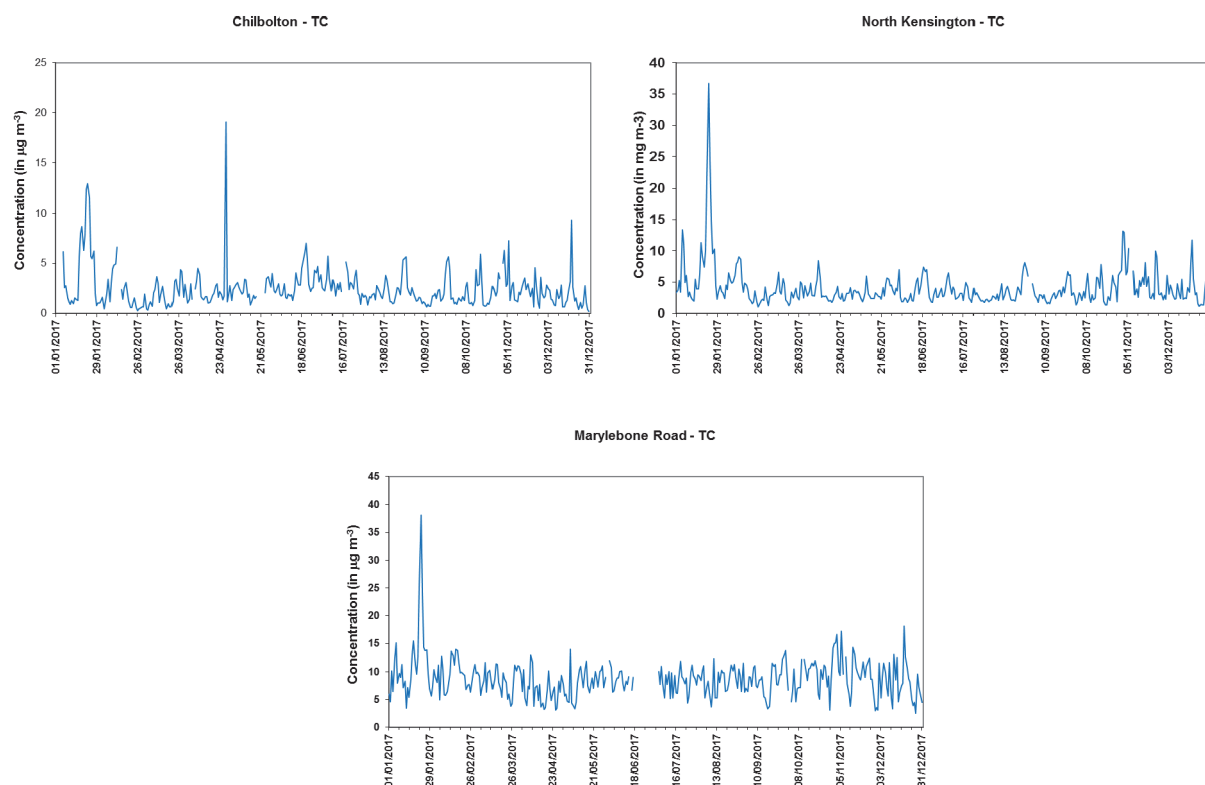


Figure 4-2 PM₁₀ TC concentrations at Chilbolton, North Kensington and Marylebone Road during 2017

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

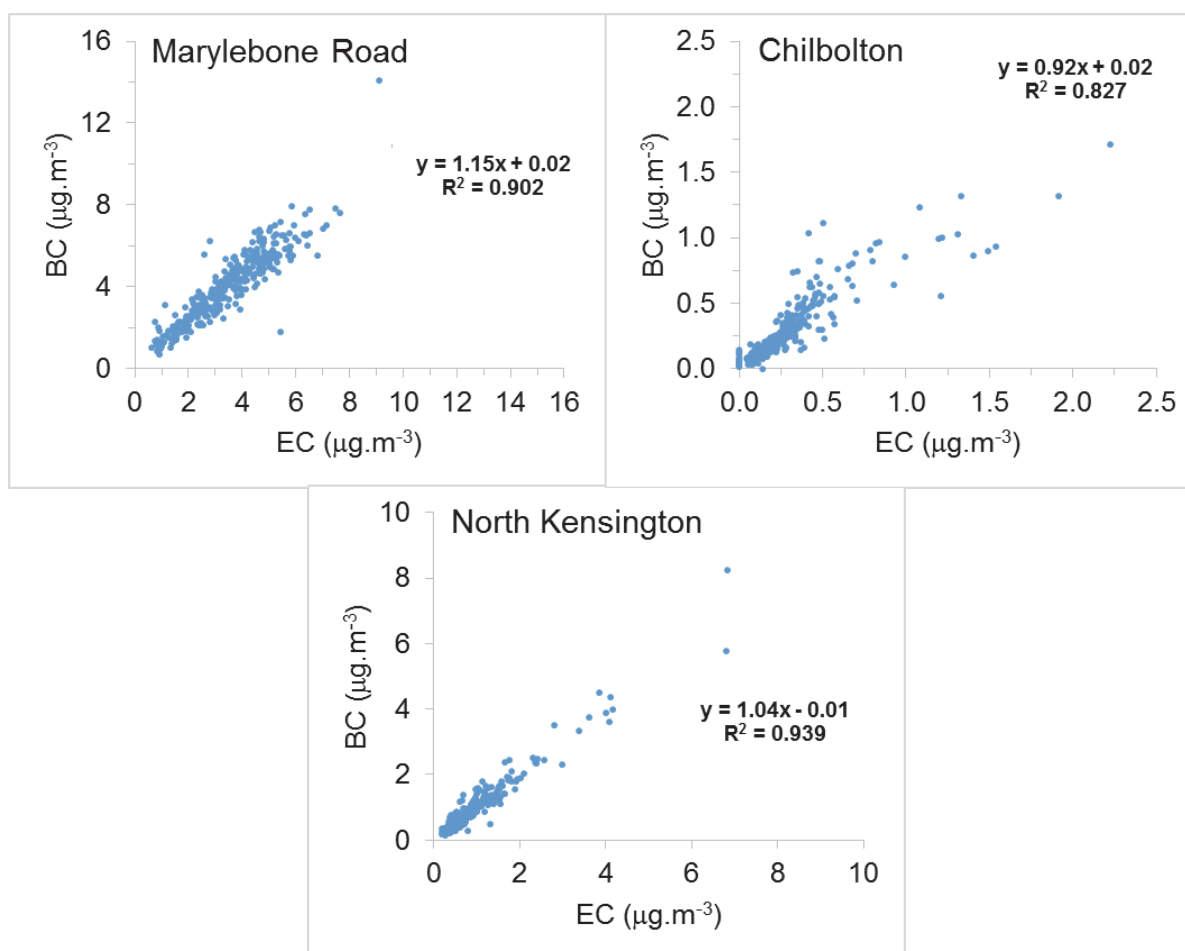


Figure 4-3 Comparison between PM_{2.5} BC and PM₁₀ EC at the 3 sites in 2017

It can be seen that there is a generally good linear relationship between the Elemental Carbon and Black Carbon concentrations ($R^2 > 0.82$ 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%. This is consistent with published work.⁴

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

Year	Harwell/Chilbolton		North Kensington		Marylebone Road	
	Relationship	R ²	Relationship	R ²	Relationship	R ²
2009	N/A*	N/A	$1.05x + 0.20$	0.858	$1.36x - 0.69$	0.776
2010	$1.32x + 0.06$	0.555	$1.37x - 0.32$	0.734	$1.28x + 0.56$	0.946
2011	$1.52x + 0.18$	0.844	$1.26x + 0.07$	0.810	$1.50x - 0.35$	0.924
2012	$1.84x + 0.06$	0.908	$1.42x + 0.17$	0.906	$1.43x + 0.01$	0.898
2013	$1.74x + 0.17$	0.865	$1.59x + 0.33$	0.871	$1.47x + 0.39$	0.679
2014	$2.02x - 0.01$	0.802	$1.68x - 0.00$	0.872	$1.32x + 0.25$	0.819
2015	$1.67x - 0.03$	0.833	$1.64x - 0.17$	0.893	$1.23x + 0.28$	0.901
2016	$1.31x + 0.03$	0.887	$1.08x + 0.03$	0.958	$1.25x + 0.26$	0.953
2017	$0.92x + 0.02$	0.827	$1.04x - 0.01$	0.939	$1.15x + 0.02$	0.902

*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 and 2017 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 2017 was 97% for Chilbolton and 49% for Auchencorth Moss. The poor data capture for Auchencorth Moss was due to recurrent pump failures which have now been resolved. Figure 4-44 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.

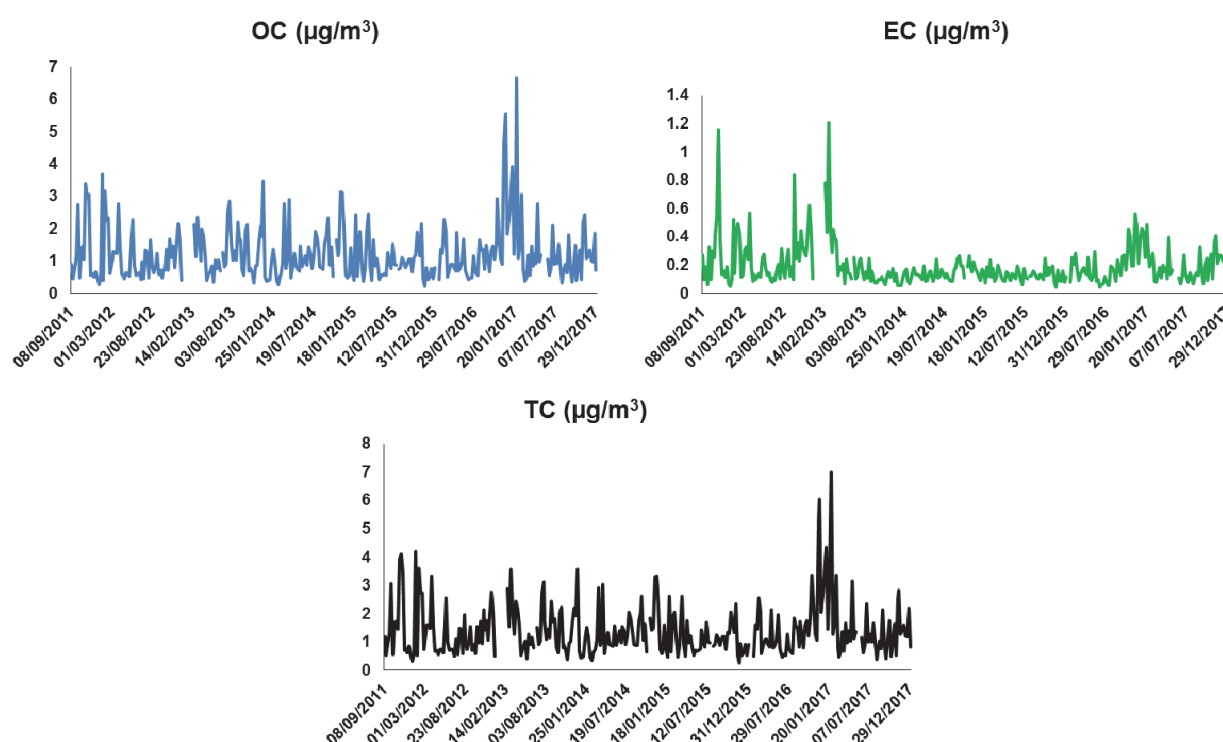


Figure 4-4 Time series of OC, EC and TC in the PM_{2.5} fraction at Harwell/Chilbolton since the installation of the sampler (weekly samples) (µg/m³)

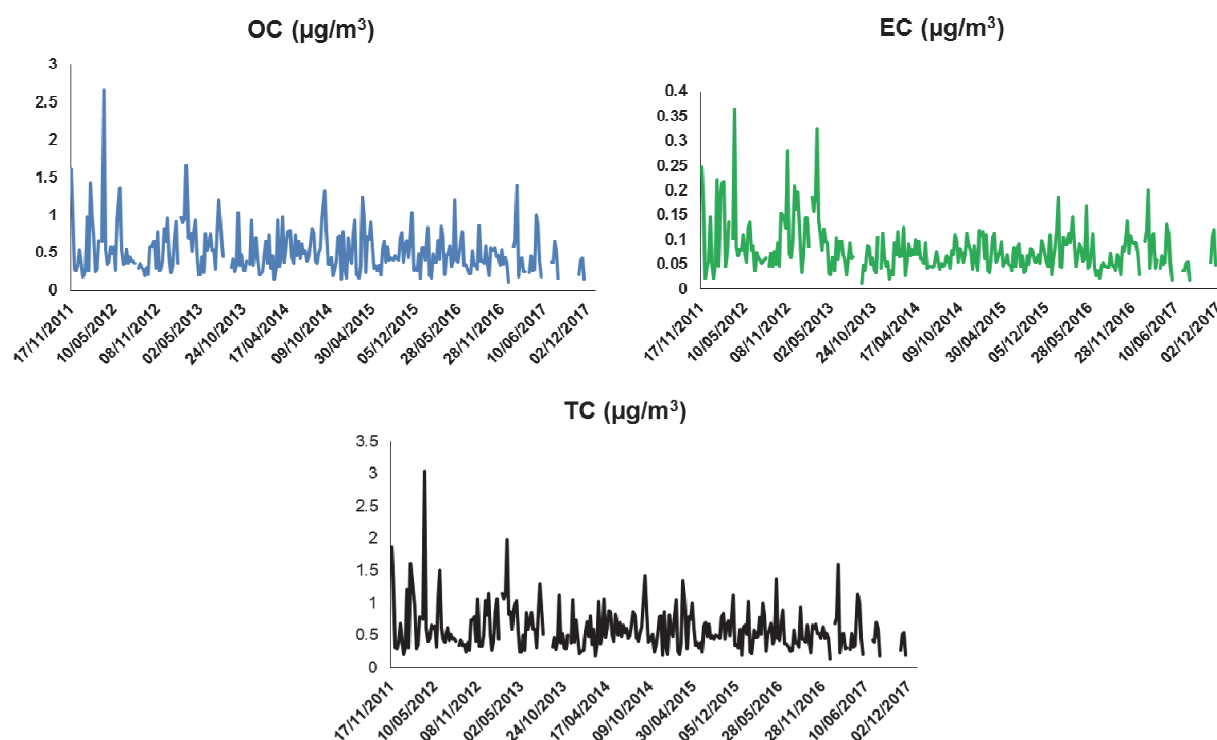


Figure 4-5 Time series of OC, EC and TC in the PM_{2.5} fraction at Auchencorth Moss since the installation of the sampler (weekly samples) (µg/m³)

The PM_{2.5} carbon concentrations at Chilbolton were compared with weekly averages from the PM₁₀ filters from the Partisol (Figure 4-6).

As seen in previous years, the PM_{2.5} data is generally lower than the PM₁₀ 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. The comparably poor regression for the EC data, 0.6863, is considered to be due to the two pollution episodes which occurred in late January and on 27 April 2017. Excluding the data from these two events improves the regression to 0.9065, due to increased contributions to the EC in only the PM₁₀ fraction.

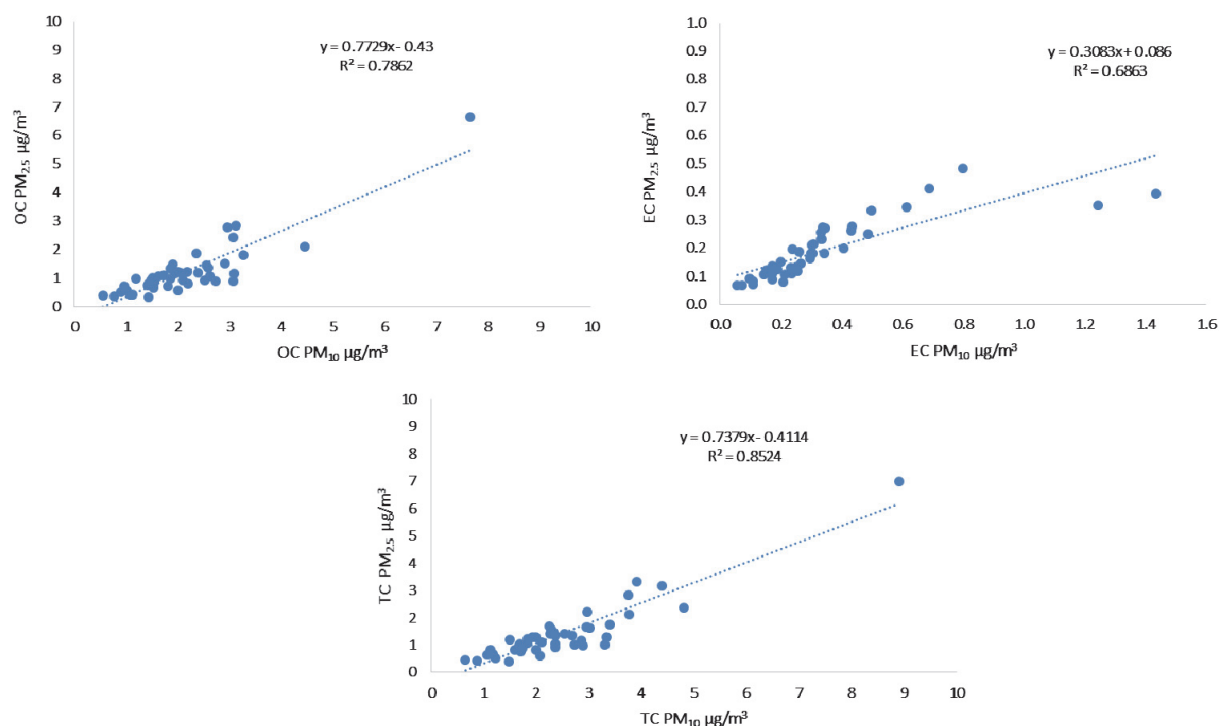


Figure 4-6 Comparison between PM₁₀ OC/EC weekly averages and PM_{2.5} OC/EC at Chilbolton

4.3 AUTOMATIC PM₁₀ ANION AND CATION MEASUREMENTS

The two URG 9000B – AIM instruments were installed at the two sites in London in February 2011. These instruments measure hourly concentration of chloride (Cl⁻), nitrate (NO₃⁻), sulphate (SO₄²⁻), sodium (Na⁺), ammonium (NH₄⁺), potassium (K⁺), magnesium (Mg²⁺) and calcium (Ca²⁺) in the PM₁₀ size fraction.

Prior to February 2011, daily anion measurements were made in this Network at Harwell, North Kensington and Marylebone Road using a filter based method. The two URG instruments at the London sites replaced the manual method giving a higher time resolution measurements and adding information on cation content of PM₁₀. At Harwell a MARGA instrument was already in operation, under a different Network.

The annual data capture (averaged using all of the ions) was 46% for Marylebone Road and 76% for North Kensington. The comparably poor data capture for Marylebone Road was as a result of various instrument break downs.

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

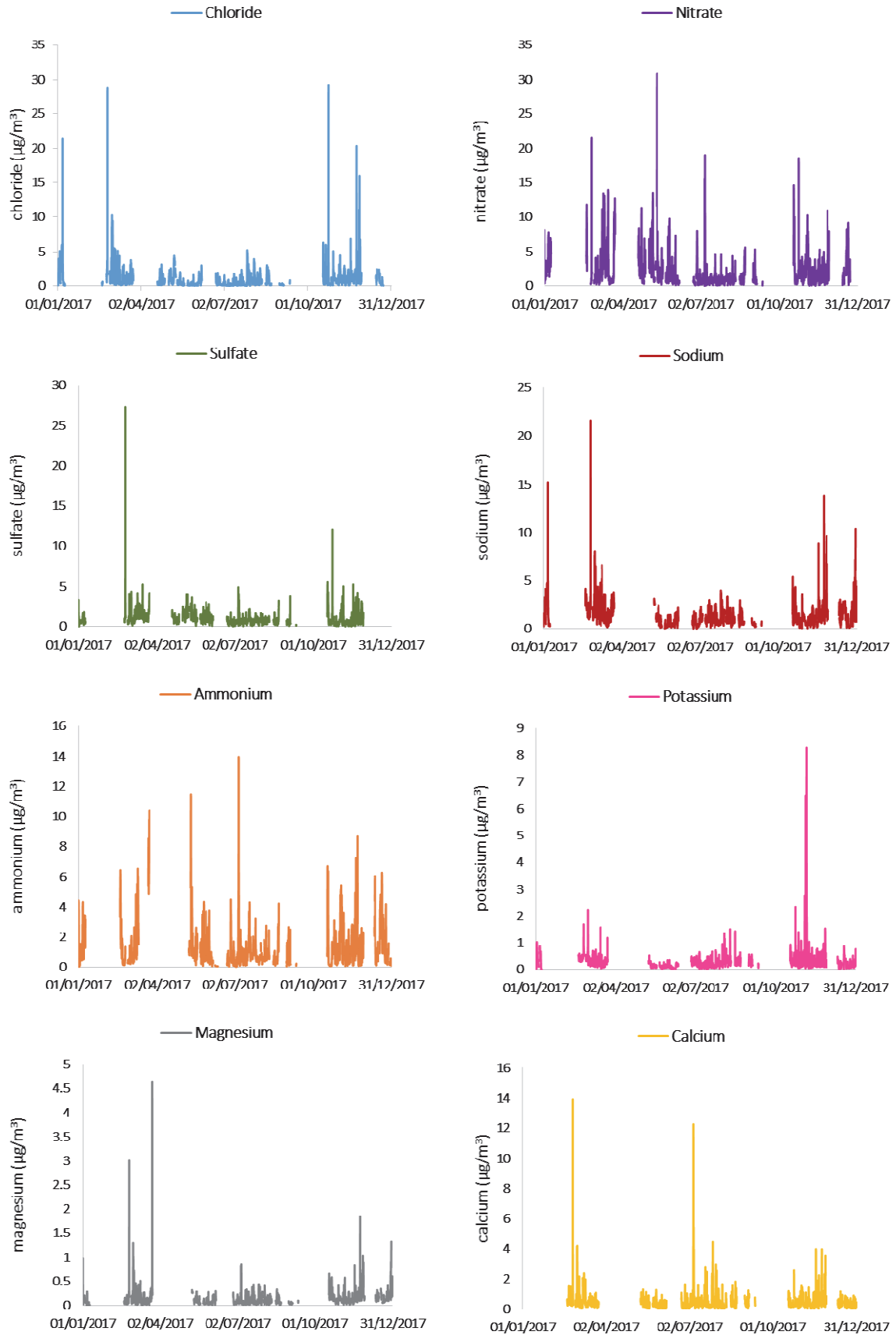


Figure 4-7 Time series for ion concentrations at Marylebone Road in 2017

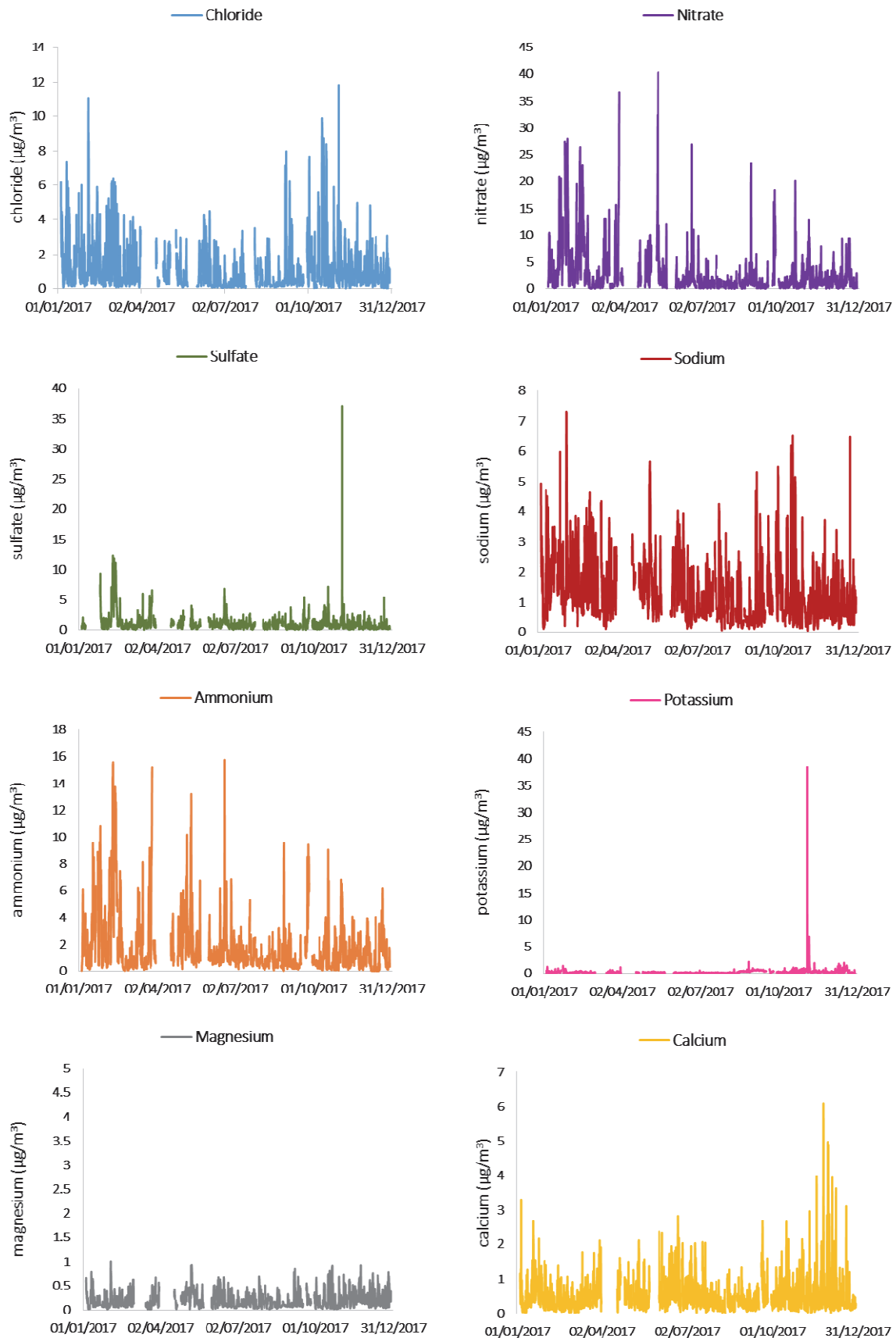


Figure 4-8 Time series for ion concentrations at North Kensington in 2017

Figure 4-9 shows the latter part of the pollution episode seen at North Kensington towards the end of January, as described in Section 4.1.1. There were various ion chromatography instrument issues experienced at Marylebone Road during January so this episode was not captured at that site.

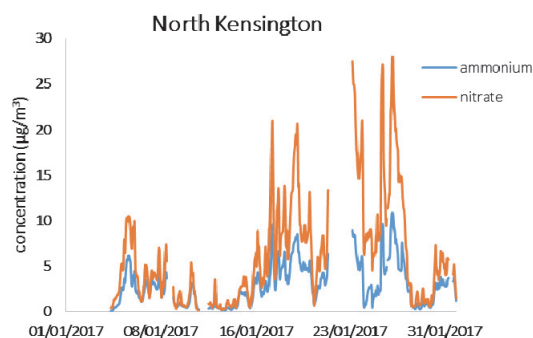


Figure 4-9 Pollution episode on 20-26 January 2017 at North Kensington in London.

Figure 4-10 shows the concentration of NO_3^- , SO_4^{2-} and NH_4^+ at North Kensington during the 10-13 February episode. Once again, during this time period, the instrument at Marylebone Road suffered sampling problems.

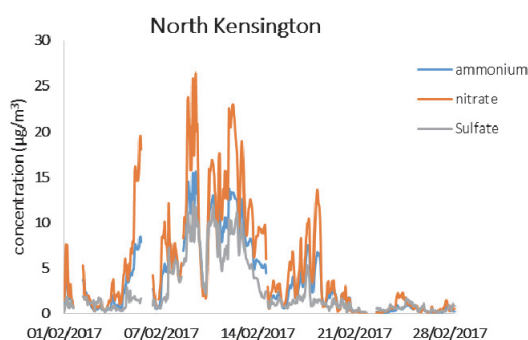


Figure 4-10 Mid-February 2017 pollution episode at North Kensington.

The onset of the end of March episode was partially captured at the North Kensington site, as shown in Figure 4-11. Raised NO_3^- levels at the end of March are thought to be due to springtime applications of slurry and fertiliser in agricultural regions in Europe. The presence of SO_4^{2-} in the measured particulate can indicate contributions from both local and distant combustion sources. This type of long-range transport episode has become common at this time of year.⁷

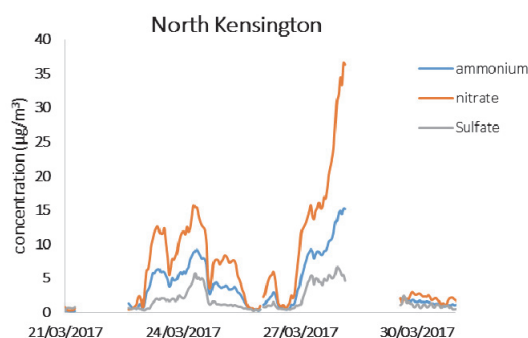


Figure 4-11 Onset of the end of the March pollution episodes captured at North Kensington.

Figure 4-12 shows Higher K^+ concentrations (along with raised NH_4^+ and NO_3^- levels) at the beginning of November at both sites; these are due to fireworks and bonfires at the start of the weekend (Friday 3 November) and the two succeeding evenings.

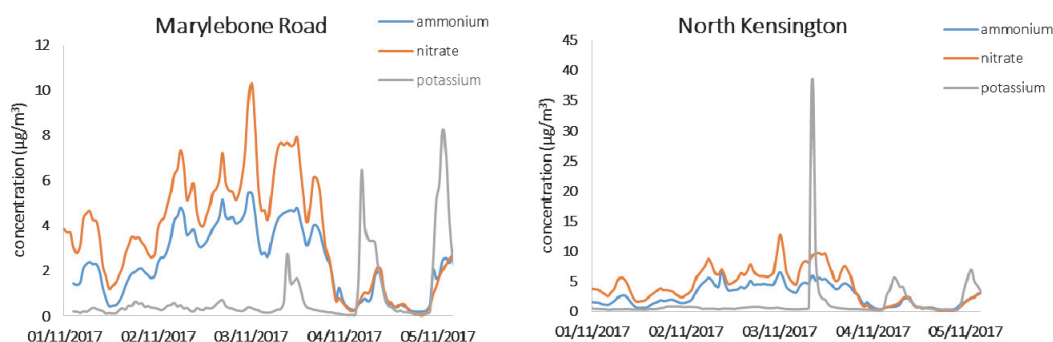
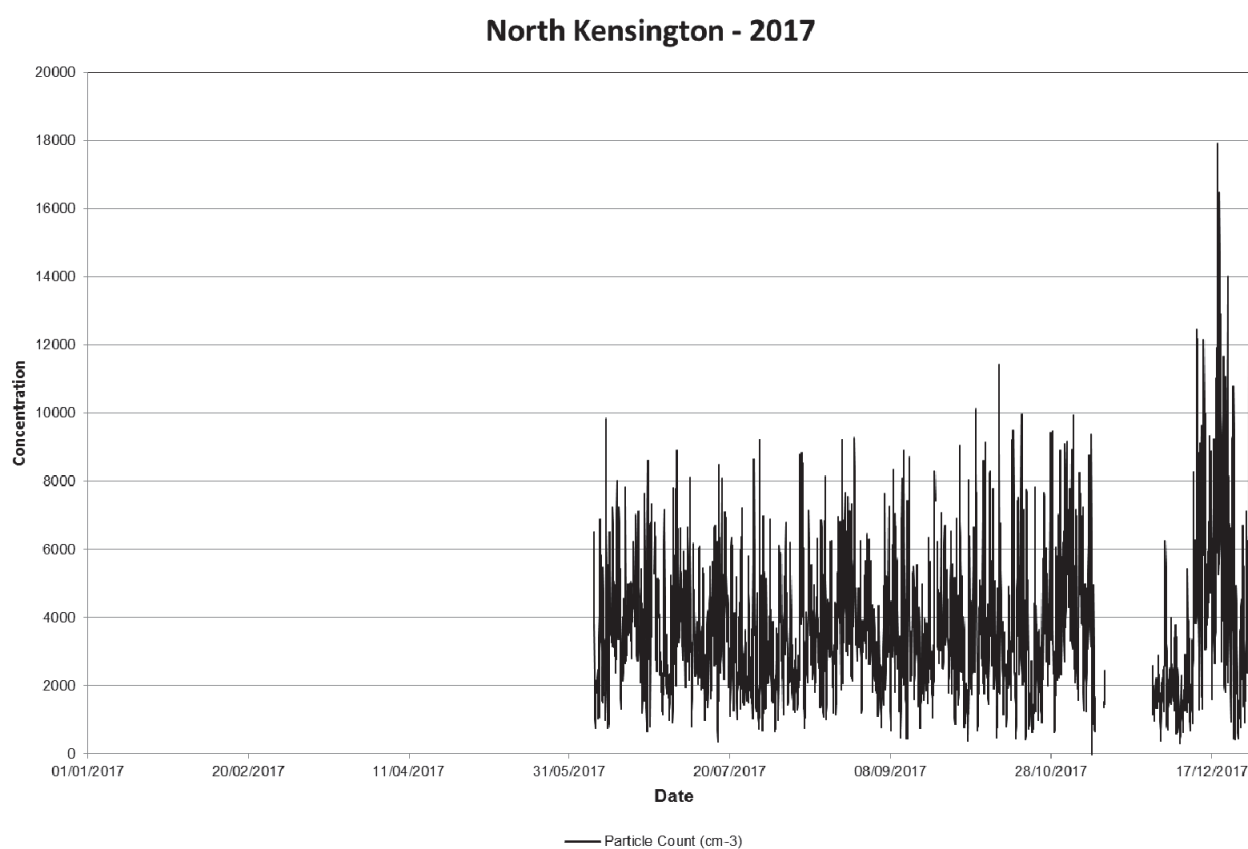


Figure 4-12 Early November pollution episode at the two sites in London.

4.4 PARTICLE NUMBER CONCENTRATIONS 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 2017 are shown in Figure 4-13. There is no data for the Harwell/Chilbolton site as there was no data recorded for the CPC present.



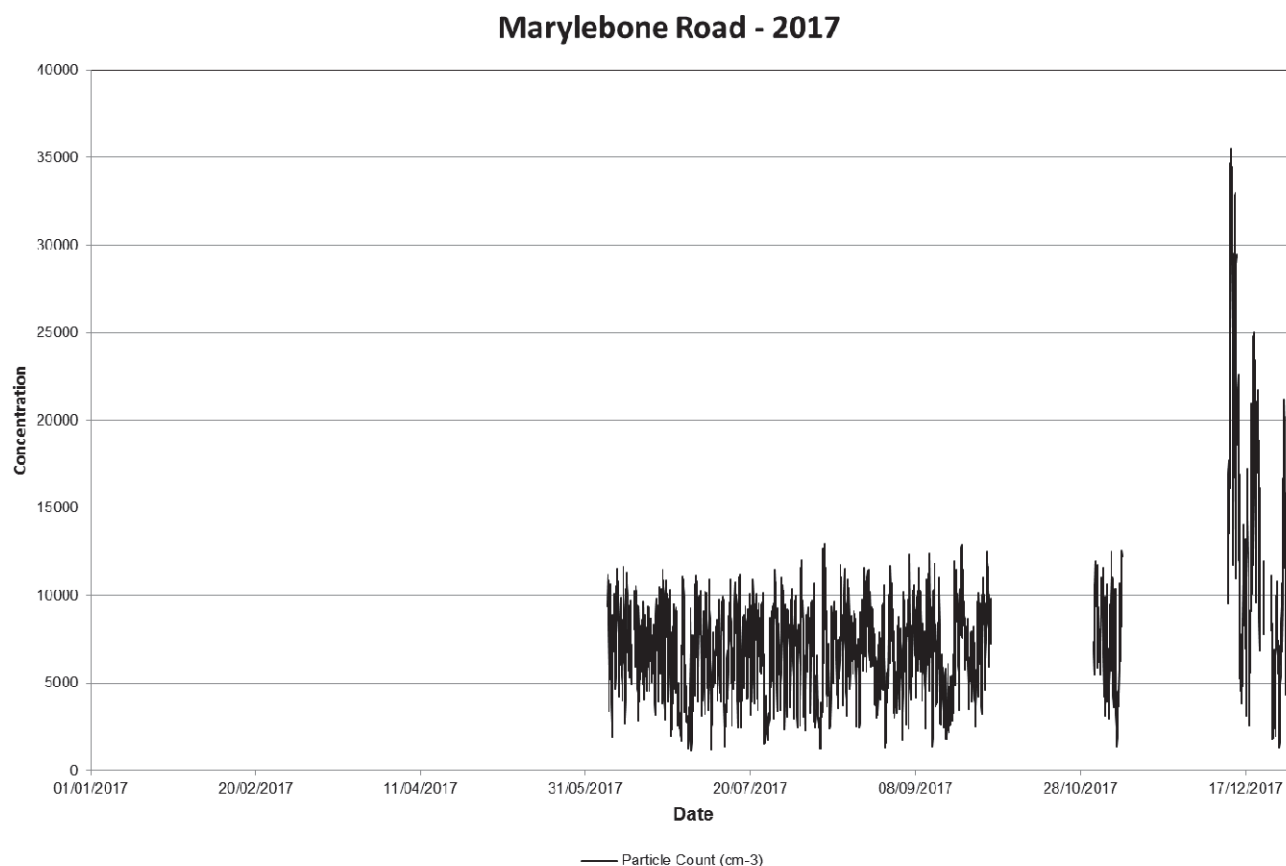


Figure 4-13 Hourly particle number concentrations at North Kensington and Marylebone Road

As described in 2.3.1, during 2017 the TSI 3022A CPCs were replaced with TSI 3772-CEN CPCs, as they had been operated beyond their useful life. Three new CPC CEN compliant instruments (TSI 3772-CEN) have been installed in mid-2017, one each at the Marylebone Road, North Kensington and Chilbolton sites. New drier systems have also been 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 2018).

Due to software differences between the new and old CPCs the correct communication software was unavailable for the Chilbolton site in 2017. The instruments at North Kensington and Marylebone Road were installed in June 2017.

The average data captures for the CPC instruments during 2017 (from June) were 87% and 76% respectively for North Kensington and Marylebone Road.

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 2017 were 73%, 82% and 58% respectively for Chilbolton, North Kensington and Marylebone Road.

For all three sites, the main data gaps were due to problems with the new drier systems.

The production of data from SMPS instruments is a complicated process, summarised schematically in Figure 4-14. 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 4-15. The overall effect of the two corrections is to increase the particle number counts at smaller sizes and to increase the total particle count.

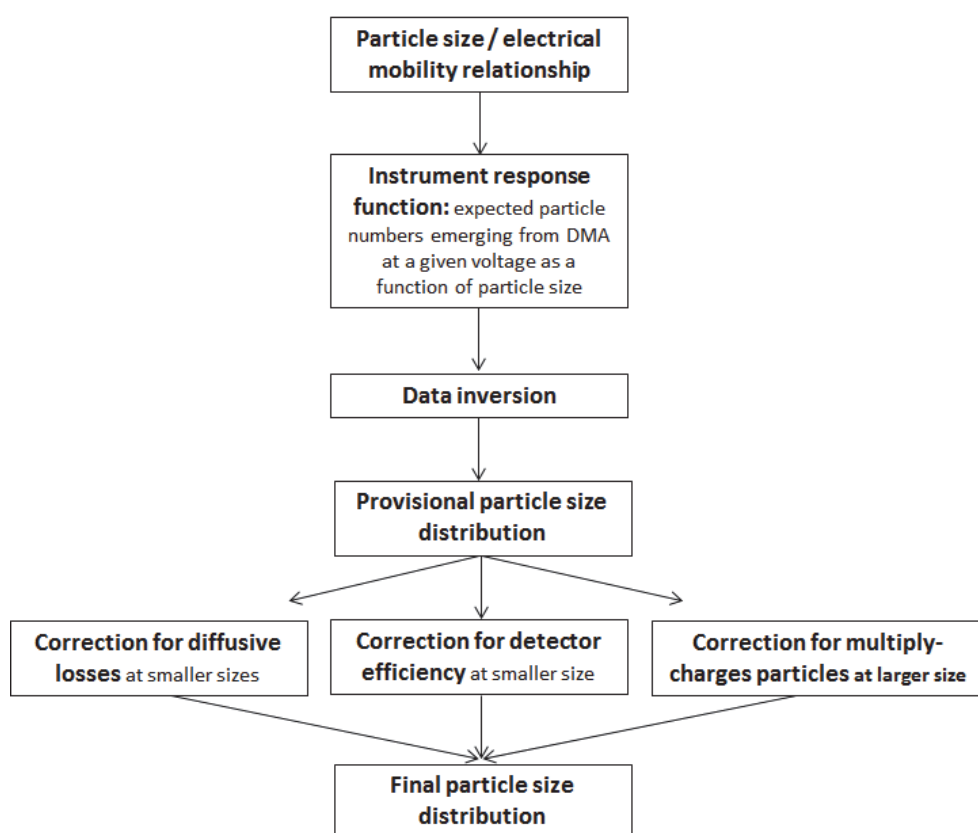


Figure 4-14 Schematic of the internal data processing of SMPS measurements in the Network

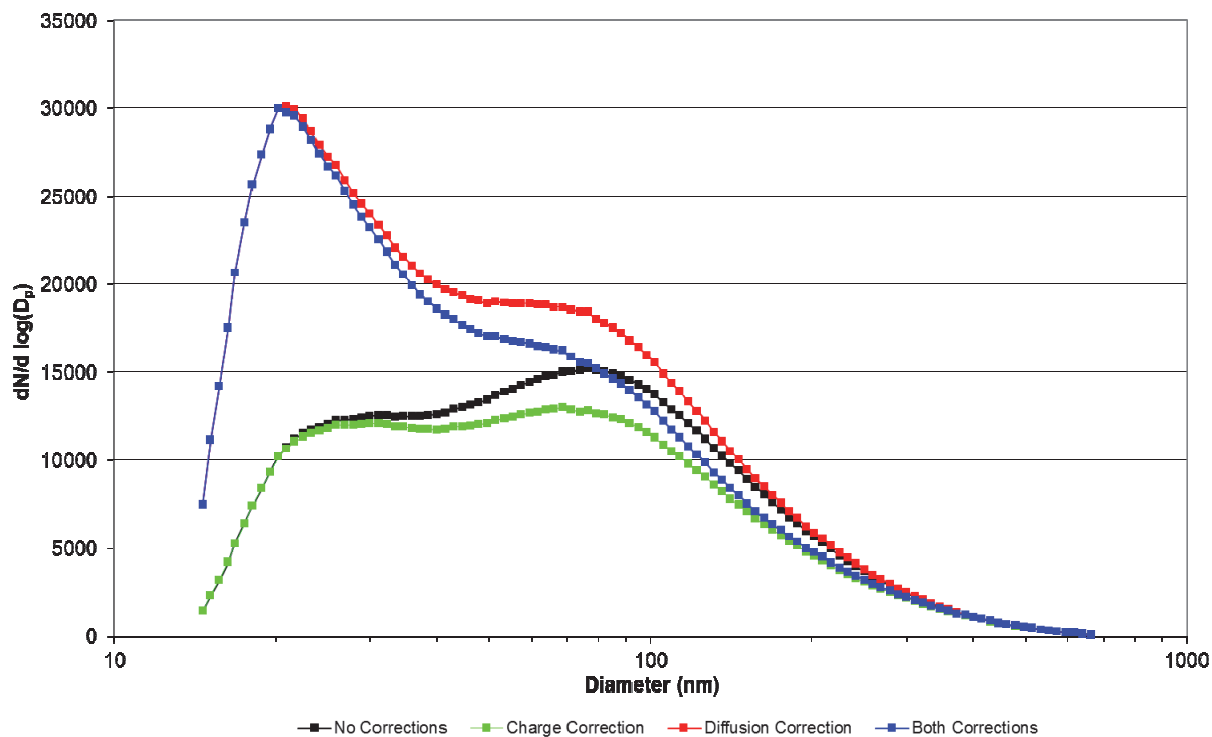


Figure 4-15 Effect of the multiple charge, the diffusion loss and their combined correction in the SMPS size spectrum

The counts in each particle size bin measured during 2017 are presented as monthly averages in Figure 4-16 and as annual averages in Figure 4-17.

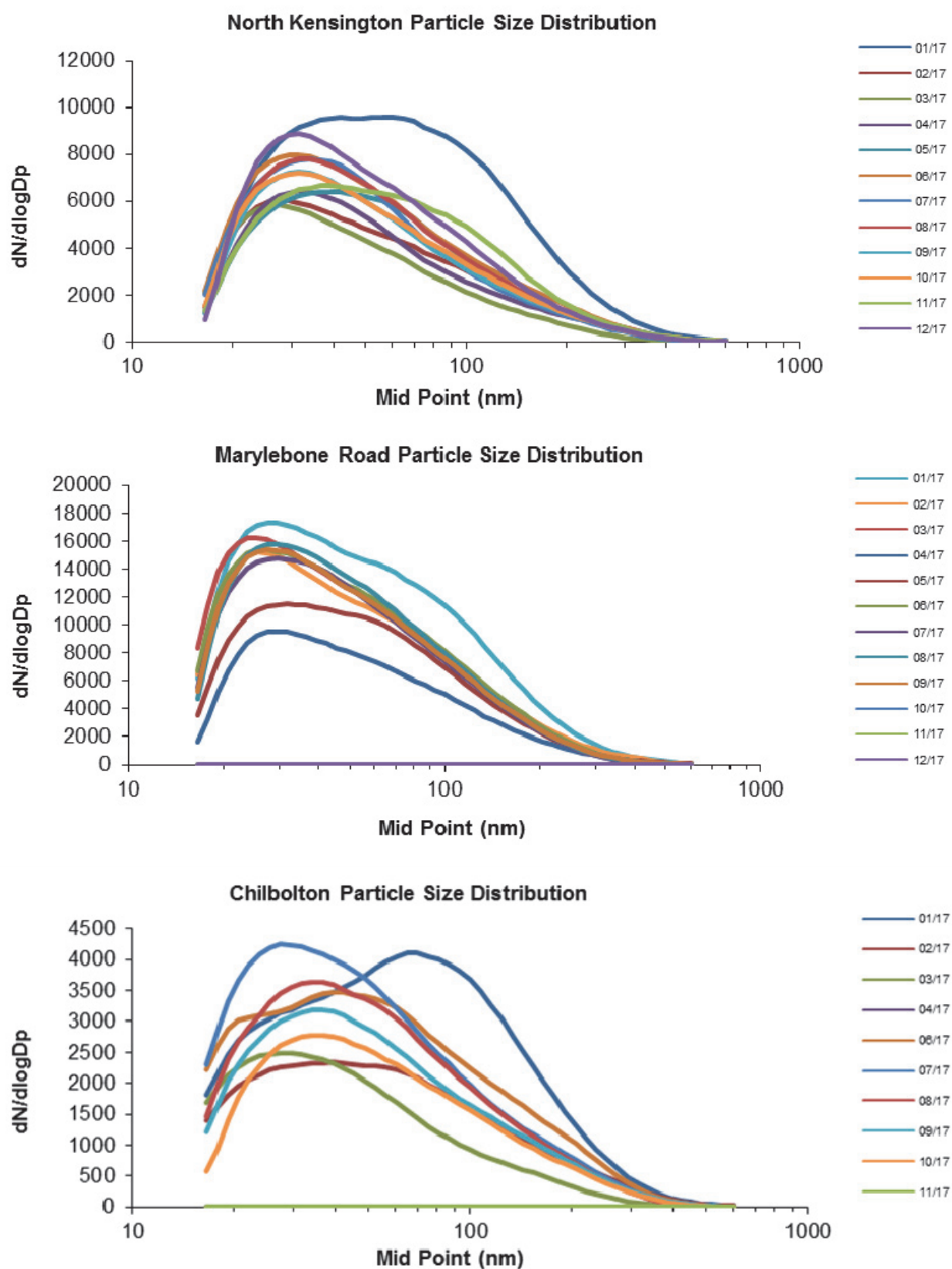


Figure 4-16 Monthly averaged particle size distributions at the Network sites during 2017

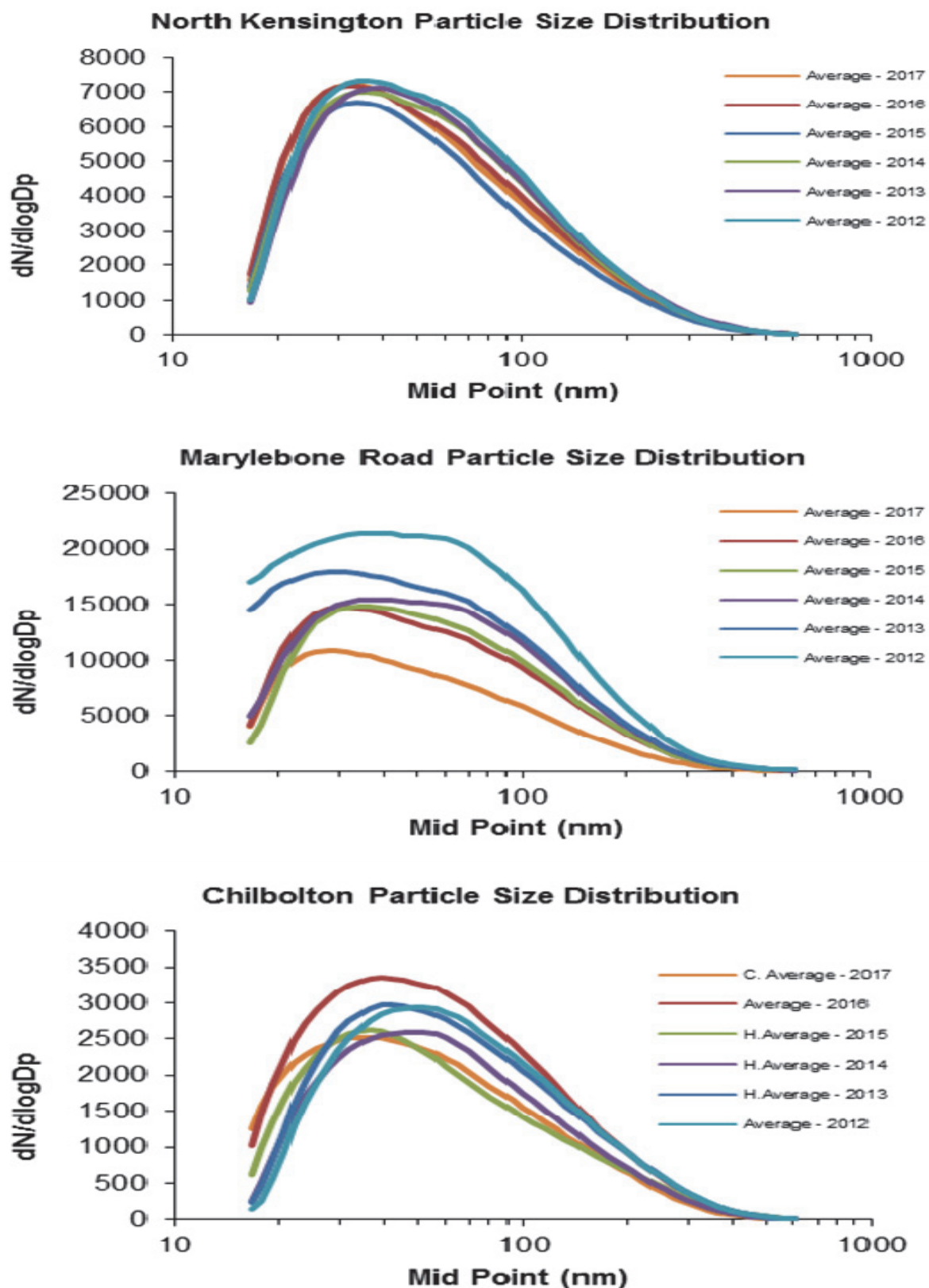


Figure 4-17 Comparison of the 2012, 2013, 2014, 2015, 2016 and 2017 annual-averaged size distributions

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.

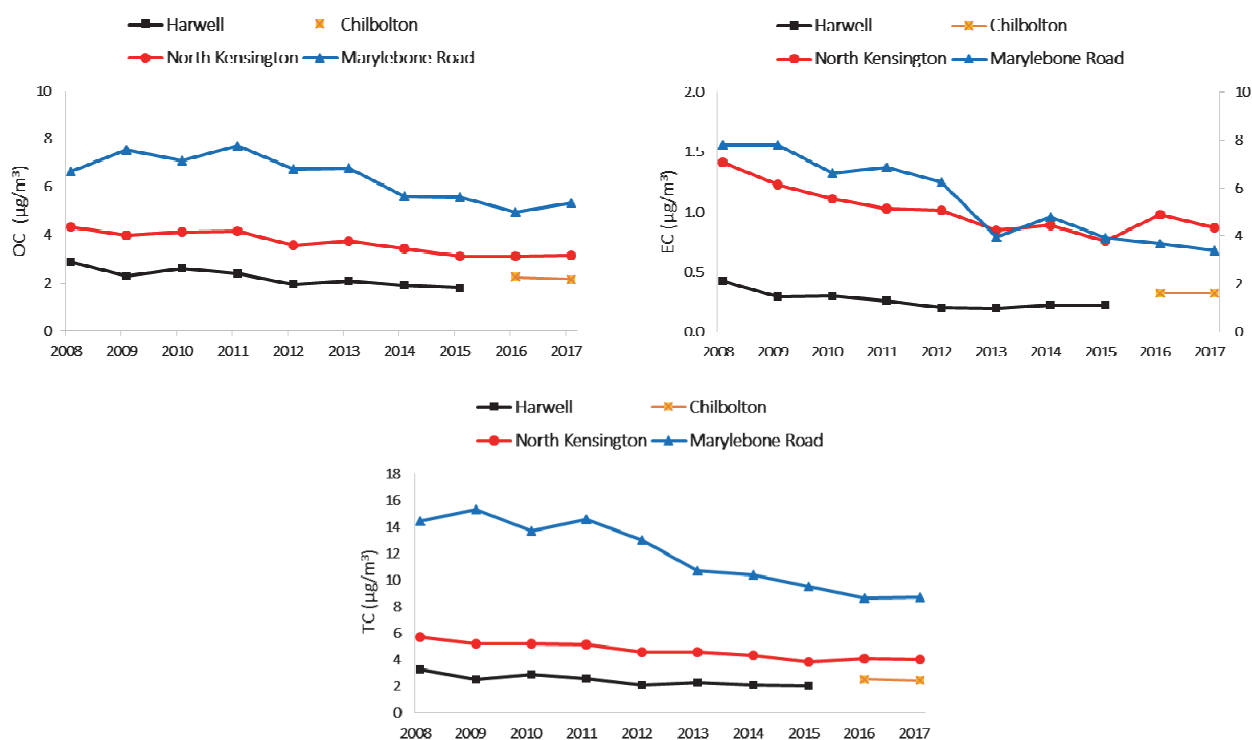


Figure 4-18 Annual trends for OC, EC and TC measurements. Note: The EC values for Marylebone Road are shown on the right-hand axis

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.

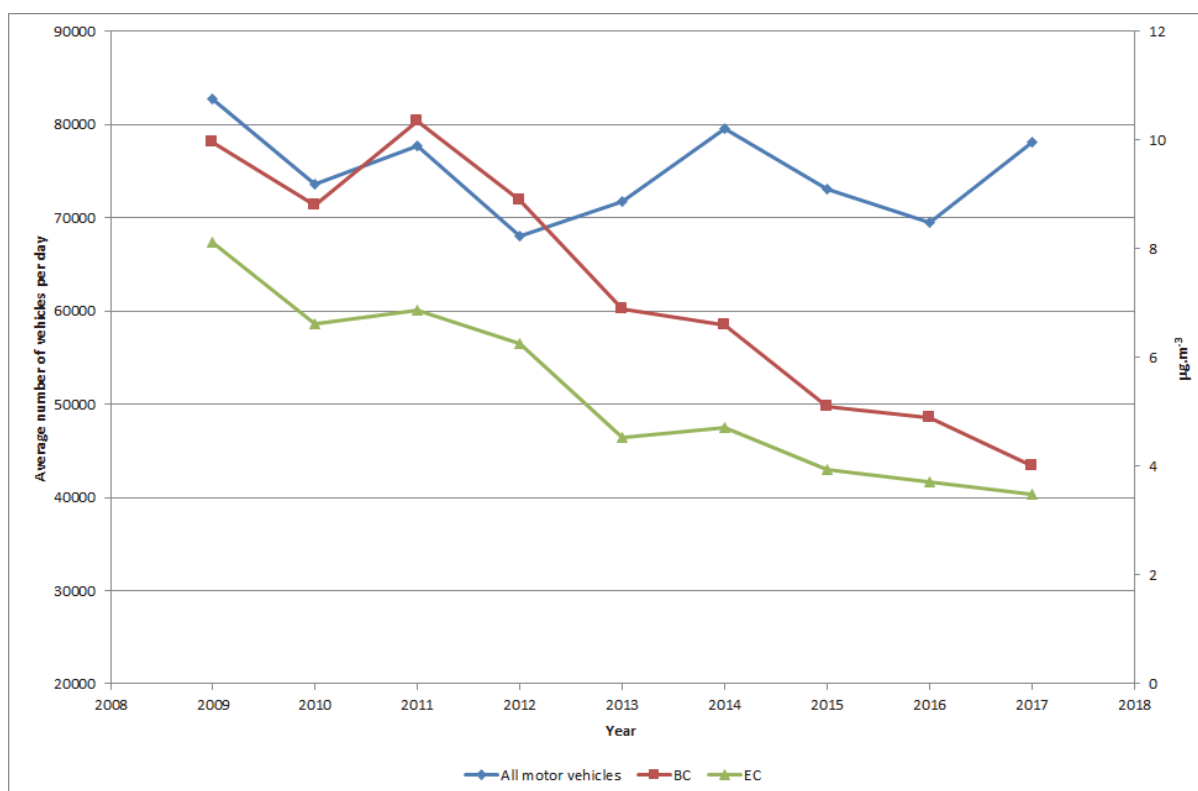


Figure 4-19 Annual Average Black Carbon, Elemental Carbon and Motor Vehicles per day at Marylebone Road for the period 2009 – 2017

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 2017. 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 4-20 is Figure 4-19 replotted with the number of motor vehicles per day passing the Marylebone Road monitoring site replaced by [100 – percentage of low emission buses in the London bus fleet].

Table 4-3 Composition of London bus fleet, 2010 to 2017⁶

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

**Figure 4-20 Annual Average Black Carbon, Elemental Carbon and [100 – percentage of low emission buses in the London bus fleet] for the period 2009 – 2017.**

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 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, though Chilbolton consists of two years' data to date.

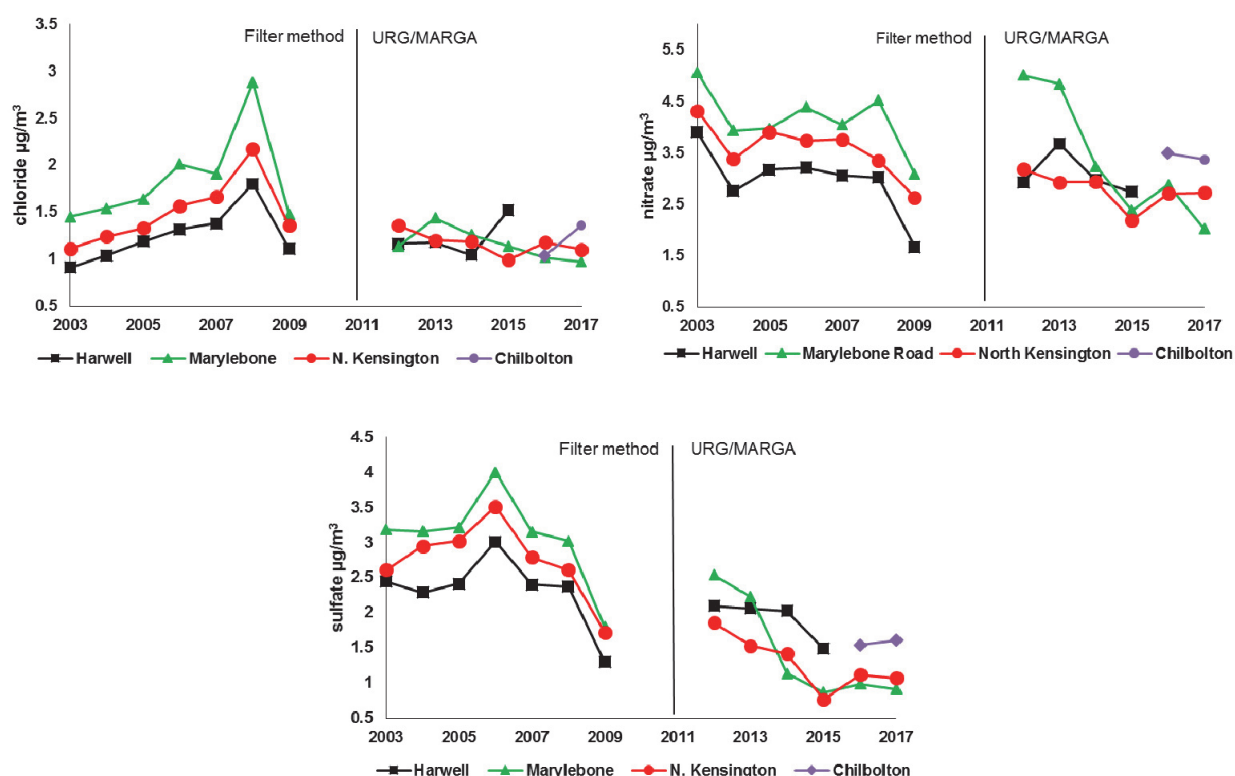


Figure 4-21 Anion long-term annual trends (clockwise chloride, nitrate and sulphate). The 2012 – 2017 data for Harwell/Chilbolton have been derived from the MARGA measurements.

4.5.3 Particle number concentrations

Figure 4-22 shows long-term annual trends for CPC measurements at all sites. 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

Legislation enacted in June 2007⁸ 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 2007¹⁰ 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.

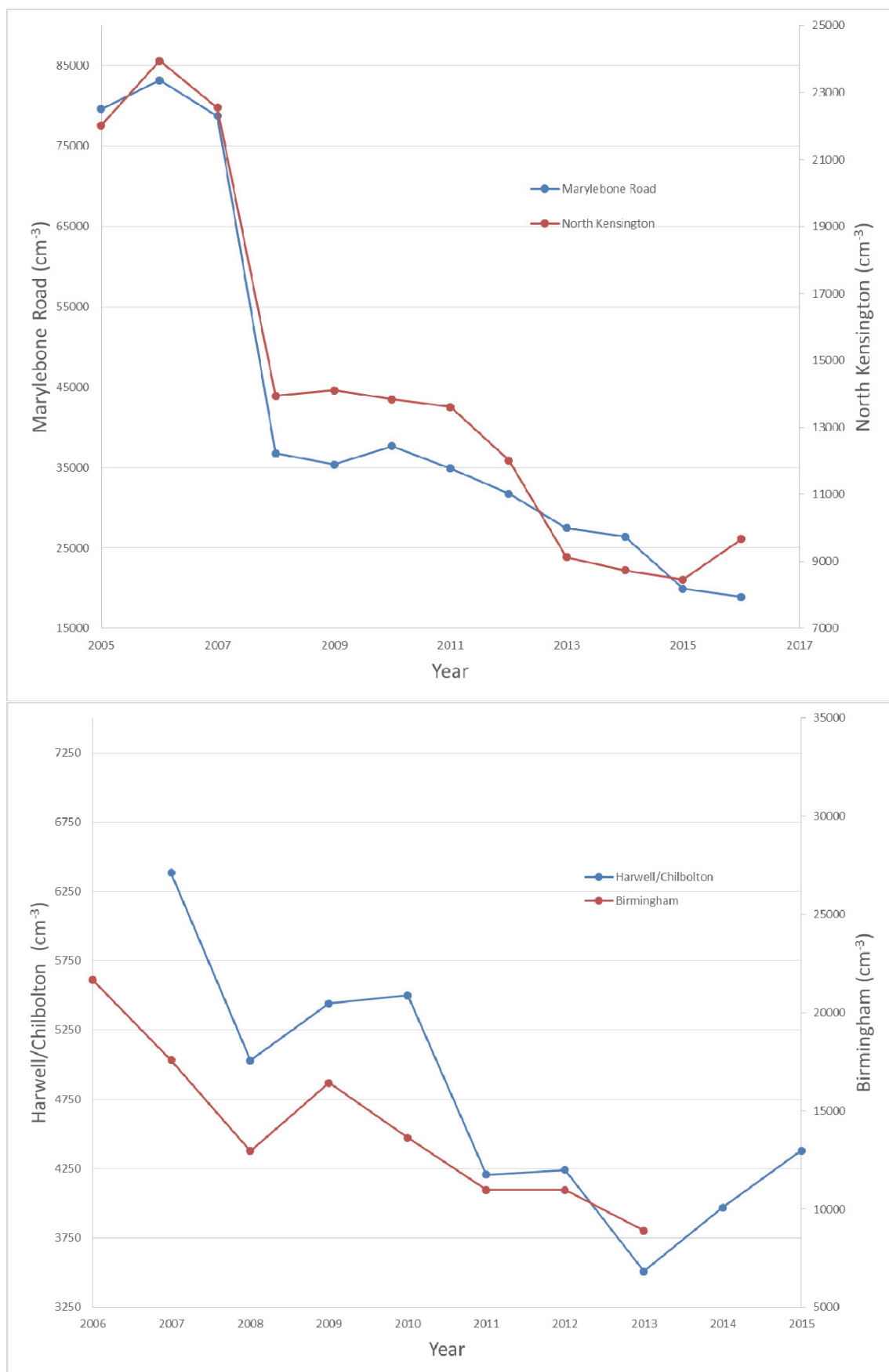


Figure 4-22 Historic CPC long-term annual trends at all sites. No data are available since 2014 for the Birmingham site. The Harwell site moved to Chilbolton in 2016.

4.6 DIURNAL, WEEKLY AND MONTHLY PROFILES

Diurnal, weekly and monthly profiles have been plotted in Figures 4-23, 4-24, and 4-25 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 4-24 indicates the existence of both $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 . The lowest concentrations of NO_3^- and NH_4^+ in the afternoon are attributed to the dissociation of NH_4NO_3 at higher temperatures during the day.

Figure 4-24 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, 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.

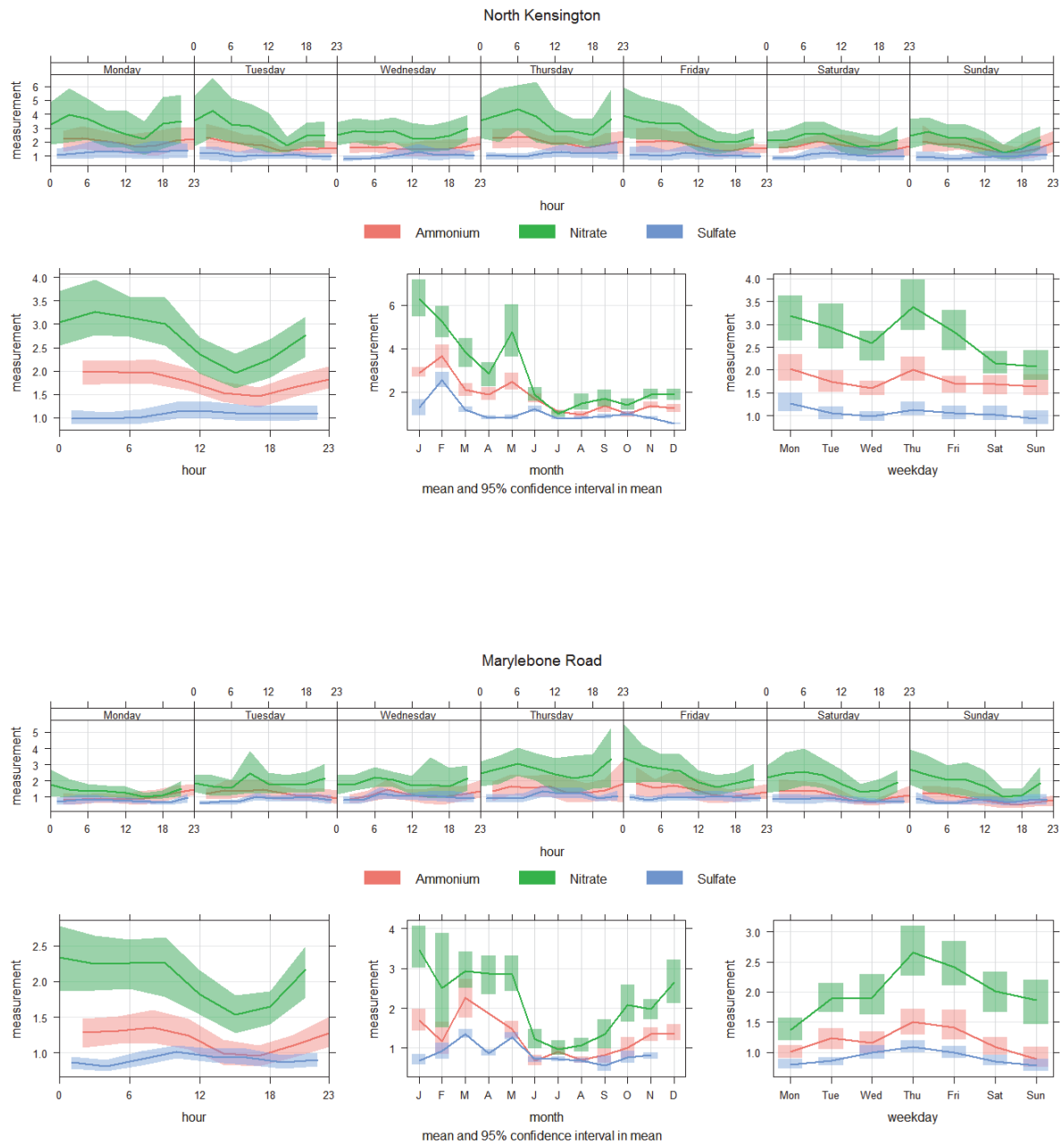


Figure 4-23 Diurnal, weekly and monthly profiles for and NH_4^+ , NO_3^- and SO_4^{2-} during 2017 at North Kensington (top) and Marylebone Road (bottom).

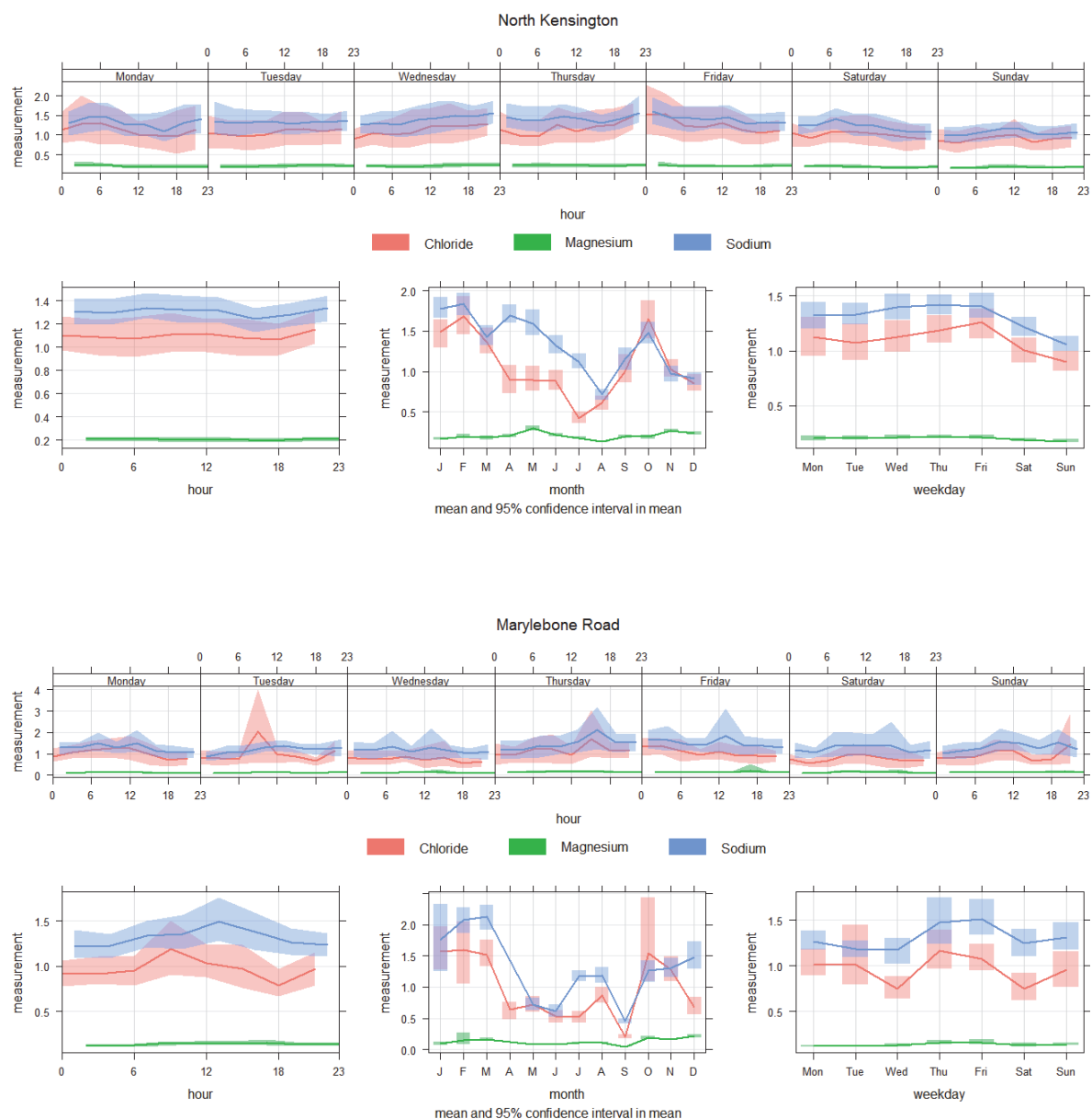


Figure 4-24 Diurnal, weekly and monthly profiles for Cl^- , Mg^{2+} and Na^+ concentrations during 2017 at North Kensington (top) and Marylebone Road (bottom).

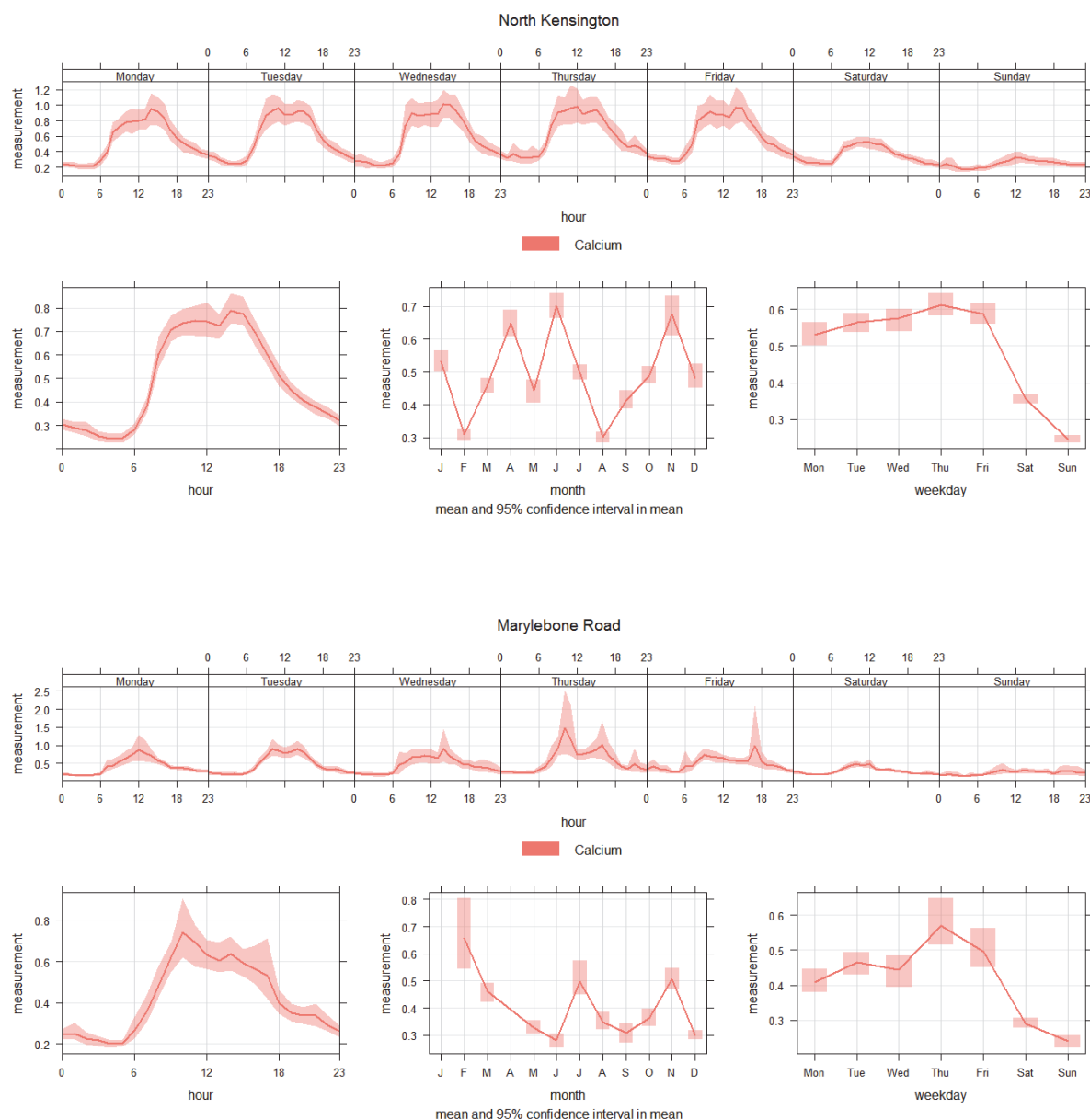


Figure 4-25 Diurnal, weekly and monthly profiles for Ca^{2+} during 2017 at North Kensington (top) and Marylebone Road (bottom).

4.6.2 Profile for number concentrations

The data for the diurnal, weekly and monthly profiles for number concentrations in 2017 are limited because there is only data for seven months from North Kensington and 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 there is a minimum in summer as a combination of vertical dilution during warm months due to a higher mixing layer, and the summer break which reduces anthropogenic activities.

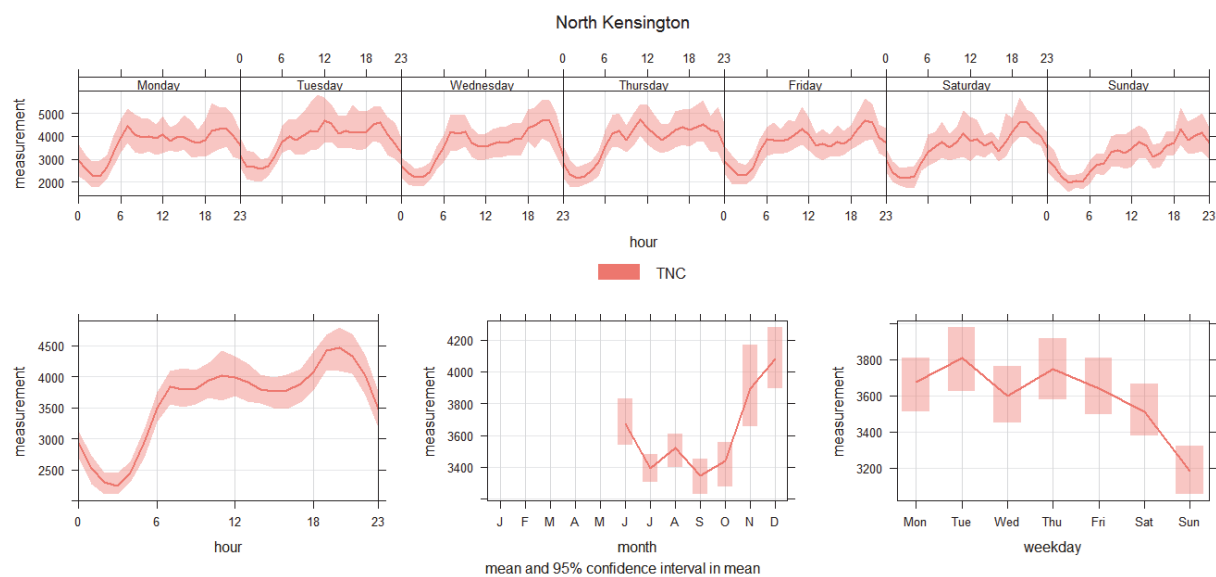


Figure 4-26 Diurnal, weekly and monthly profiles for number concentrations in 2017 at North Kensington

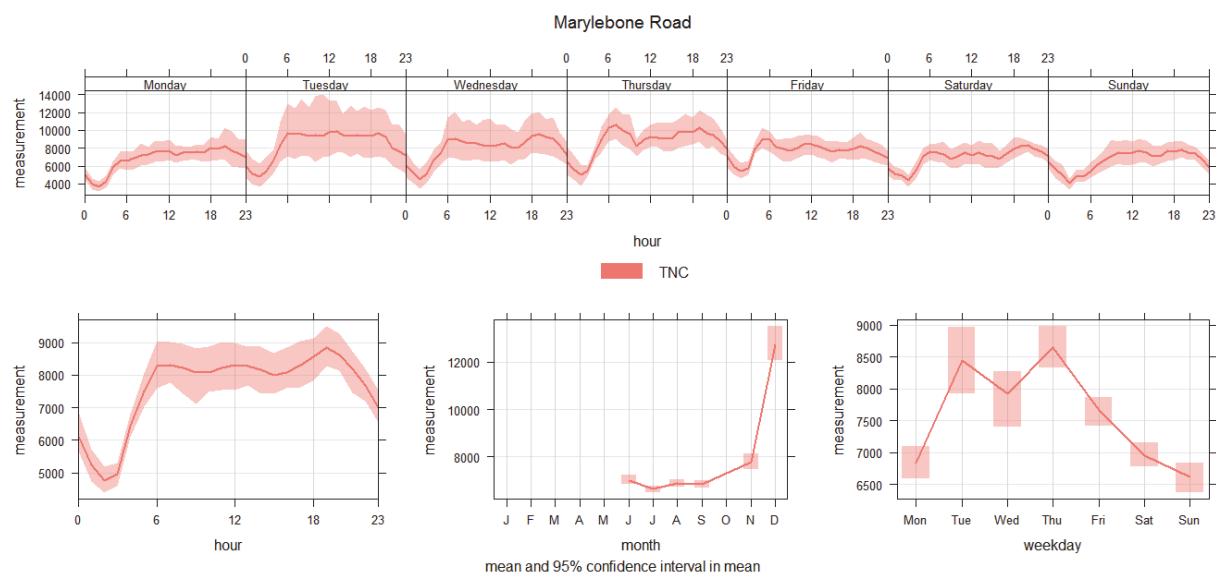


Figure 4-27 Diurnal, weekly and monthly profiles for number concentrations in 2017 at Marylebone Road

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

Daily measurements of sulphate, and monthly measurements of nitrate, chloride and ammonium are made at a number of rural sites through the Ammonia and Acid Deposition Monitoring Networks.

As part of the UK implementation of the EMEP monitoring strategy, two rural sites, Auchencorth Moss and Harwell (now moved to Chilbolton), have been established to monitor, *inter alia*, particulate matter. The measurements of relevance to this network are those of:

- Sulphate, nitrate, ammonium, sodium, potassium, calcium and magnesium ions in both the PM₁₀ and PM_{2.5} size fractions, on an hourly basis, using a steam-jet aerosol collector.
- Black Carbon by aethalometry, with supplementary analysis of filter samples for EC and OC (which is explicitly performed within this network).

5.2 UPDATE ON 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 PM_{2.5} (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 PM_{2.5} 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 SMPSSs, 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 2017 were as follows:

WG 34:

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" by Sonya Beccaceci, Richard J. C. Brown, David M. Butterfield et al was completed and published in Environmental Science: Processes and Impacts **18** 1561-1571 (2016).

The UK relies on automated instrumentation, instead of a filter based method, to report ion concentrations to Europe. During the latest 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.

Funding was sought 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, as funding has not been obtained, WG 34 cannot develop a standard on the equivalence of automatic measurements of NO₃⁻, SO₄²⁻, Cl⁻, NH₄⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, in PM_{2.5}. Therefore, WG 34 has been disbanded.

WG 35:

The standard EN 16909, "Ambient air - Measurement of elemental carbon (EC) and organic carbon (OC) collected on filters" was published in March 2017.

Two new work items are in progress; "Measurement of elemental carbon (EC) and organic carbon (OC) in PM₁₀ and PM_{coarse}" 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.

The following paper was published: Standardisation of a European measurement method for organic carbon and elemental carbon in ambient air: results of the field trial campaign and the determination of a measurement uncertainty and working range, Richard J. C. Brown, Sonya Beccaceci, David M. Butterfield, Paul G. Quincey, Peter M. Harris et al, *Environmental Science: Processes & Impacts* **19** 1249-1259 (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

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- ² NPL report “2017 Annual Report for the UK Black Carbon Network”
- 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>
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- 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.
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