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NPL REPORT ENV 39

AIRBORNE PARTICULATE CONCENTRATIONS AND NUMBERS IN THE UNITED KINGDOM

Annual report 2019

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SEPTEMBER 2021

Airborne Particulate Concentrations and Numbers in the United Kingdom: Annual report 2019

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ISSN: 2059-6030

https://doi.org/10.47120/npl.ENV39

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EXECUTIVE SUMMARY

This report was prepared by the National Physical Laboratory (NPL) and the Environmental Research Group (ERG) at King's College London (KCL) as part of the UK Airborne Particulate Concentrations and Numbers (PCN) contract managed by the Environment Agency (EA), provided on behalf of the Department for the Environment, Food and Rural Affairs (Defra) and the Devolved Administrations (the Scottish Government, the Welsh Government and the Department of the Environment in Northern Ireland). ERG moved from KCL to Imperial College London (ICL) during 2020.

This Annual Network Report for 2019 contains:

- A summary of network operations and quality procedures
- Description of the instruments used on the Network
- A graphical presentation of all ratified network data from 2019
- Data capture for each instrument
- Comparison of 2019 data with data from recent years.

The Network operated instruments at four monitoring sites: the London roadside site Marylebone Road, the London urban background site Honor Oak Park, and the rural sites Chilbolton, in south-east England, and Auchencorth Moss, in Scotland.

Weekly measurements of Organic Carbon and Elemental Carbon (OC/EC) in the $PM_{2.5}$ fraction, required by the European directive 2008/50/EC, continued throughout the year at the two rural sites, Chilbolton, and Auchencorth Moss. Daily measurements of OC/EC were changed from the PM_{10} fraction to the $PM_{2.5}$ fraction at Honor Oak Park in February 2019, and at Marylebone Road in October 2019. Daily PM_{10} measurements of OC/EC at Chilbolton were discontinued in October 2019.

Hourly $PM_{2.5}$ ion chromatography measurements were made at Honor Oak Park throughout the year. The size fraction of similar measurements at Marylebone Road was changed from PM_{10} to $PM_{2.5}$ in January 2019. Concentrations of chloride, nitrate, sulfate, sodium, ammonium, potassium, magnesium, and calcium ions in ambient air were measured at these sites. An Aerosol Chemical Speciation Monitor (ACSM) operated by ICL at Honor Oak Park provided hourly measurements of ammonium, nitrate, sulfate, and organic aerosols in $PM_{2.5}$.

Hourly total particle number concentrations were measured using condensation particle counters (CPCs) at Chilbolton, Honor Oak Park and Marylebone Road. Particle number size distributions were also measured using scanning mobility particle sizers (SMPSs) at the same sites.

Across 2018 and 2019, the network instruments have switched from sampling PM_{10} to sampling $PM_{2.5}$ to align with the shift in focus towards $PM_{2.5}$ as a more relevant metric for health effects.

Some notable features of the data are:

- Annual average EC concentrations at Marylebone Road have decreased rapidly and steadily from around 8 μg m^{-3} in 2009 to around 2 μg m^{-3} in 2019. EC at other sites, and OC at all sites, have shown a more gradual decline.

- Annual average particle number concentrations at Marylebone Road have remained relatively constant in the range 7,000 to 10,000 cm^{-3} since the rapid decrease from around 80,000 cm^{-3} in 2007-2008, which was attributed to the introduction of low sulfur vehicle fuel.

The Network data are available electronically via the Defra UK-Air website[1].

CONTENTS

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), organic and elemental carbon concentrations, and anion and cation concentrations. An Aerosol Chemical Speciation Monitor (ACSM) is operated by Imperial College London (ICL) (formerly King's College London (KCL).

This report shows a summary of the 2019 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 2019 was structured in the same way as the previous year, with the CPC in Birmingham not yet operating, as it is awaiting the finalisation of a data collection setup. King's College London continued its role as the Central Management and Control Unit (CMCU). From July 2020, this team is now based at Imperial College London . It carried out activities including routine collection of data from site, initial data validation and instrument fault finding, and routine liaison with the Local Site Operators (LSO) and the Equipment Support Unit (ESU). NPL continued its role of overall coordination and management, together with QA/QC activities, which includes site audits, instrument calibrations, data ratification and reporting.

2.2 NETWORK STRUCTURE

The measurement programme during 2019 is shown in Table 2-1.
[1] In January 2019, the URG PM_{10} head at Marylebone Road was changed to a $PM_{2.5}$ head.
[2] At the end of February 2019, the PM_{10} head of the Partisol at Honor Oak Park was changed to $PM_{2.5}$.
[3] In October 2019, the PM_{10} head on the Partisol at Marylebone Road was changed to a $PM_{2.5}$.
[4] At the end of October 2019, the Partisol PM_{10} at Chilbolton was removed.

Table 2-1 Network structure in 2019

SITE	Hourly PM_{10} or $PM_{2.5}$ Ions	Daily PM_{10} or $PM_{2.5}$ OC/EC	Weekly $PM_{2.5}$ OC/EC	CPC	SMPS	Hourly ACSM $PM_{2.5}$
Chilbolton (Rural background)		X [4]	X	X	X	
Auchencorth Moss (Rural background)			X			
London Marylebone Road (Urban Roadside)	X [1]	X [3]		X	X	
London Honor Oak Park (Urban background)	X	X [2]		X	X	X

Site locations are shown in Figure 2-1 and site details are available through the Defra UK Air website.

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

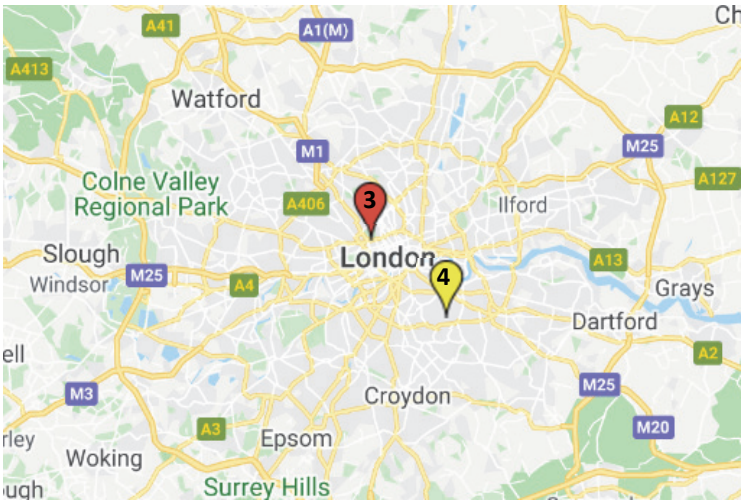

Figure 2-1 Network sites in 2019

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 the Condensation Particle Counter (CPC) TSI model 3772-CEN, installed at the sites in June 2017, replacing the older TSI 3022a models.

The CPC instrument works by passing a 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 CEN Technical Specification for CPC measurements, CEN/TS 16976, outlines the measurement criteria for the control of humidity in the sampled aerosol.

When the new Condensation Particle Counter (CPC) TSI model 3772-CEN instruments were installed in 2017, new drier systems manufactured by TSI were installed with them. After some initial teething problems, a solution comprising 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 CPC, SMPS and drying unit equipment at a typical site.

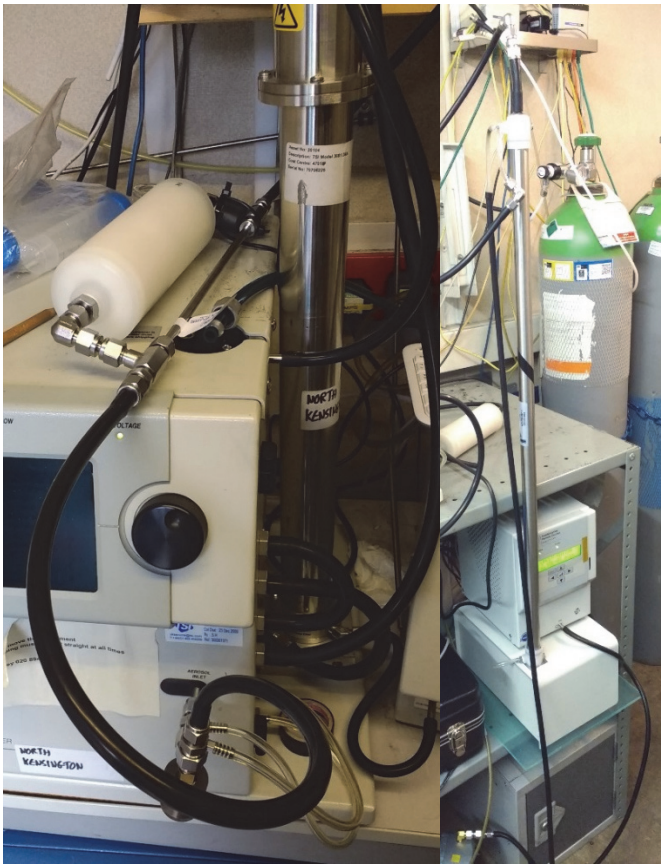

Figure 2-2 Typical configuration of CPC, SMPS and drying units at the Network sites

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} (changed to $PM_{2.5}$ in February 2019 and October 2019 for Honor Oak Park and Marylebone Road, respectively), was made using a Thermo Partisol 2025 sequential air sampler (Figure 2-3 (a)). The same model was used at Chilbolton for daily sampling with a PM_{10} head. This sampler was removed at the end of October 2019. Weekly measurements of $PM_{2.5}$ were made at Chilbolton and Auchencorth Moss using a Leckel SEQ47/50 sequential sampler (Figure 2-3 (b)). Ultrapure quartz filters (Pallflex® Tissuquartz™ 2500QAT-UP) were used for the sampling.

The elemental and organic carbon analysis was carried out using the Sunset Laboratory Inc. thermal/optical carbon analyser, model 5L similar to that shown in Figure 2-4. In the laboratory, a 1.5 cm^2 punch was taken from each filter and analysed.

The procedure involves heating the sample to remove 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 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.

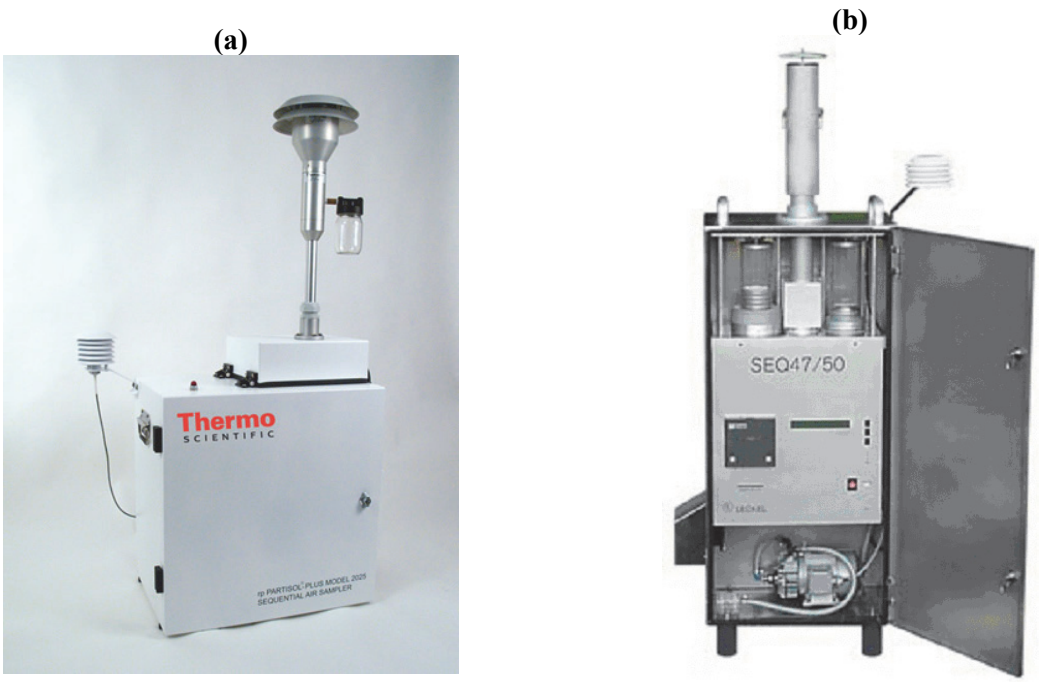

Figure 2-3 (a) Thermo Partisol 2025 sampler (b) Leckel SEQ47/50 sampler

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

2.3.4 URG – AIM 9000B (PM_{10} and $PM_{2.5}$ anion and cation measurements)

The URG – AIM (Ambient Ion Monitor) 9000-B (
Figure 2-5) 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 have their 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 µm ($PM_{2.5}$) or 10 µm (PM_{10}) 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. The two Ion Chromatography systems then 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. 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. The size selective head at Marylebone Road was changed from PM_{10} to $PM_{2.5}$ on 9 January 2019. At Honor Oak Park this change had already been carried out at the end of November 2018.

Figure 2-5 URG – 9000B Ambient Ion Monitor

2.3.5 ACSM - Aerosol Chemical Speciation Monitor

The Aerodyne Research Inc. (ARI) Aerosol Chemical Speciation Monitor (ACSM) measures aerosol mass and chemical composition of non-refractory submicron aerosol particles in real-time in ambient air. It uses established Aerosol Mass Spectrometer technology to provide quantitative chemical composition measurements for particulate ammonium, nitrate, sulfate, chloride, and organics. It is designed for continuous monitoring of aerosol composition with long-term (weeks) of unattended operation.

The instrument operates by sampling air into a high vacuum system through a particle aerodynamic lens. The particle lens focuses submicron aerosol (~40 - 1000 nm aerodynamic diameter) into a narrow beam which is directed to a resistively heated particle vaporiser, typically operated at 600°C, mounted inside the ionisation chamber of a mass spectrometer where non-refractory components in/on the particle flash vaporise on impact. The vaporised constituents are ionised by electron impact then analysed with a quadrupole mass spectrometer which reports aerosol mass spectra (<200 amu). These spectra are used to extract the chemically speciated aerosol mass loadings. Figure 2-6 below, shows a schematic diagram of the set up.

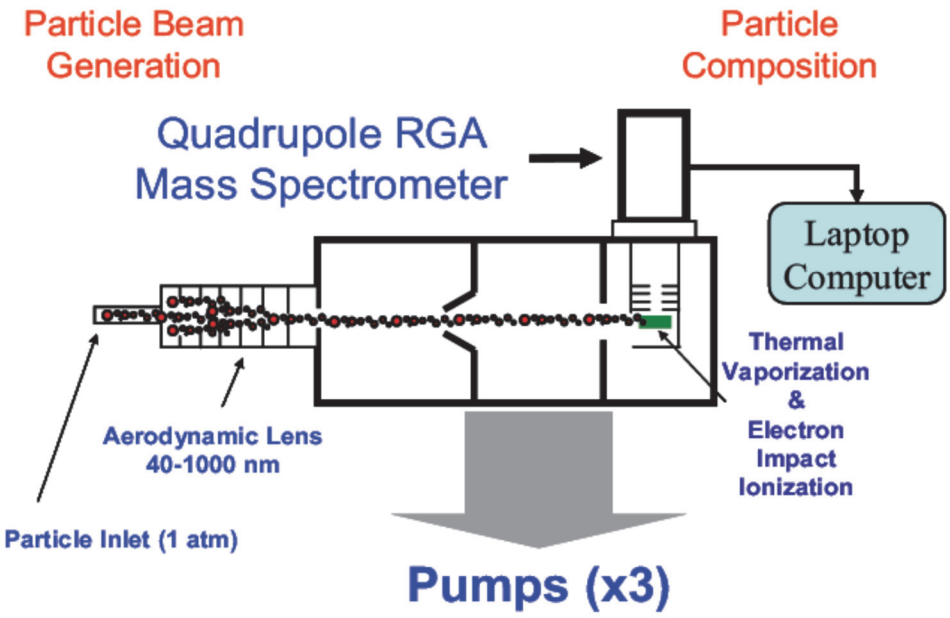

Figure 2-6 ARI Aerosol Speciation Chemical Monitor schematic

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 ICL Duty Officer is available to advise LSOs 365 days per year.
- Scheduled instrument services.
- An annual audit of all sites, LSOs and instruments conducted by an independent NPL team.
- Regular calibrations are carried out automatically, or manually, by the LSO or NPL, and calibration checks 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). This calibration data is used to produce a scaling factor to apply to the measurement data.
- For OC/EC analysis, field blank filters are 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 Environment Agency monitoring programmes are also used to check the validity of the measurements.

3.2 SCHEDULED INSTRUMENT SERVICE AND CALIBRATION

NPL received ISO 17025 accreditation for CPC calibration in 2008, and therefore since January 2009, the network CPCs have been serviced and calibrated at NPL. Since January 2010, the SMPS instruments have also been serviced and calibrated at NPL. From 2019, calibrations also included an additional stepwise SMPS size calibration for individual instruments as well as the multi-instrument simultaneous checks to improve quality.

The 2025 Partisols at Chilbolton, Honor Oak Park and Marylebone Road were serviced by the ESU, Air Monitors (ACOEM), during 2019. Under the new Network contract, starting 1 November 2019, the Environment Agency’s Ambient Air Monitoring (AAM) team took over Partisol servicing and callout duties (the Honor Oak Park Partisol was serviced in November). The Leckel SEQ47/50s at Auchencorth Moss and Chilbolton were serviced by the ESU, Enviro Technology Services. These 6-monthly 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 laboratory blank filter and a filter spiked with a traceable standard solution.

The URG-AIMs at Honor Oak Park and Marylebone Road were serviced by the ESU, Enviro Technology Services during 2019. NPL continue to make the ion chromatography system calibration standards from traceable stock standard solutions and carry out quarterly calibrations.

The ACSM at Honor Oak Park is supported by ICL staff who perform monthly flow checks and *ad hoc* instrument tuning, and pinhole and inlet cleaning. Repairs are carried out by the ICL operator following Aerodyne advice and procedures. The instrument is calibrated biannually using laboratory ammonium sulfate and ammonium nitrate standards.

4 NETWORK DATA

4.1 DAILY OC/EC MEASUREMENTS

4.1.1 OC/EC and Total Carbon (TC = OC + EC)

Daily measurements of OC (Organic Carbon) and EC (Elemental Carbon) collected on filters are provided by this Network at three sites: Chilbolton (rural background), London Honor Oak Park (urban background) and London Marylebone Road (urban roadside). The existing PM_{10} sampling heads were changed to $PM_{2.5}$ at Honor Oak Park at the end of February 2019 and in October 2019 at Marylebone Road. At the end of October 2019, the Partisol (PM_{10}) at Chilbolton was removed. These daily PM_{10} measurements at Chilbolton were due to be replaced by daily $PM_{2.5}$ measurements using the weekly-sampling $PM_{2.5}$ Leckel sampler already situated there. Note that a change from weekly to daily sampling was scheduled to be made in June 2020, to provide information on composition during short term pollution events or diurnal variations. This aims to support improved source apportionment and assessment of emissions in space and time.

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, essentially soot, 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 2019 were 77%, 98% and 79% at Chilbolton, London Honor Oak Park and London Marylebone Road, respectively. Please note, however, that because sampling at Chilbolton was stopped at the end of October, the year-to-date data capture for Jan-Oct was 93%. The time series of OC, EC and TC (Total Carbon – the sum of OC and EC) are displayed in Figure 4-1, Figure 4-2, Figure 4-3, and Figure 4-4 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.

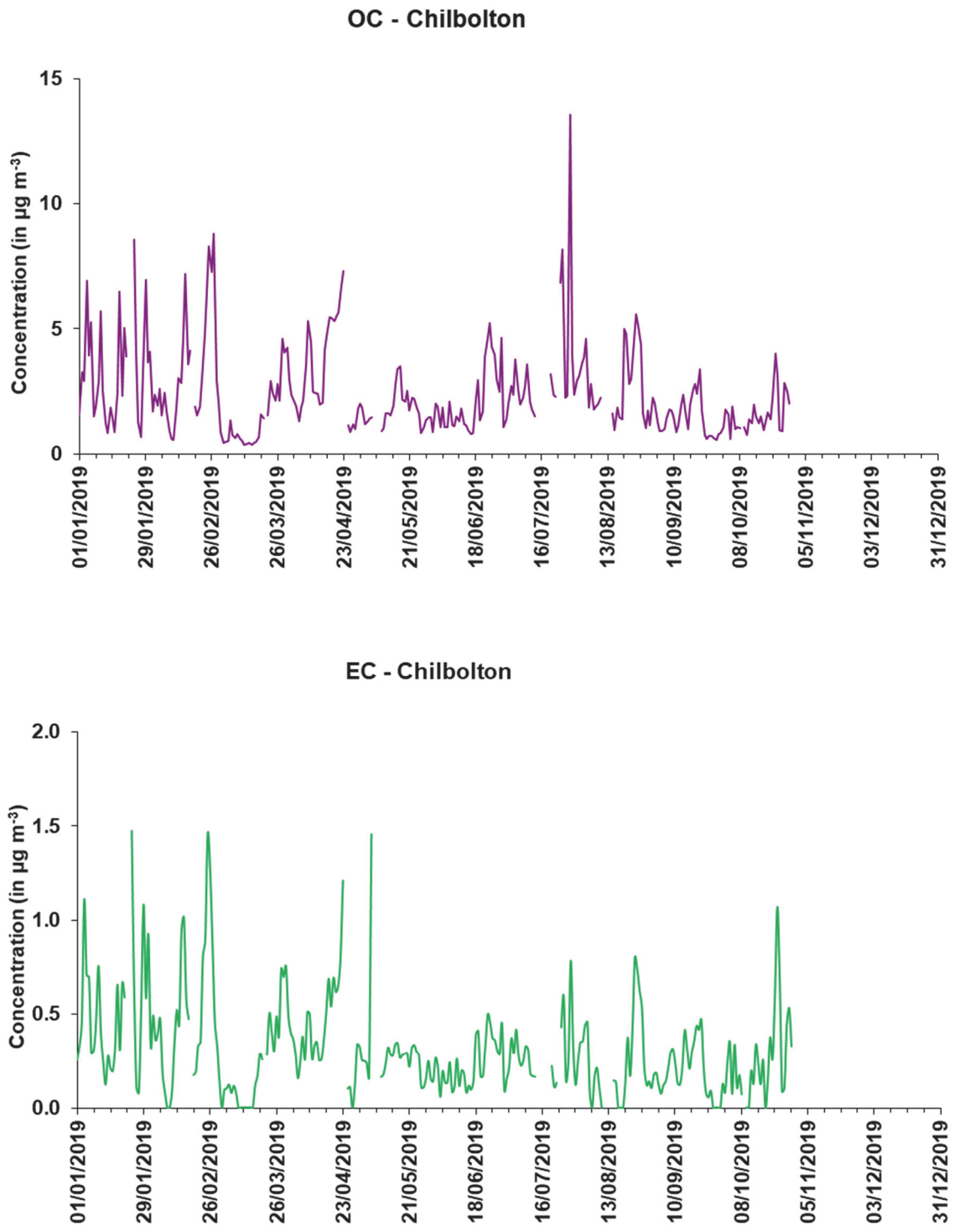

Figure 4-1 PM_{10} OC and EC concentrations (µg m^{-3}) at Chilbolton up until October 2019

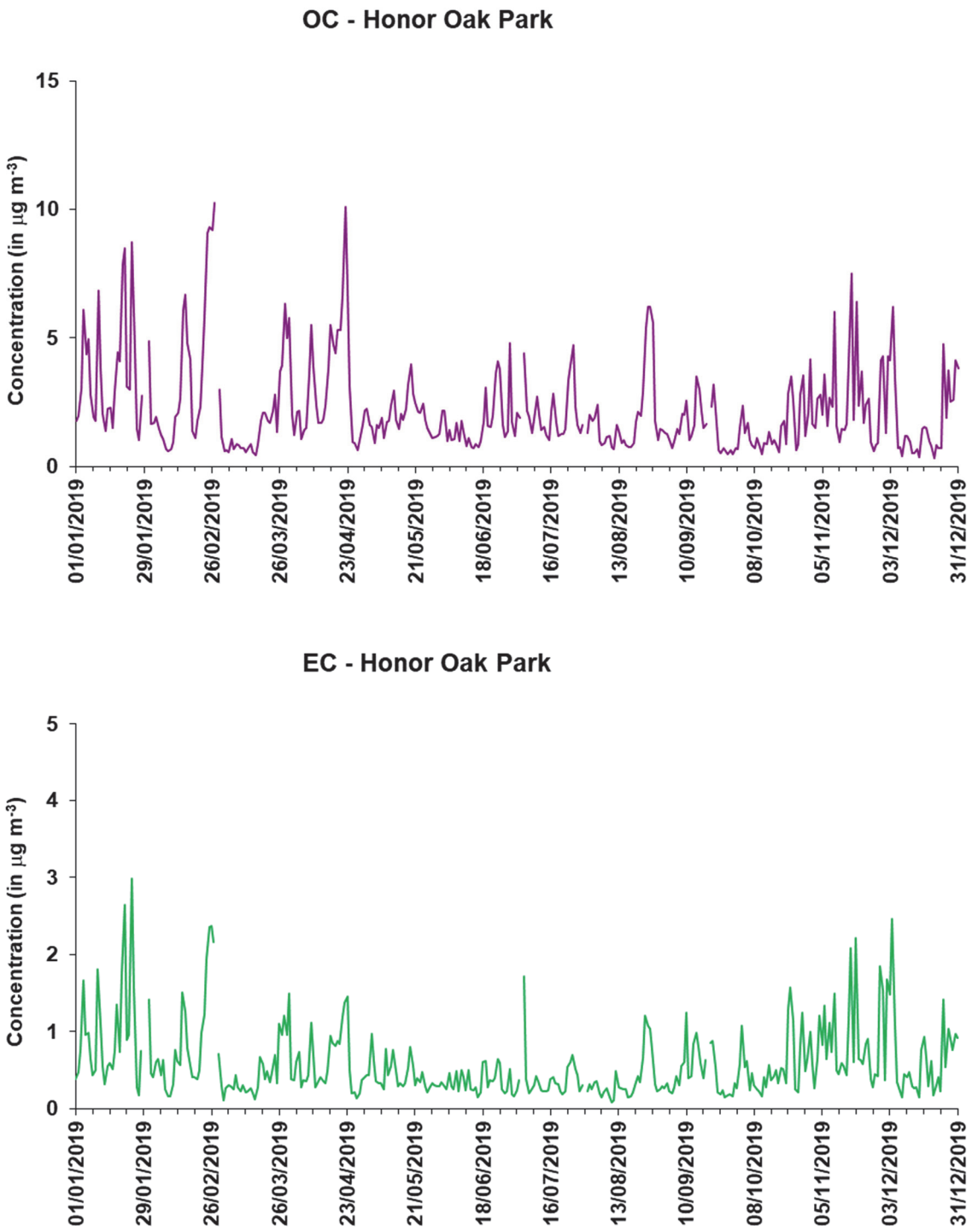

Figure 4-2 OC and EC concentrations at Honor Oak Park during 2019 (size selection changed from PM_{10} to $PM_{2.5}$ at the end of February)

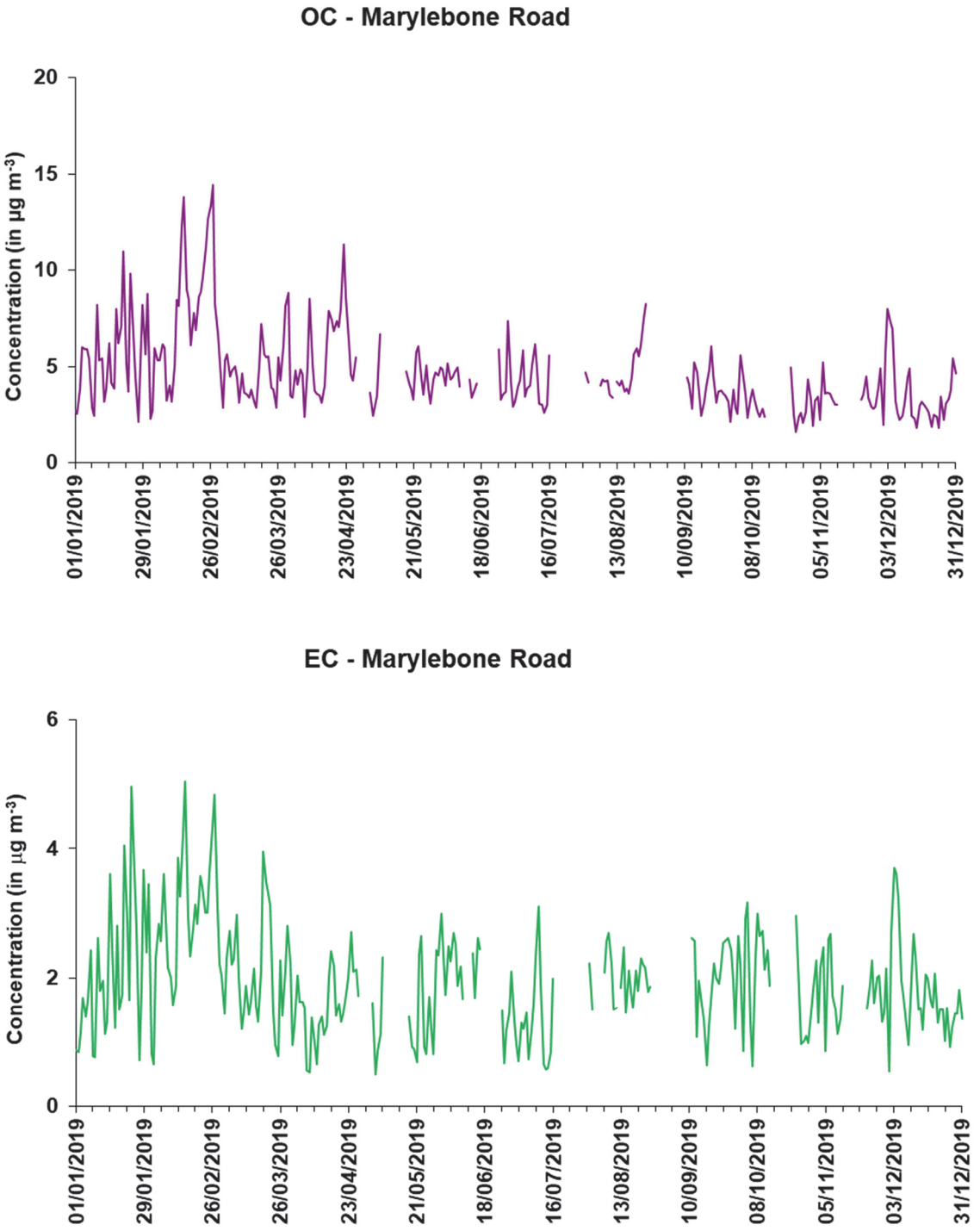

Figure 4-3 OC and EC concentrations at Marylebone Road during 2019 (size selection changed from PM_{10} to $PM_{2.5}$ at the end of October 2019)

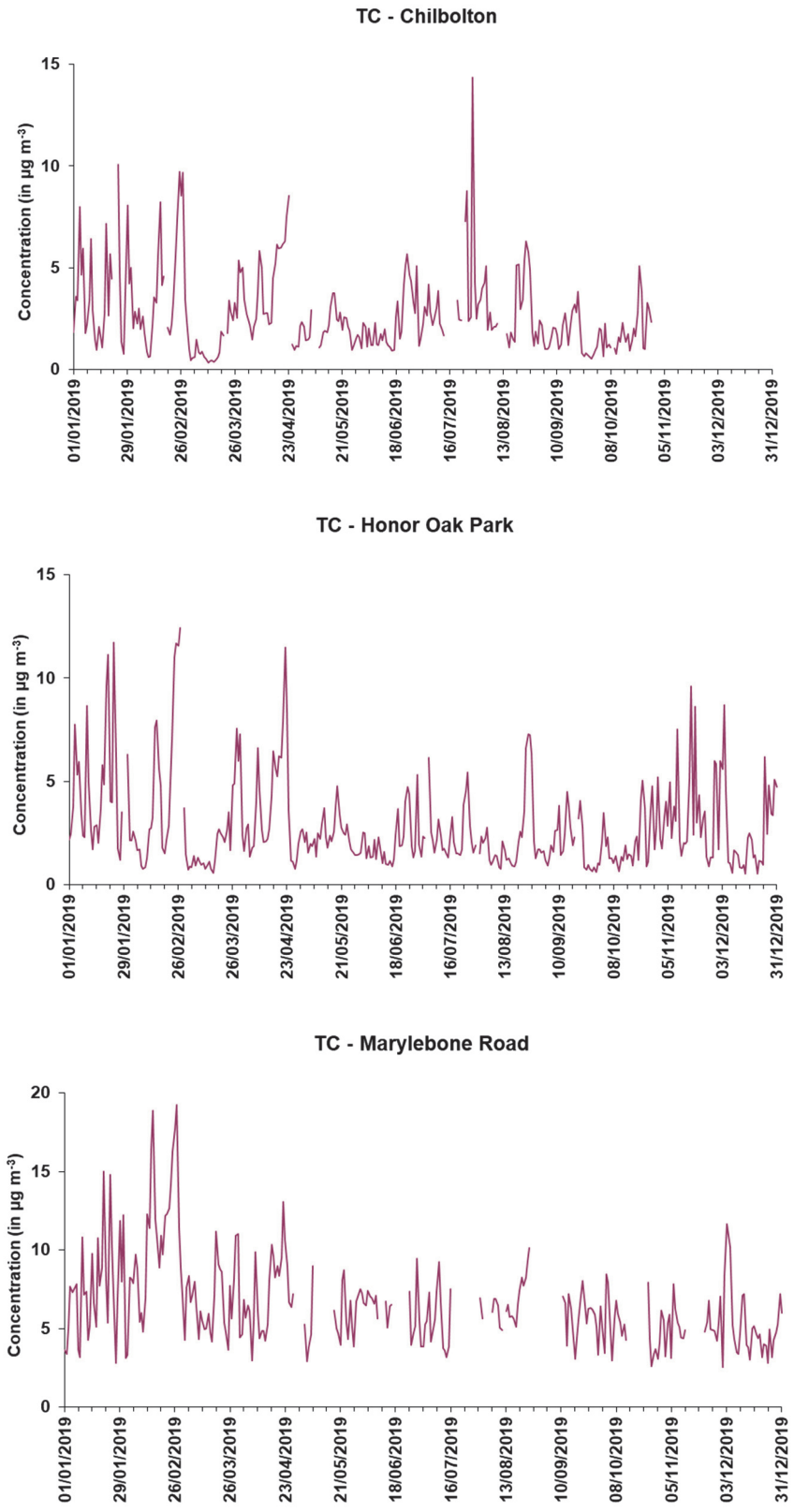

Figure 4-4 PM_{10} TC concentrations during 2019: at Chilbolton up until October 2019; at Honor Oak Park (size selection changed from PM_{10} to $PM_{2.5}$ at the end of February 2019); and Marylebone Road (size selection changed from PM_{10} to $PM_{2.5}$ at the end October 2019)

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 Chilbolton, Marylebone Road, and until 2018 at North Kensington, using aethalometer instruments as part of the Defra Black Carbon Network[2]. 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 4-5. The regression is calculated according to the Reduced Major Axis (RMA) method[3].

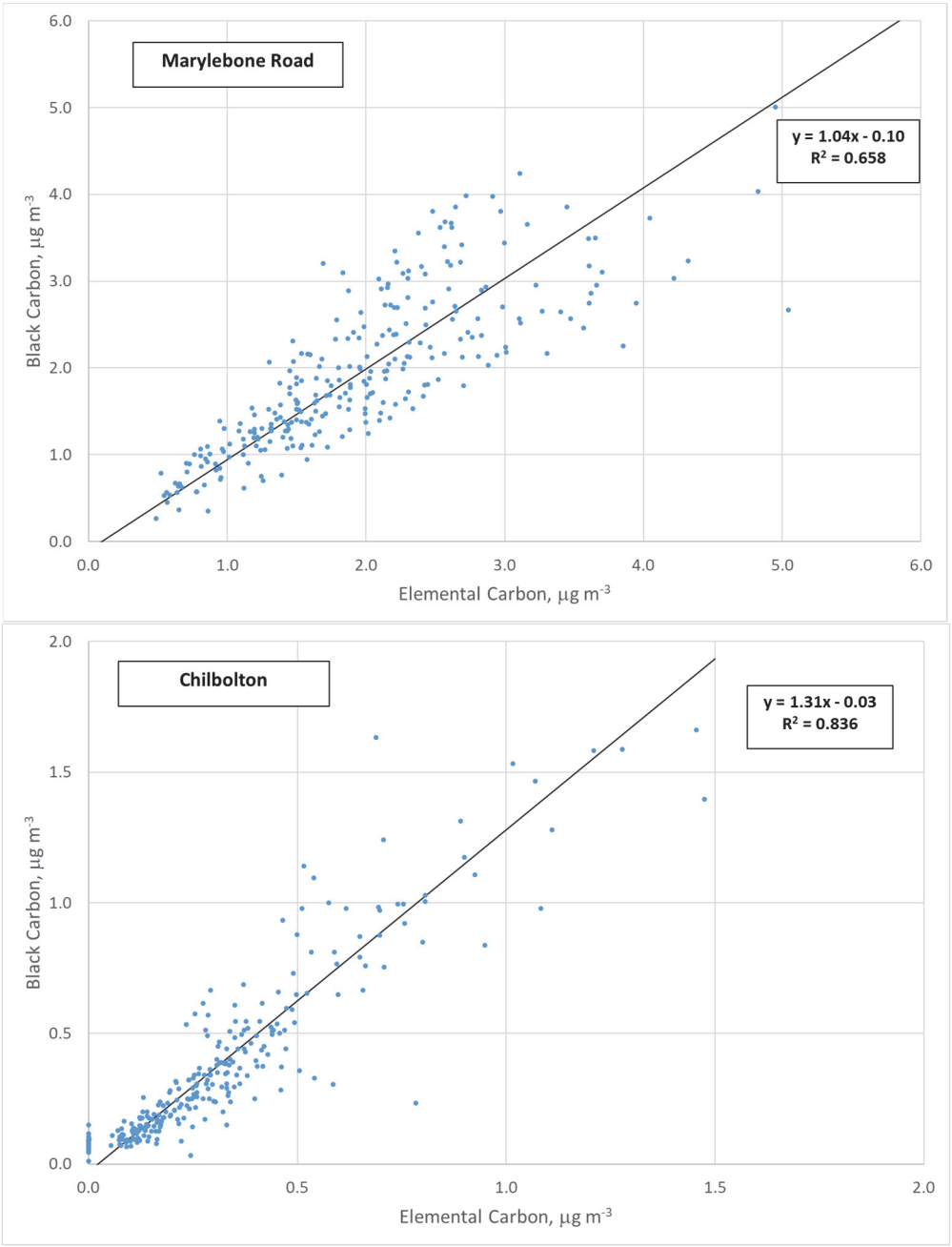

Figure 4-5 Comparison between $PM_{2.5}$ BC and $PM_{10\&2.5}$ EC at the Marylebone Road and Chilbolton sites in 2019

It can be seen that there is a generally good linear relationship between the Elemental Carbon and Black Carbon concentrations, and with comparable slopes. The relationship between Black Carbon and Elemental Carbon has been quite variable year to 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.

Table 4-1 Relationship between Black Carbon ($PM_{2.5}$) and Elemental Carbon ($PM_{10\&2.5}$) 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
2019	1.31 x - 0.03	0.836	-	-	1.04 x - 0.10	0.658

*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 to 2019 data are from Chilbolton and so may not be directly comparable to the Harwell data in previous years.

**The EC instrument was moved to Honor Oak Park in the end of 2018.

4.2 WEEKLY 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[4], 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 has operated there from 4 February 2016. The sampler at Auchencorth Moss has been operational since 17 November 2011. Data capture for 2019 was 87% for Chilbolton and 79% for Auchencorth Moss. Figure 4-6 and Figure 4-7 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.

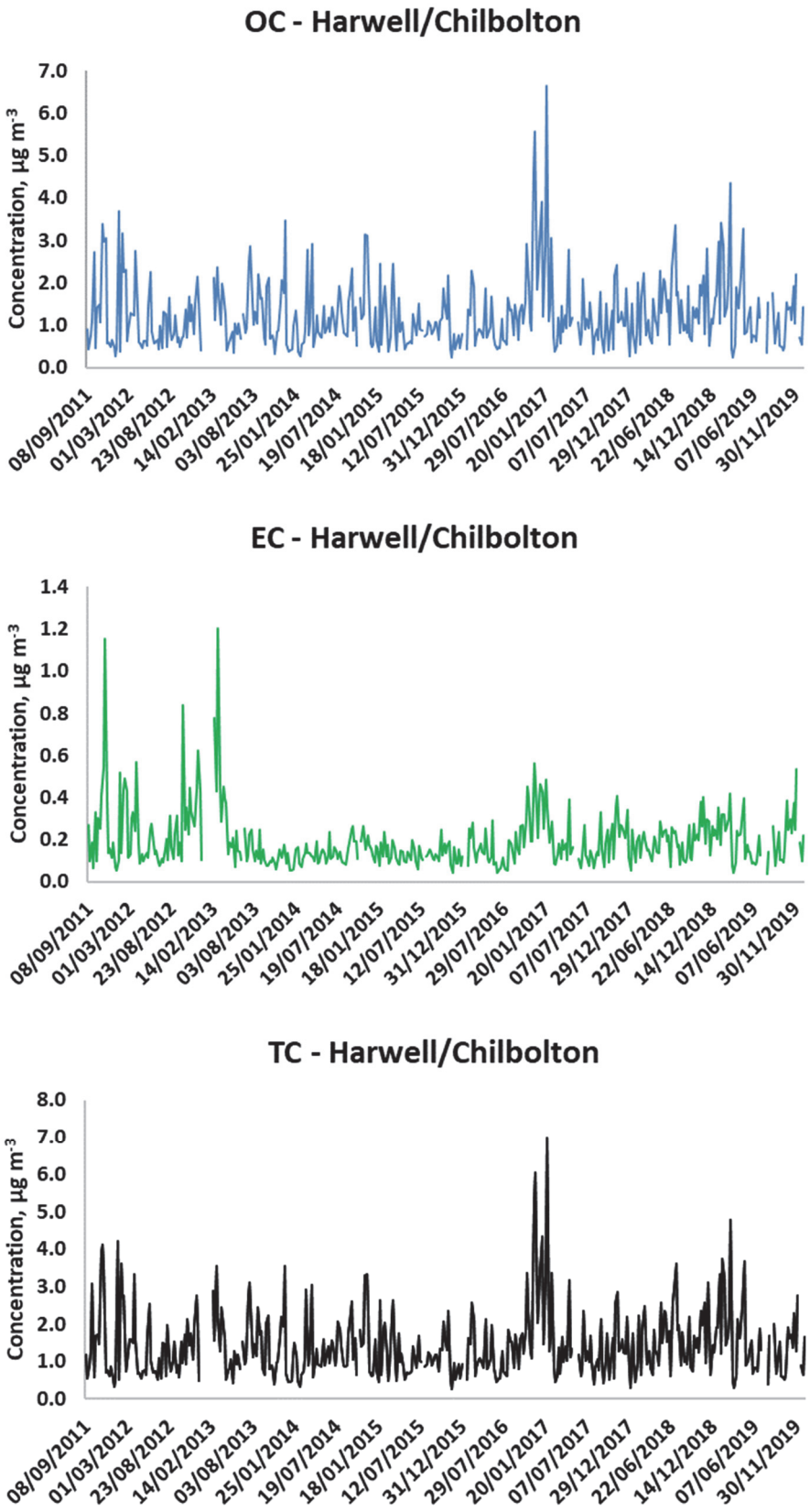

Figure 4-6 Time series of OC, EC and TC in the $PM_{2.5}$ fraction at Harwell/Chilbolton since the installation of the sampler up to the end of 2019 (weekly samples) (µg m^{-3}). The sampler moved from Harwell to Chilbolton in February 2016

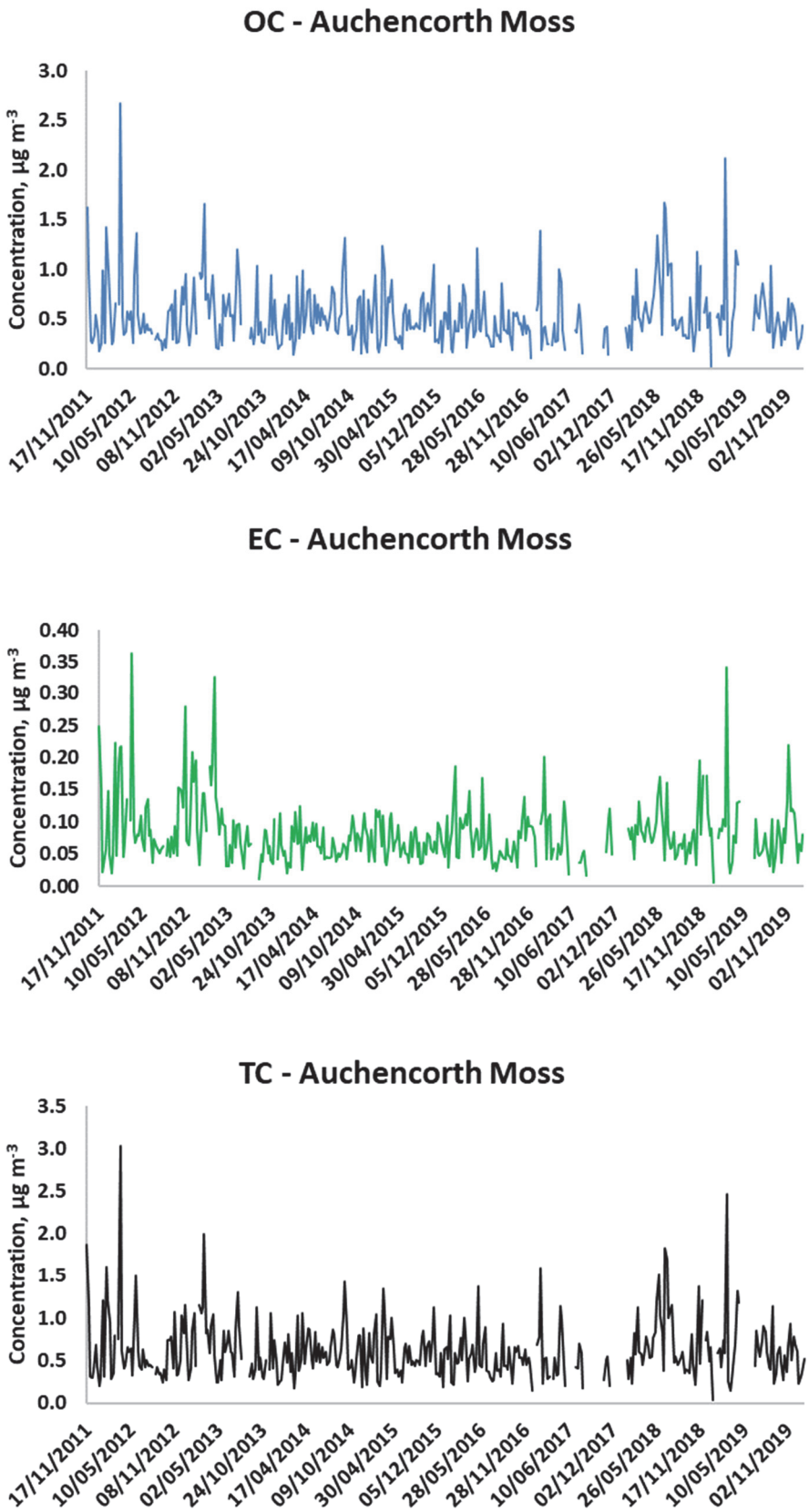

Figure 4-7 Time series of OC, EC and TC in the $PM_{2.5}$ fraction at Auchencorth Moss since the installation of the sampler up to the end of 2019 (weekly samples) (µg m^{-3})

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 4-8). 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. The lower $PM_{2.5}$ TC and OC data 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 lower EC may be an artefact due to the difficulty of determining the OC/EC split point at low concentrations.

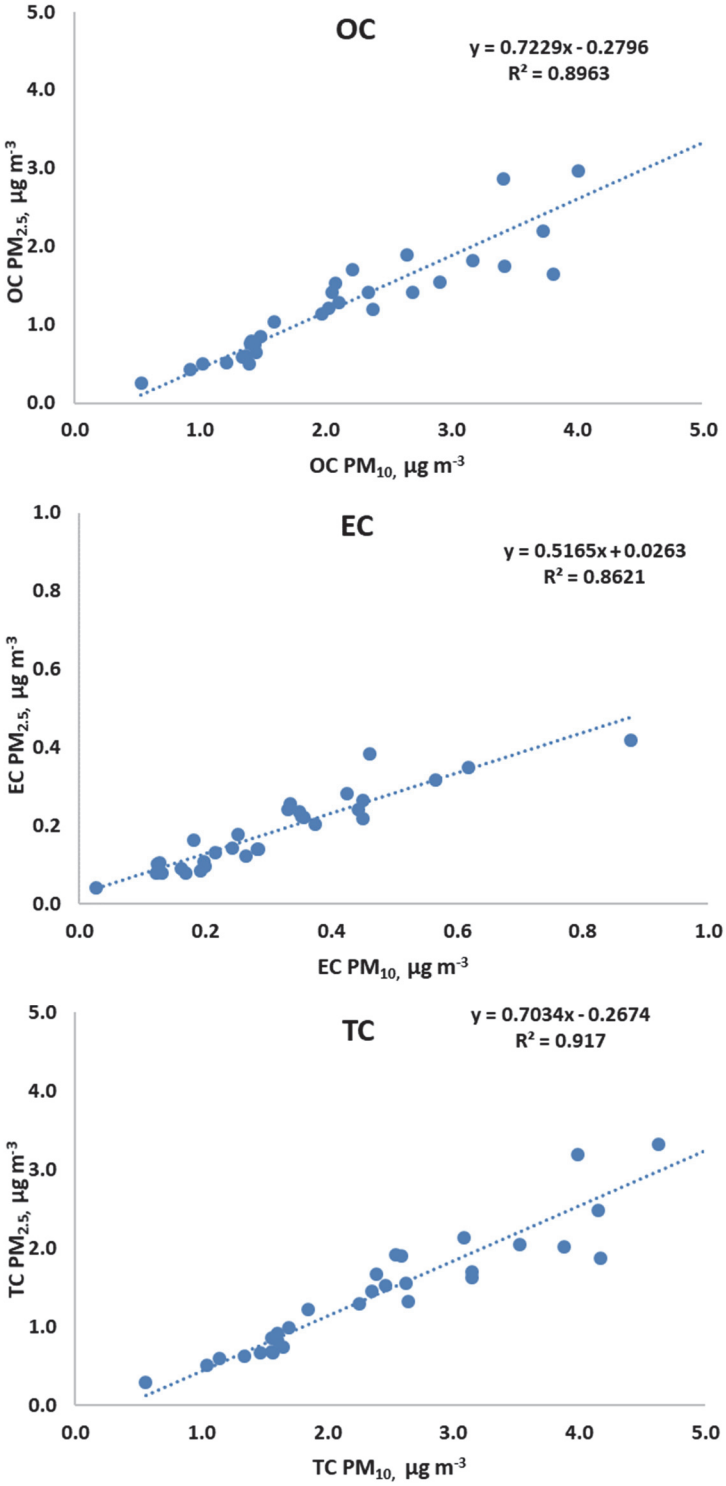

Figure 4-8 Comparison between weekly averages of PM_{10} and $PM_{2.5}$ of OC, EC and TC at Chilbolton in 2019

4.3 AUTOMATIC PM_{10} AND $PM_{2.5}$ ANION AND CATION MEASUREMENTS

The two URG 9000B – AIM instruments were installed at the two sites in London in February 2011 with PM_{10} size-selective heads. These instruments measure the hourly concentration of chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), sodium (Na^+), ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{2+}) and calcium (Ca^{2+}).

The size selective head was changed from PM_{10} to $PM_{2.5}$ in November 2018 at Honor Oak Park, and in January 2019 at Marylebone Road.

The 2019 annual data capture (averaged using all of the eight ions) was 60% for Marylebone Road (PM_{10} and $PM_{2.5}$) and 60% for Honor Oak Park ($PM_{2.5}$ only).

Figure 4-9 to Figure 4-12 show the time series at Marylebone Road and Honor Oak Park in 2019.

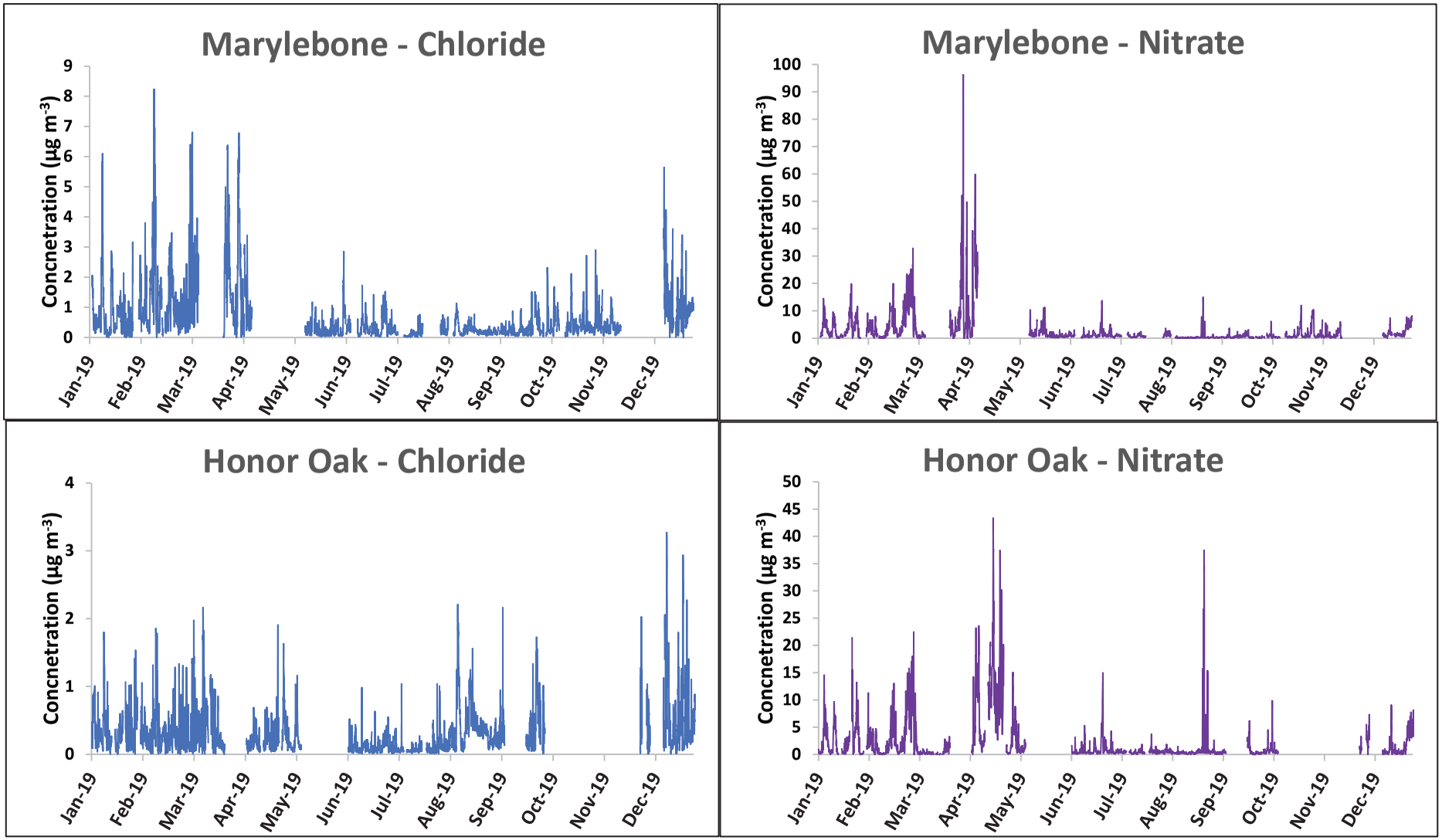

Figure 4-9 Time series for Chloride and Nitrate ion concentrations in $PM_{10/2.5}$ at Marylebone Road and $PM_{2.5}$ only Honor Oak Park in 2019 (PM_{10} changed to $PM_{2.5}$ at Marylebone on January 9th, 2019)

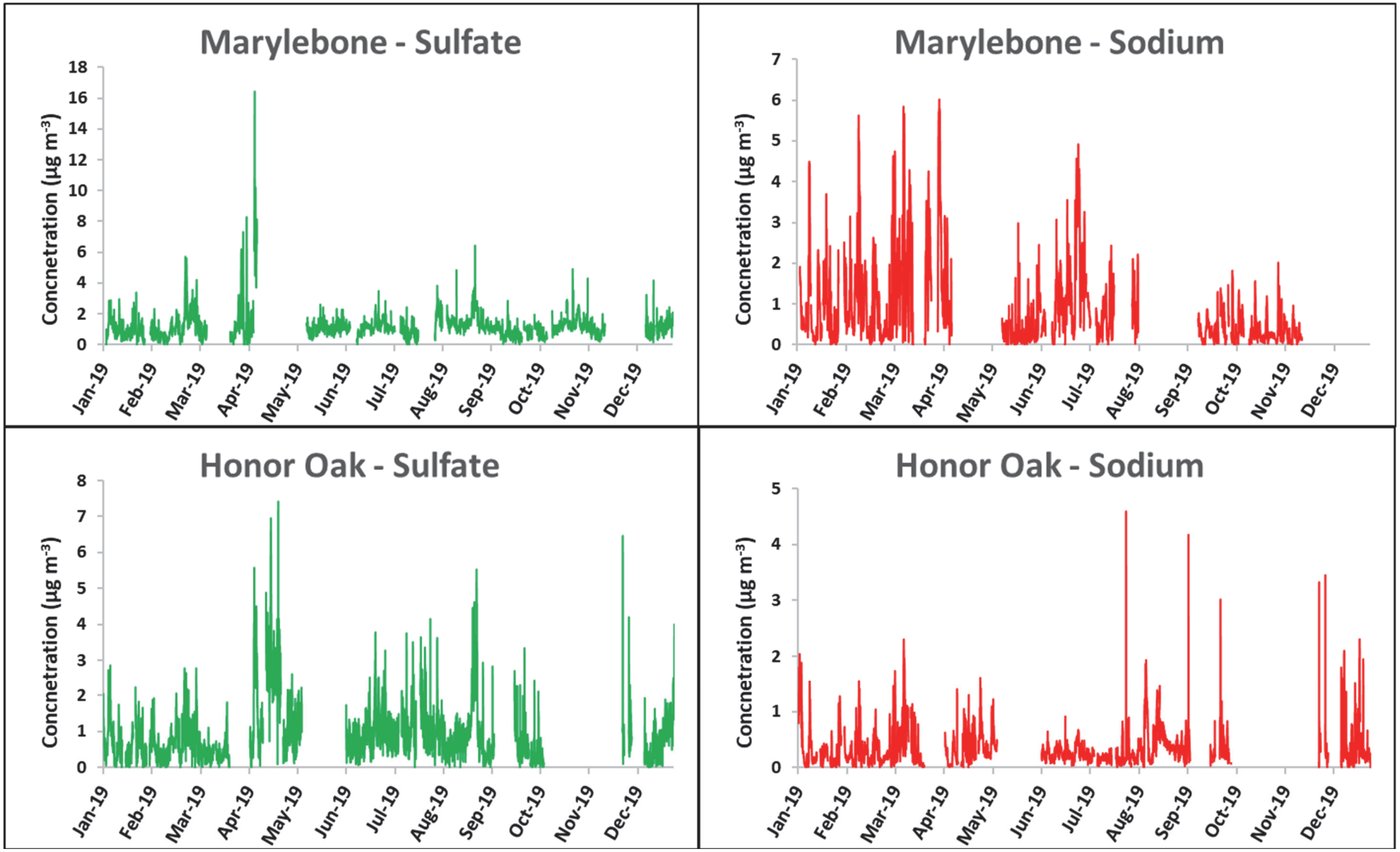

Figure 4-10 Time series for Sulfate and Sodium and Nitrate ion concentrations in $PM_{10/2.5}$ at Marylebone Road and $PM_{2.5}$ only Honor Oak Park in 2019 (PM_{10} changed to $PM_{2.5}$ at Marylebone on January 9th, 2019)

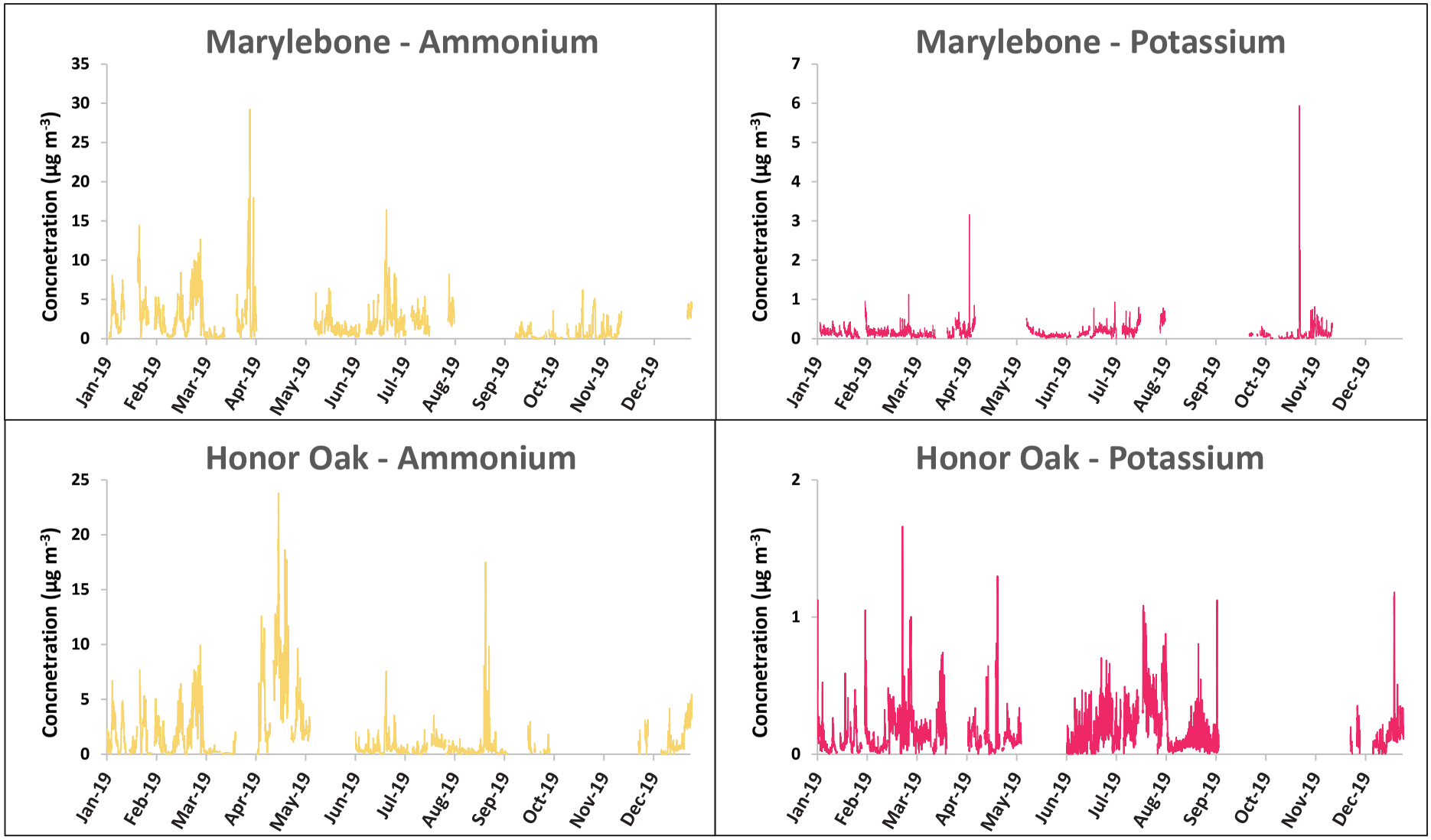

Figure 4-11 Time series for Ammonium and Potassium ion concentrations in $PM_{10/2.5}$ at Marylebone Road and $PM_{2.5}$ only Honor Oak Park in 2019 (PM_{10} changed to $PM_{2.5}$ at Marylebone on January 9th, 2019)

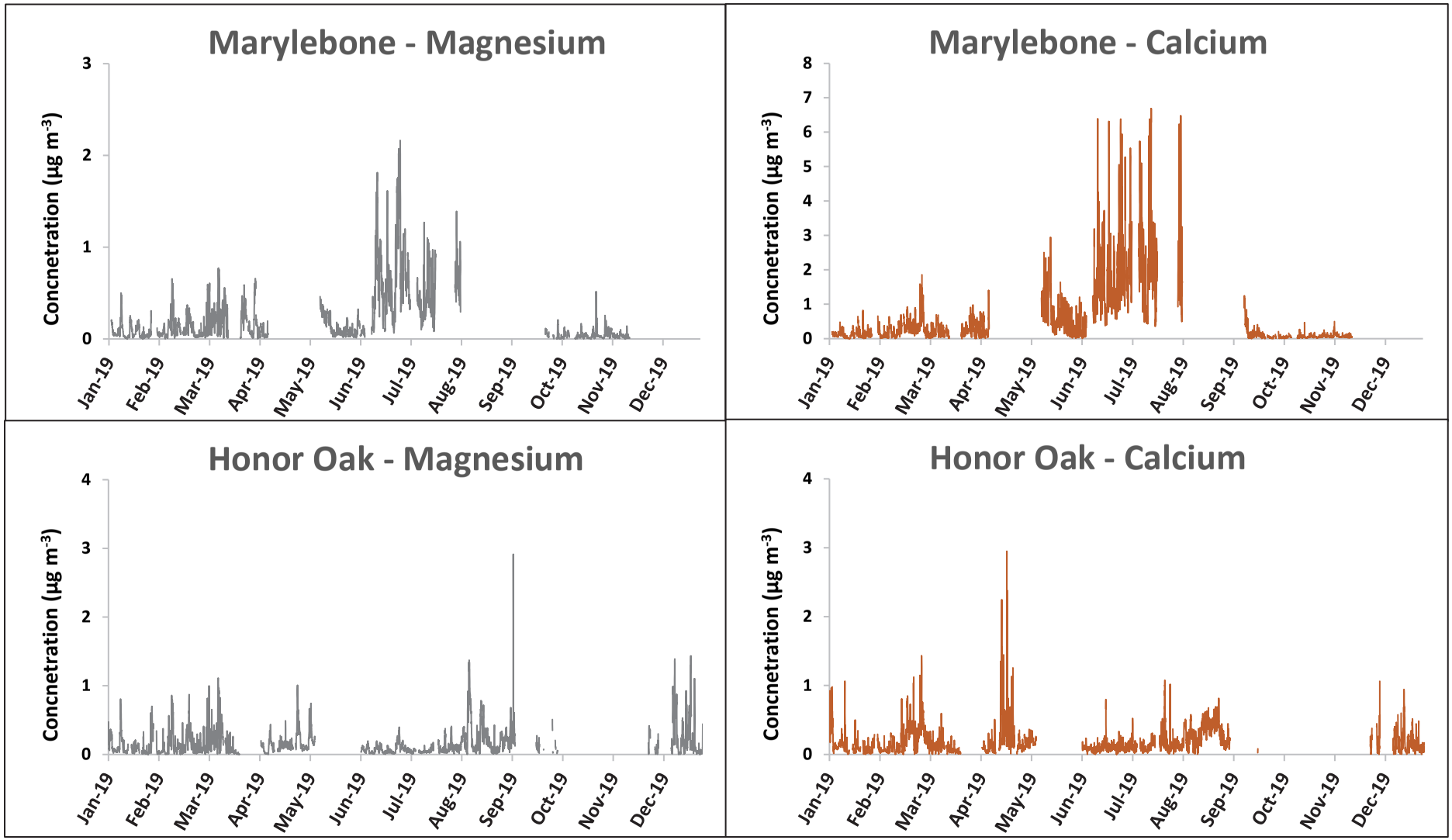

Figure 4-12 Time series for Magnesium and Calcium ion concentrations in $PM_{10/2.5}$ at Marylebone Road and $PM_{2.5}$ only Honor Oak Park in 2019 (PM_{10} changed to $PM_{2.5}$ at Marylebone on January 9th, 2019)

4.4 PARTICLE NUMBER CONCENTRATIONS AND SIZE DISTRIBUTIONS

4.4.1 Particle number concentrations (CPCs)

Time series of hourly particle number concentrations (between about 7 nm and several micrometres in diameter) measured at network sites during 2019 are shown in Figure 4-13. The average data capture for CPC instruments during 2019 were 57%, 80% and 51% respectively for Honor Oak, Marylebone, and Chilbolton.

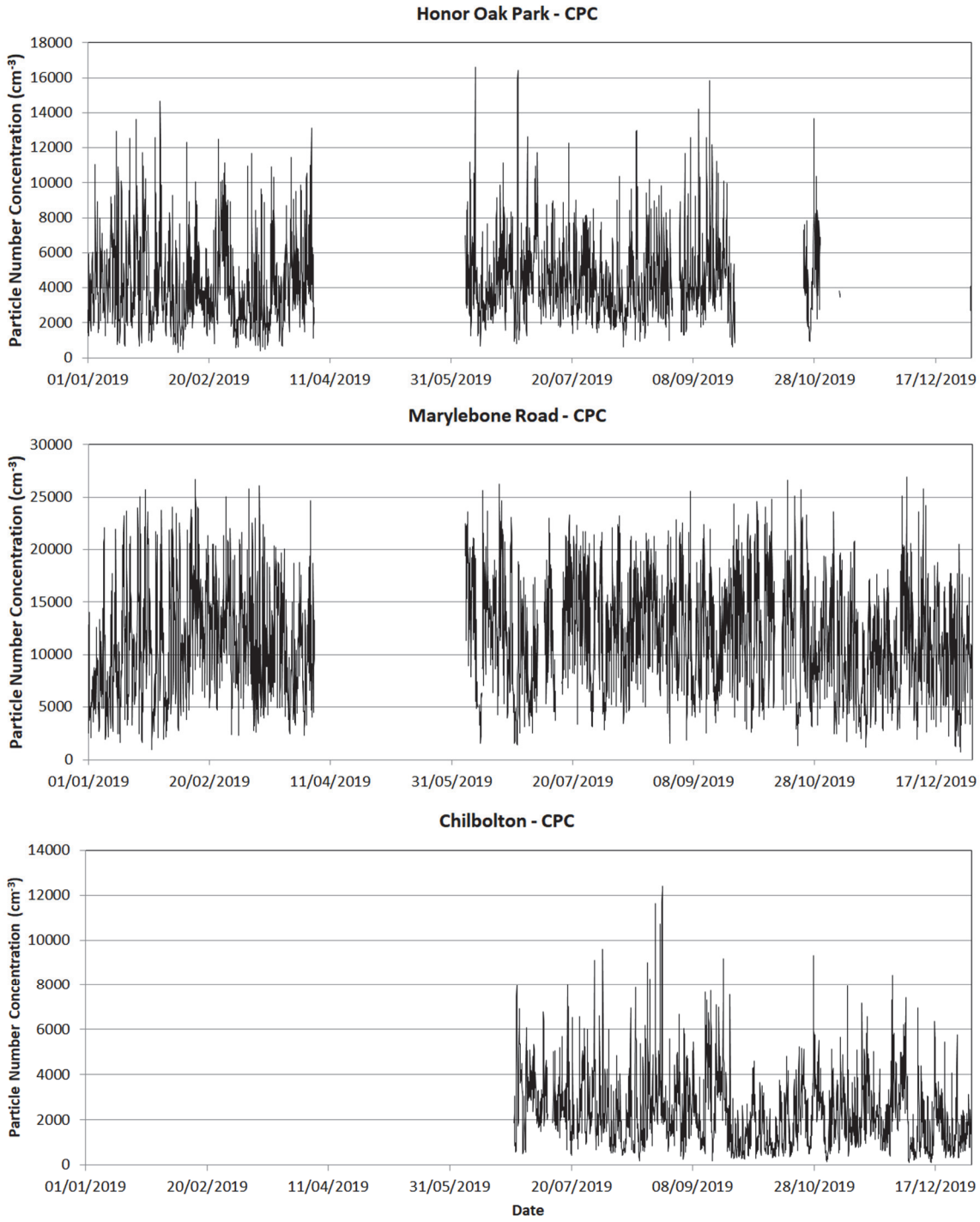

Figure 4-13 Hourly particle number concentrations at Honor Oak Park, Marylebone Road and Chilbolton in 2019

4.4.2 Particle size distributions

The average data captures for the SMPS instruments during 2018 were 54%, 36% and 65% respectively for Honor Oak Park, Marylebone Road and Chilbolton.

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.

The counts in each particle size bin measured during 2019 are presented as monthly averages in Figure 4-16 and as annual averages in Figure 4-17.

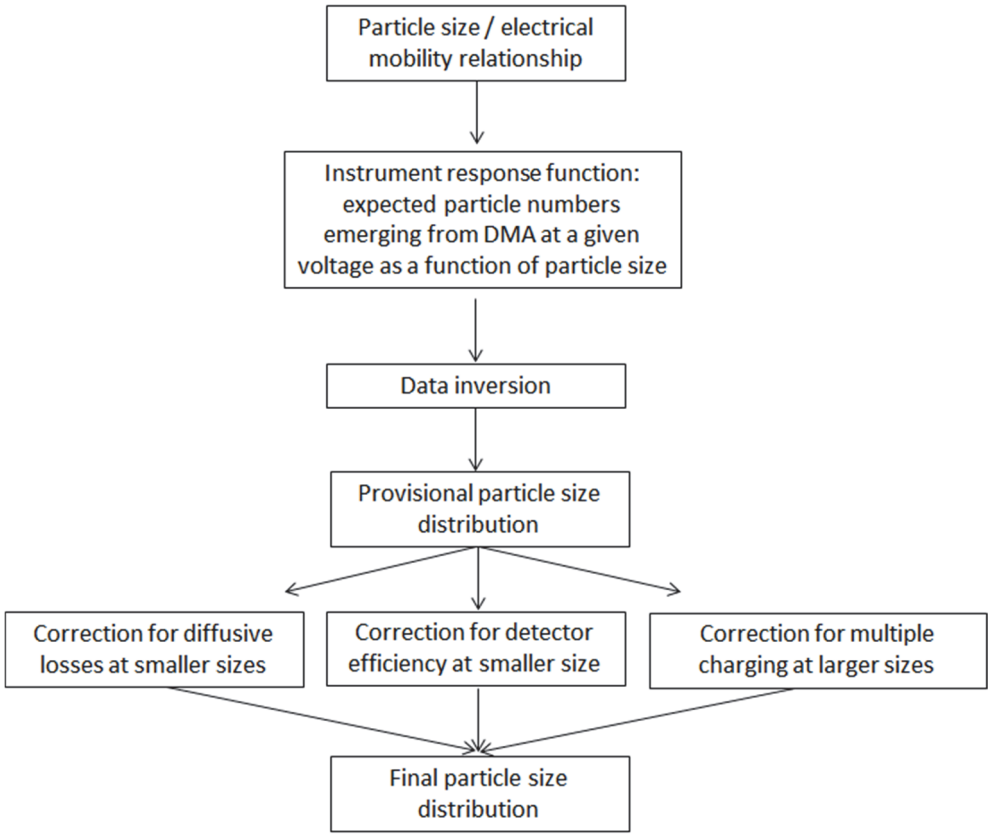

Figure 4-14 Schematic of the internal data processing of SMPS measurements in the Network

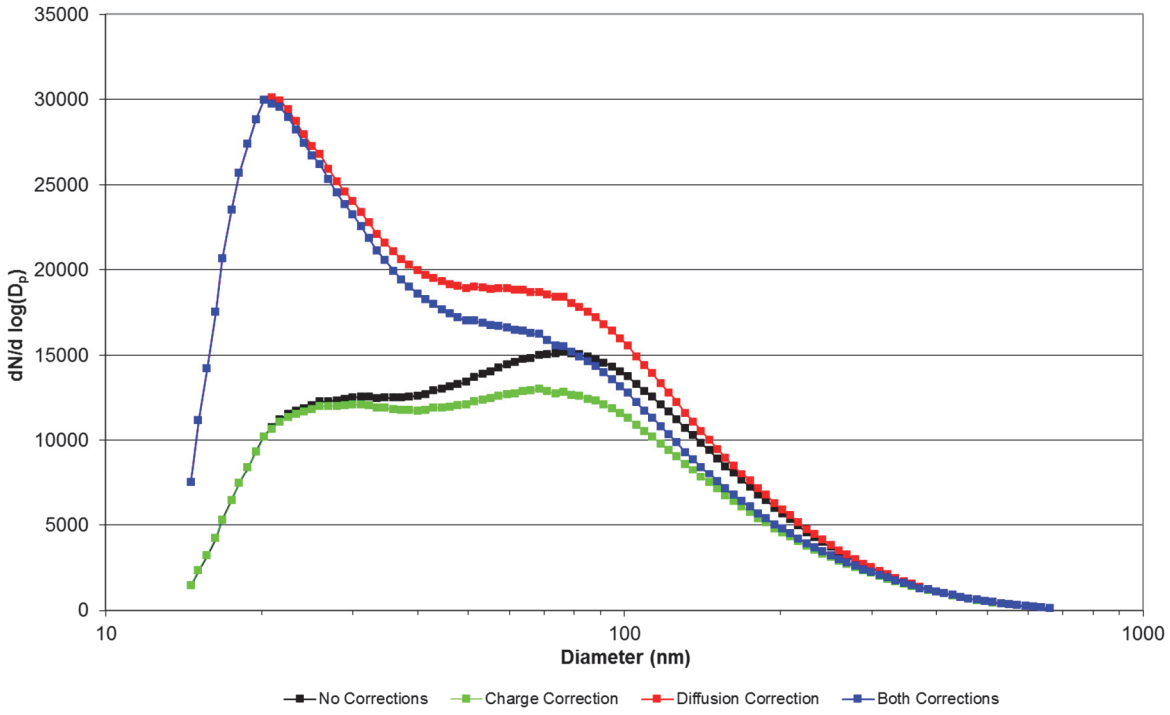

Figure 4-15 Effect of the multiple charge, the diffusion loss and their combined correction in the SMPS size spectrum

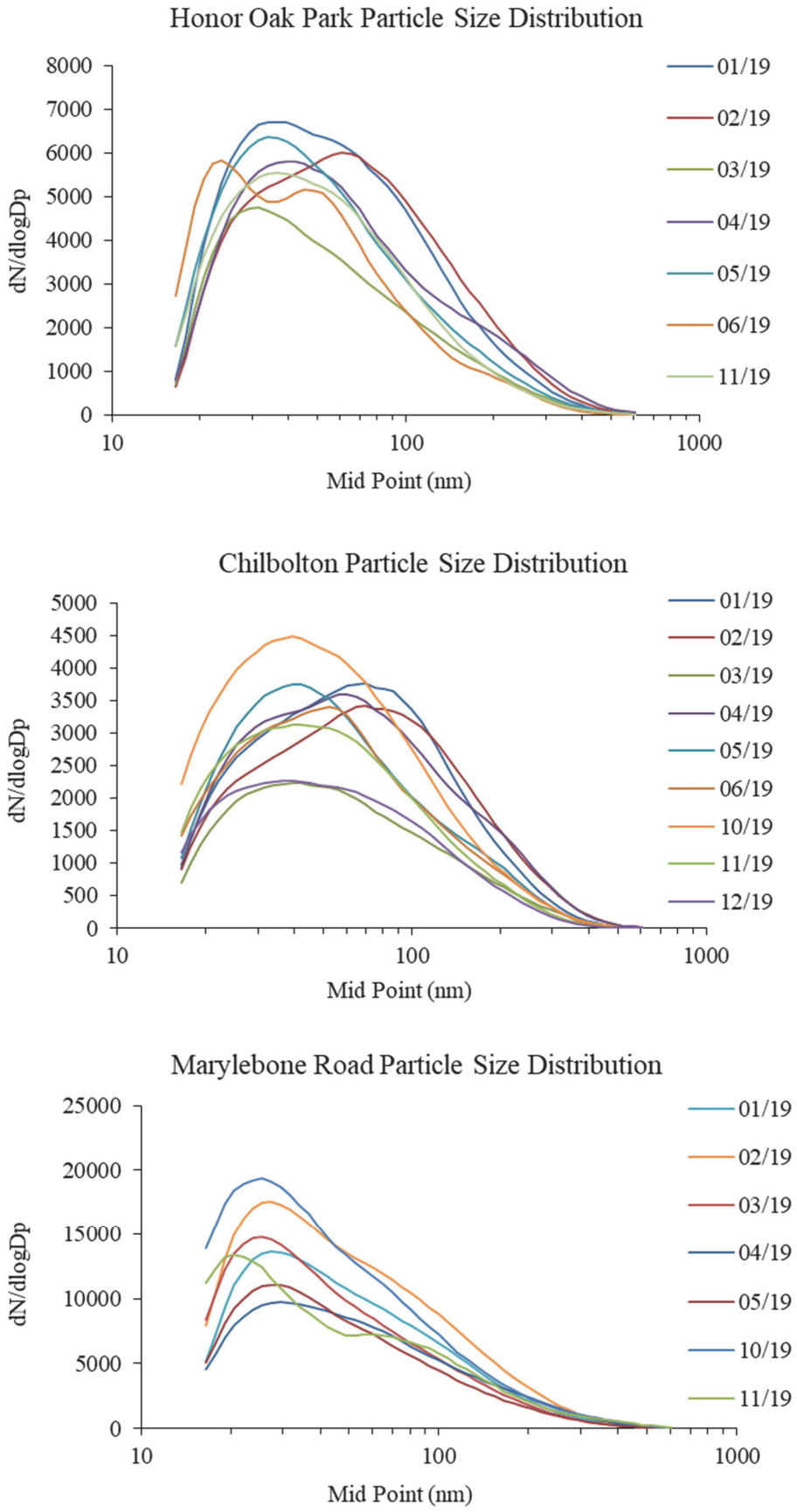

Figure 4-16 Monthly averaged particle size distributions at the Network sites during 2019

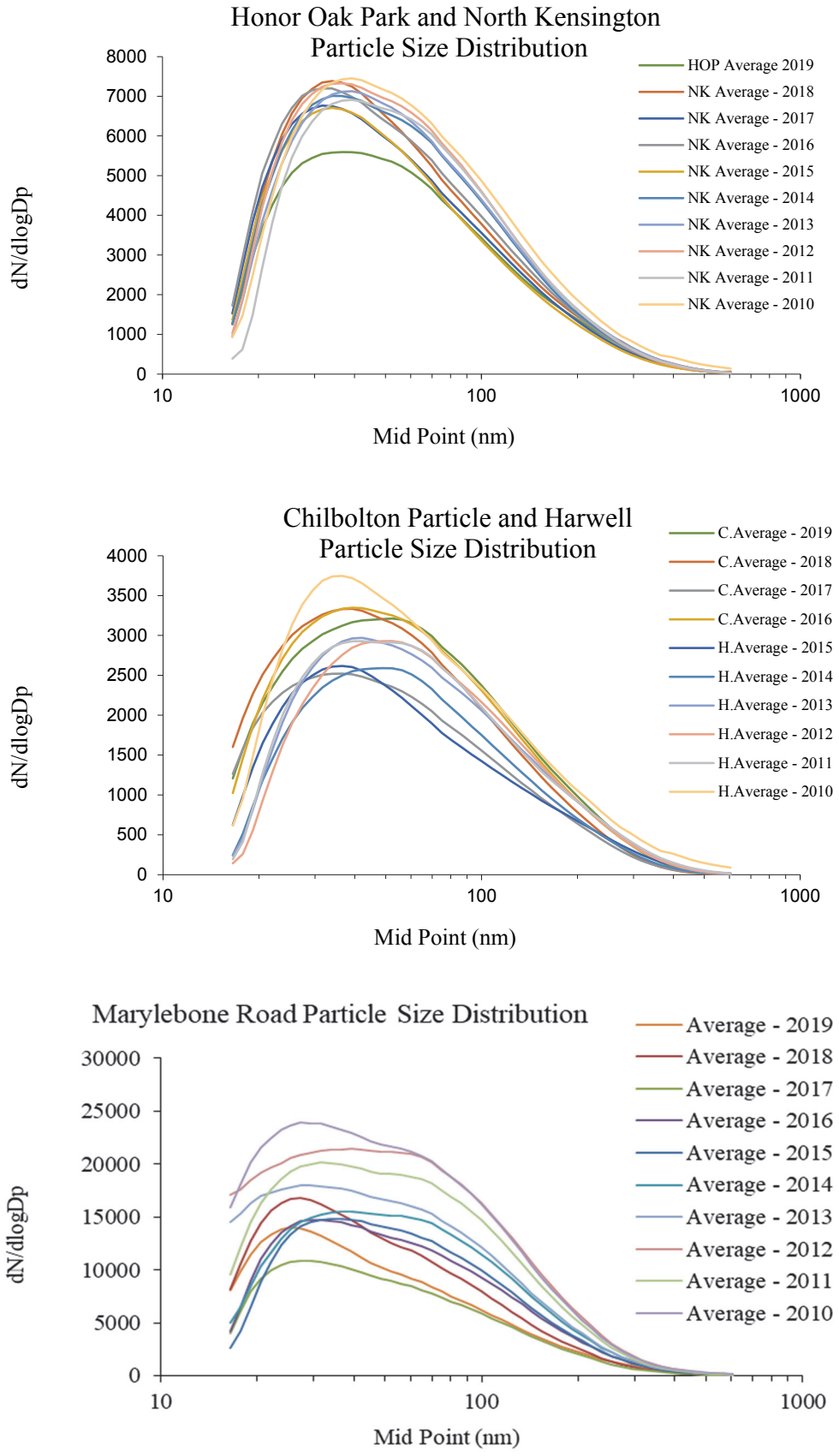

Figure 4-17 Comparison of the 2010 to 2019 annual-averaged size distributions

4.5 ACSM MEASUREMENTS

The ACSM instrument was installed at North Kensington in 2013 with a PM1 size-selective head. It was moved to Honor Oak Park and has operated there since November 2018. The instrument now measures the hourly concentrations of organics, nitrate, sulfate and ammonia in the $PM_{2.5}$ size fraction. The 2019 annual data capture (averaged using the four components) was 85%. Figure 4-18 shows the 2019 monthly averages for each component measured.

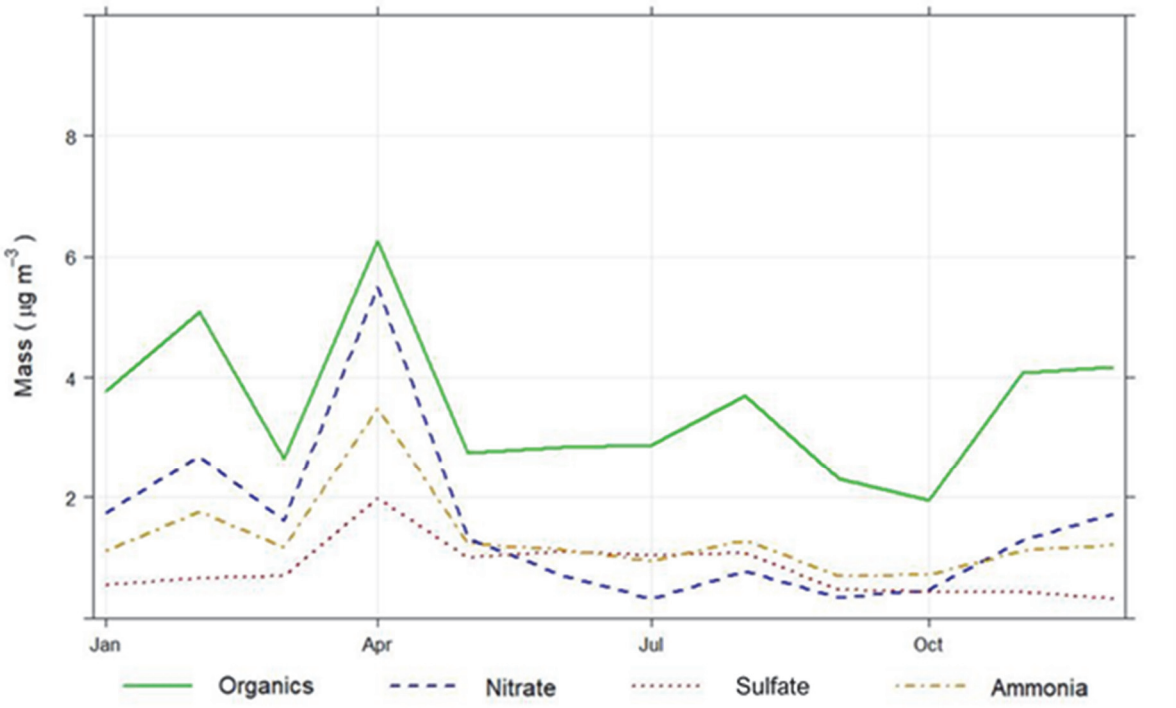

Figure 4-18 Monthly averages for 2019 ACSM data

4.6 LONG TERM TRENDS

4.6.1 Carbon measurements

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

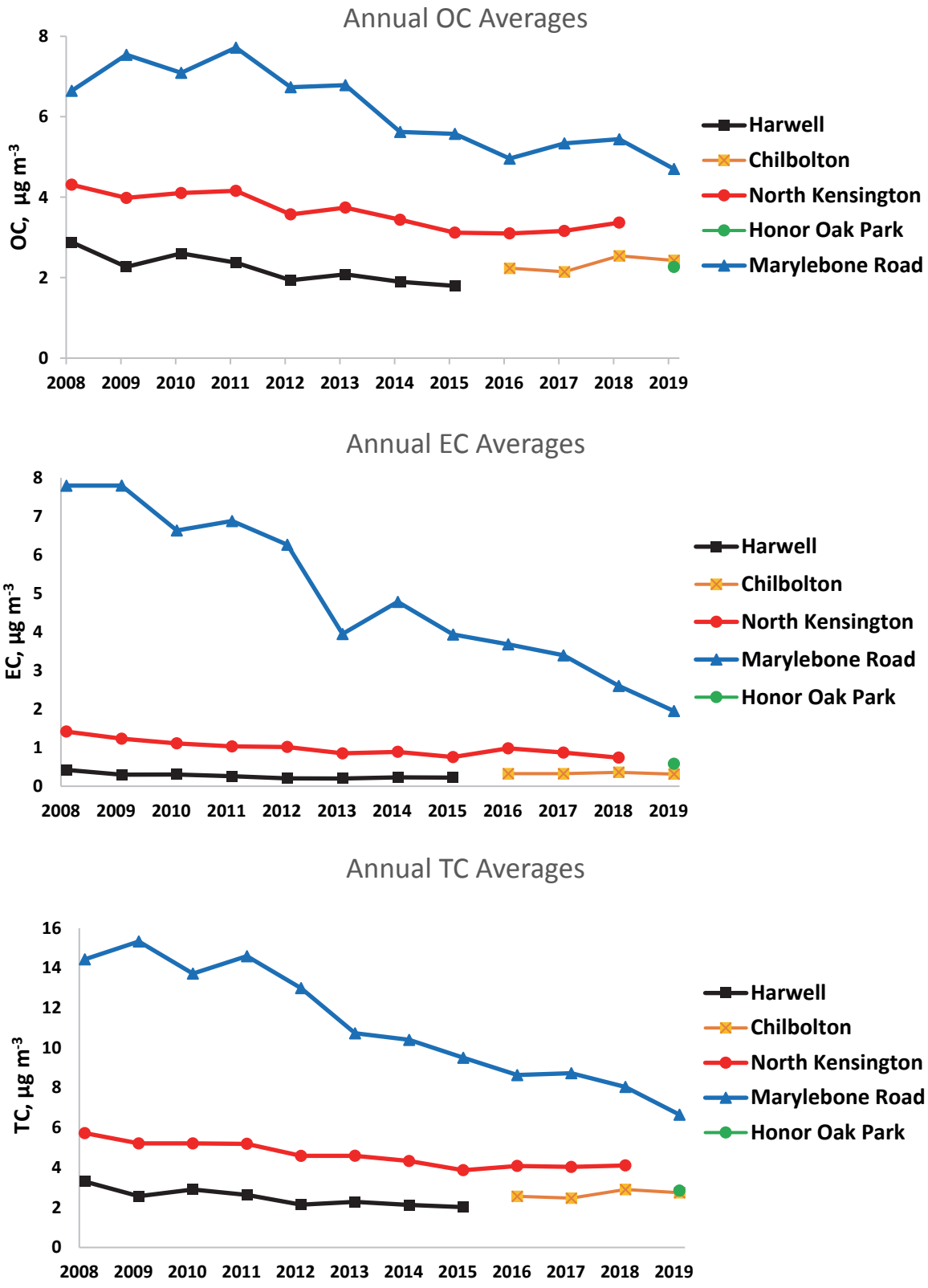

Figure 4-19 Annual trends for OC, EC and TC measurements

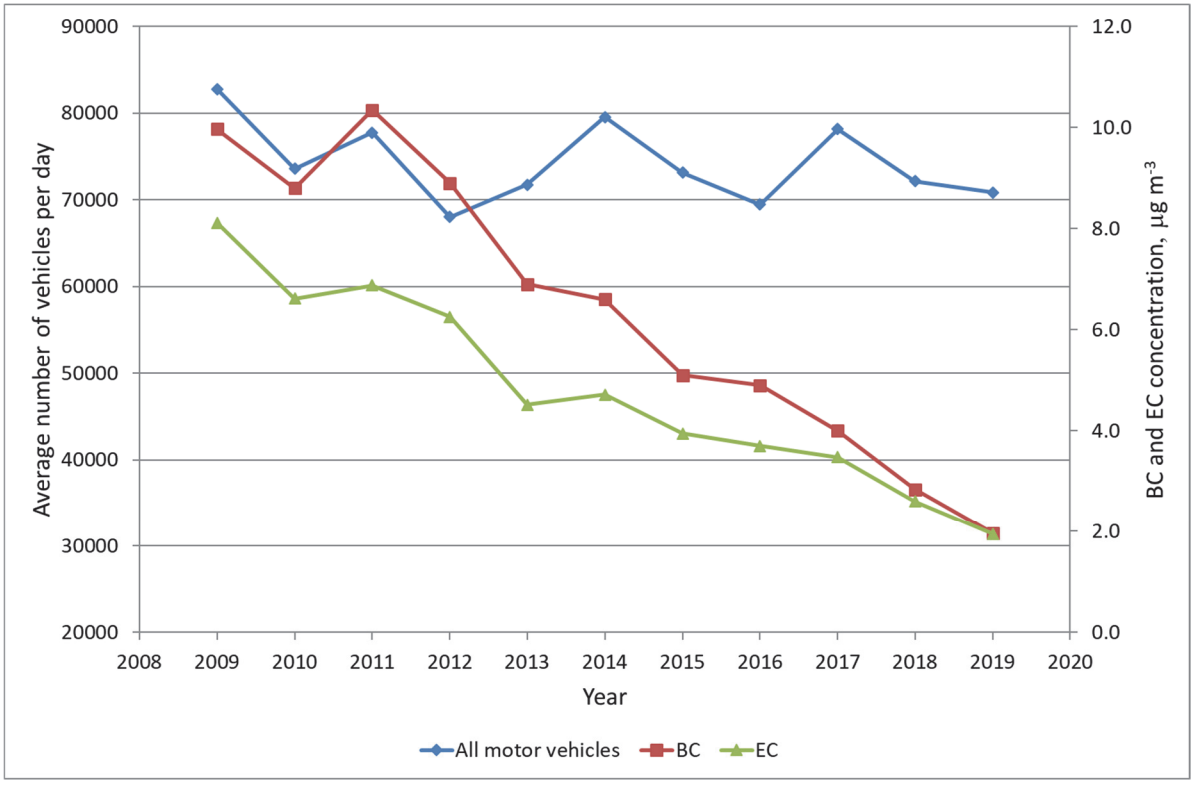

Figure 4-20 Annual Average Black Carbon, Elemental Carbon and Motor Vehicles per day at Marylebone Road for the period 2009 – 2019

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 several years. The decrease of 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[5]. Table 4-2 shows the composition of the London bus fleet over the period 2010 to 2019. 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 retrofitted 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. On 8th April 2019 the Ultra-Low Emission Zone (ULEZ) replaced the 'Toxicity Charge' (T-Charge) in central London. The emission standards for the ULEZ are: Euro IV for petrol cars and vans and Euro VI for diesel cars, vans, lorries, coaches, and buses. Although Marylebone Road itself is not included in the ULEZ, a further decrease in number of buses and coaches (especially diesel type) as well as HGVs was observed in 2019[2].

Table 4-2 Composition of London bus fleet, 2010 to 2019[5]

Bus Type	Drive train type	Number of buses									
		2010	2011	2012	2013	2014	2015	2016	2017	2018	2019
New Routemaster	Hybrid	0	0	5	8	168	432	736	953	1,000	1,000
Routemaster	Diesel	18	18	19	20	19	19	10	10	10	10
Artic	Diesel	320	260	0	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	2,435
	Fuel Cell/Hybrid	0	5	5	5	8	8	8	8	10	10
	Hybrid	27	27	33	28	23	23	18	18	13	0
	Electric	0	0	0	0	2	8	17	66	91	150
Double deck	Diesel	5,554	5,487	5,787	5,696	5,296	5,026	4,794	4,380	3,453	2,863
	Hybrid	29	79	233	352	643	799	981	1,564	2,227	2,669
	Electric	0	0	0	0	0	0	5	5	5	5
TOTAL		8,624	8,546	8,743	8,717	8,765	8,977	9,186	9,616	9,396	9,142
% low emission		0.65	1.30	3.16	4.51	9.63	14.15	19.21	27.18	35.61	41.94

4.6.2 PM_{10} and $PM_{2.5}$ anion measurements

Between 2003 and 2010, the PM_{10} 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 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 from Harwell 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 $PM_{2.5}$. The change to $PM_{2.5}$ at Marylebone Road occurred in January 2019.

Figure 4-21 shows long-term trends for the anion species.

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 sulfate has shown a distinct downward trend but has levelled off over the last 3 years.

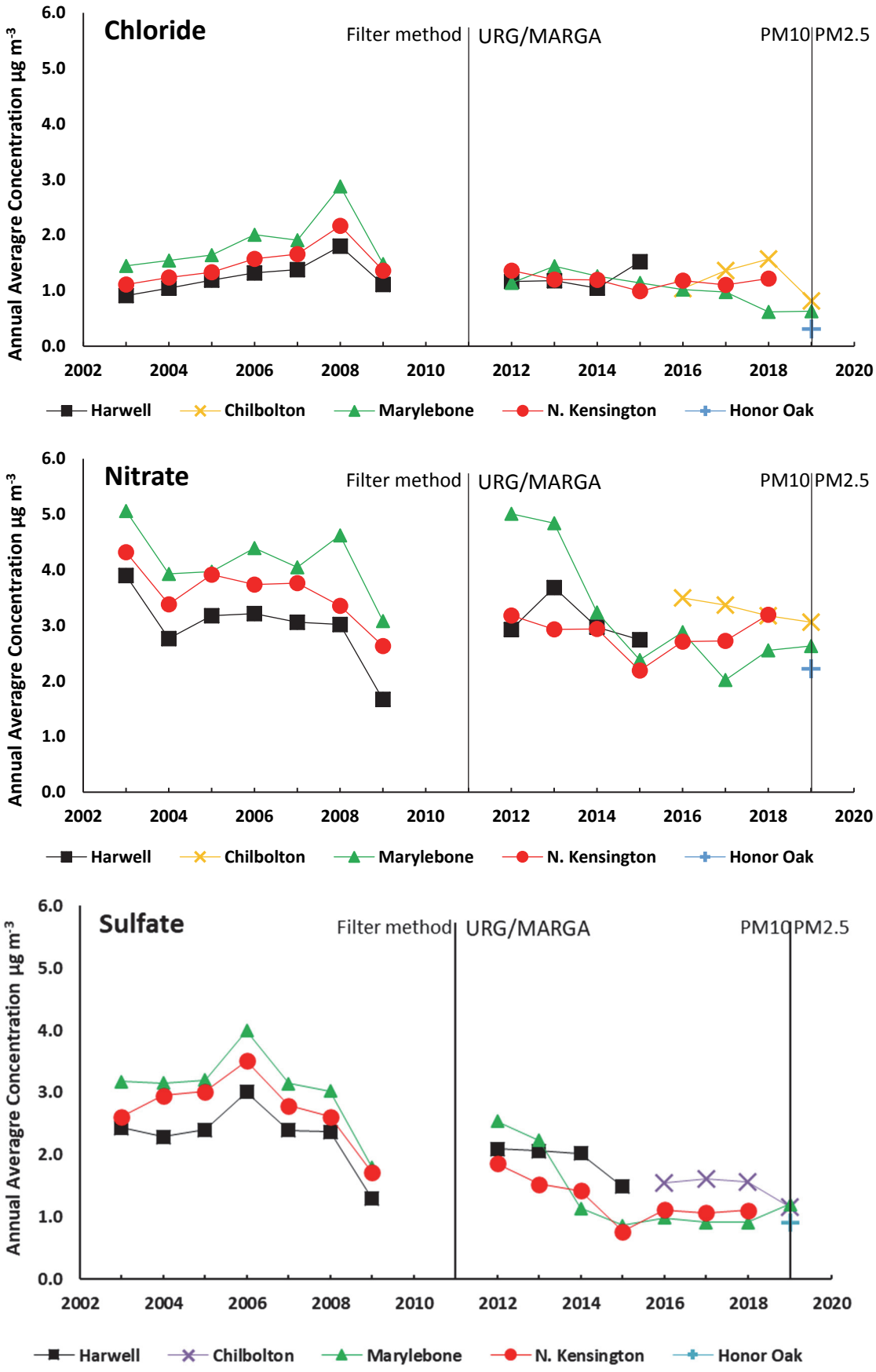

Figure 4-21 Anion long-term annual trends (chloride, nitrate and sulfate)

4.6.3 Particle number concentrations

Figure 4-22 and Figure 4-23 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 levelled off after the dramatic drop at the end of 2007 due to the introduction of sulfur-free diesel fuel and of the LEZ (Low Emission Zone)[6].

UK wide legislation[7] enacted in June 2007 required that diesel and super-unleaded petrol sold by retailers in the UK for use in road vehicles should be 'sulfur-free' (less than 50 ppm sulfur)[8] from 4th December 2007, with all UK road vehicle fuel being 'sulfur-free' (less than 10 ppm sulfur) by 1st January 2009. The LEZ[9], which covers the area of Greater London, was confirmed in May 2007, 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.

The reduction in particle number concentrations occurred immediately prior to the requirement for all diesel fuel for use in highway vehicles to be "sulfur-free" and the commencement of enforcement of the London LEZ. Measurements of airborne particle number concentrations at the two sites in London and the site in Birmingham show that over a period of few months in late 2007 concentrations were reduced by between 30% and 59 %[1]. Given the simultaneous drop of concentration at Birmingham centre (which would not be affected by the London LEZ), it is probable that the reduction at London sites is a combination of change in fuel composition and the introduction of the London LEZ.

Additional changes to the LEZ in 2012 (as detailed in section 4.6.1) do not appear to have resulted in sustained significant decrease in measured nanoparticle concentrations.

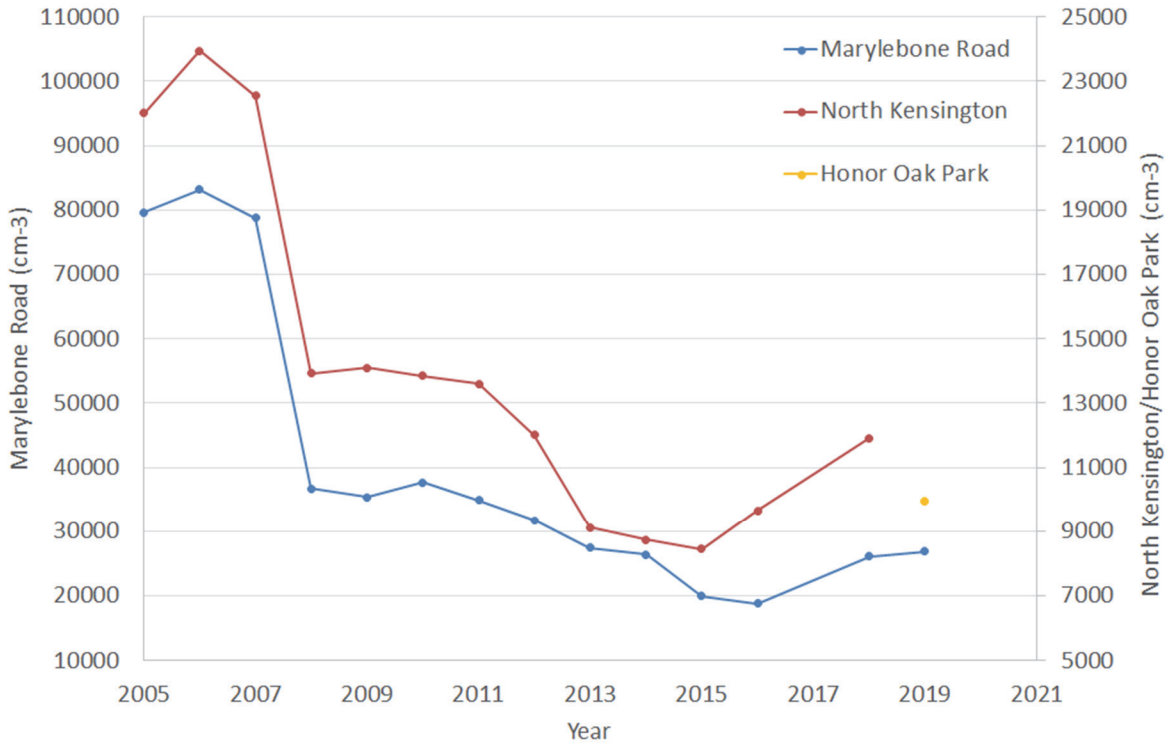

Figure 4-22 Historical CPC long-term annual trends at all London sites. The North Kensington site moved to Honor Oak Park in mid-November 2018

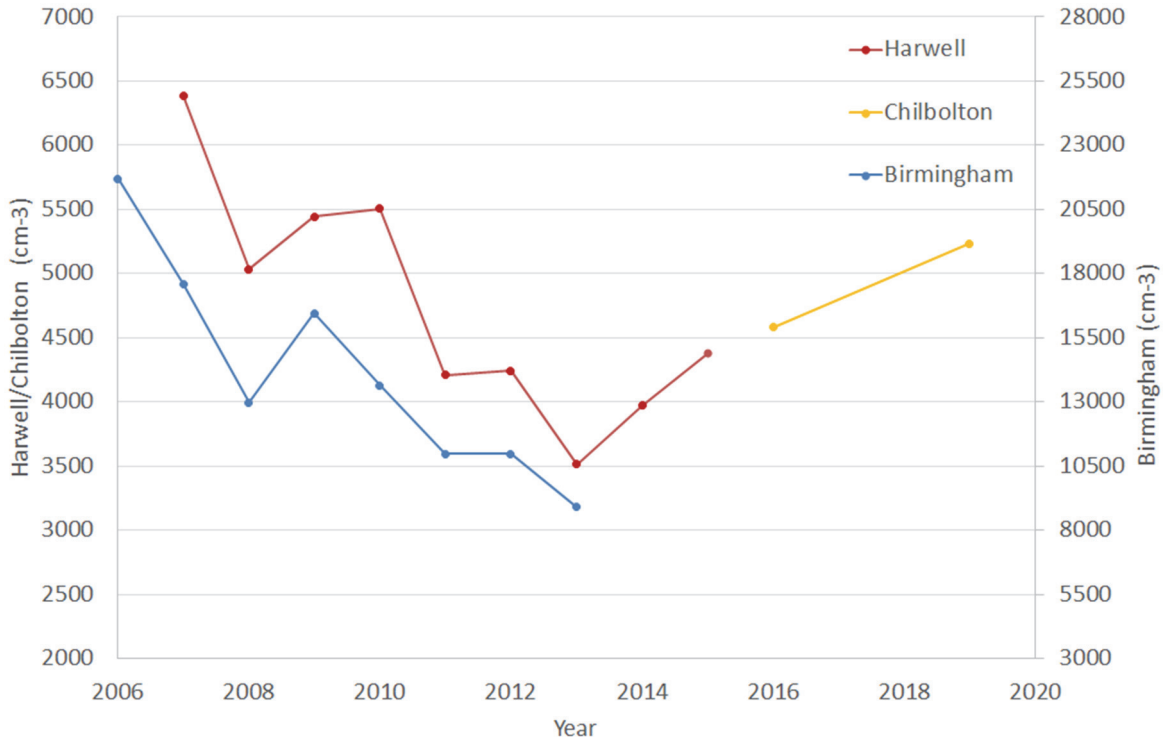

Figure 4-23 Historical CPC long-term annual trends at all Non-London sites. No data are available since 2014 for the Birmingham site. The Harwell site moved to Chilbolton in 2016. Insufficient data was available from Chilbolton for reliable averages in 2017 and 2018

4.6.4 Hourly Measurements by the ACSM Instrument

Figure 4-24 and Figure 4-25 show the long-term annual trends (using monthly averages) of the four components measured using the ACSM instrument at North Kensington and Honor Oak Park. Not enough data has yet been collected using these instruments to discern any meaningful seasonal or annual trends.

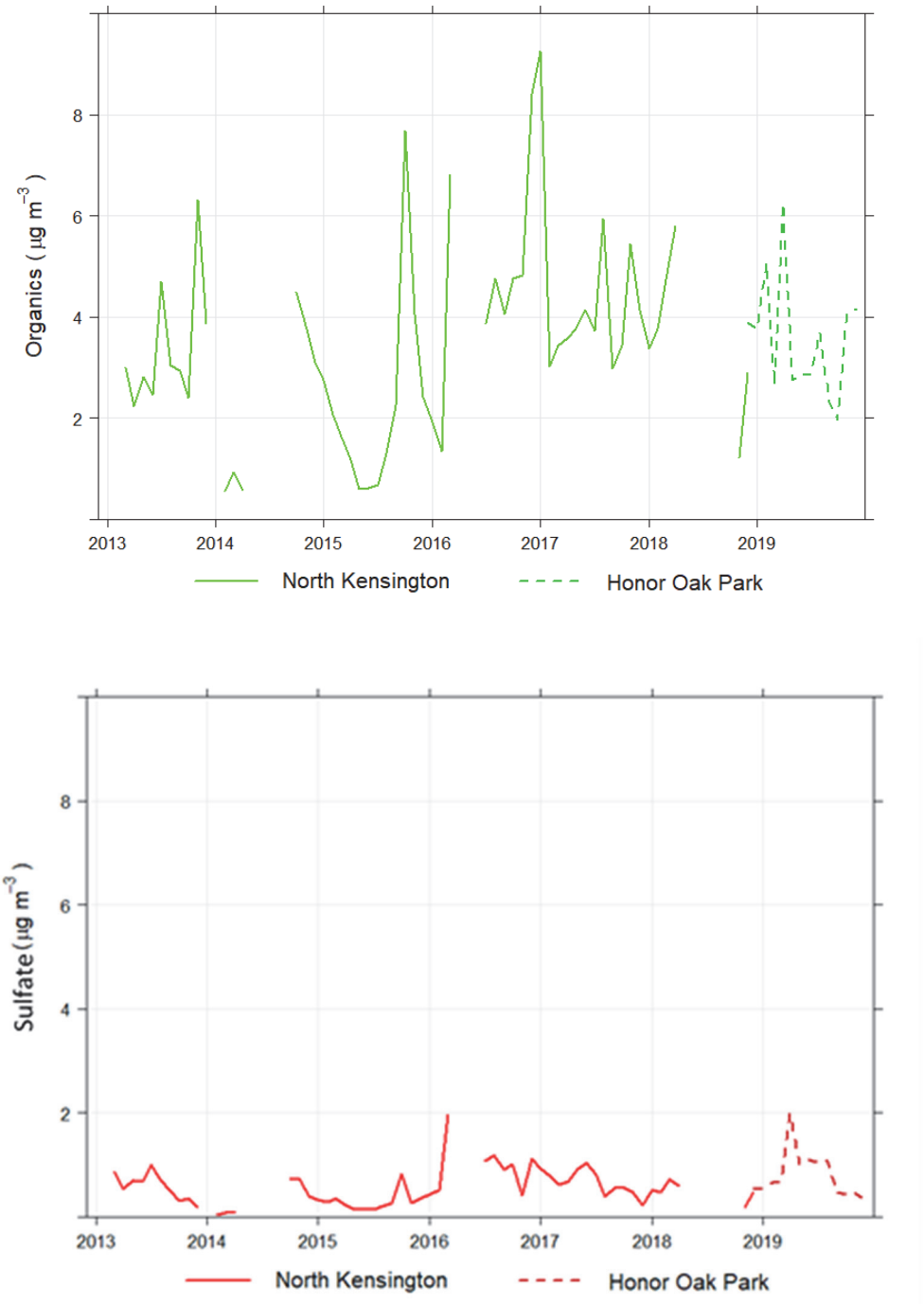

Figure 4-24 Long-term trends of Organics and Sulfate at the Urban Background site Honor Oak Park, previously North Kensington before 2019

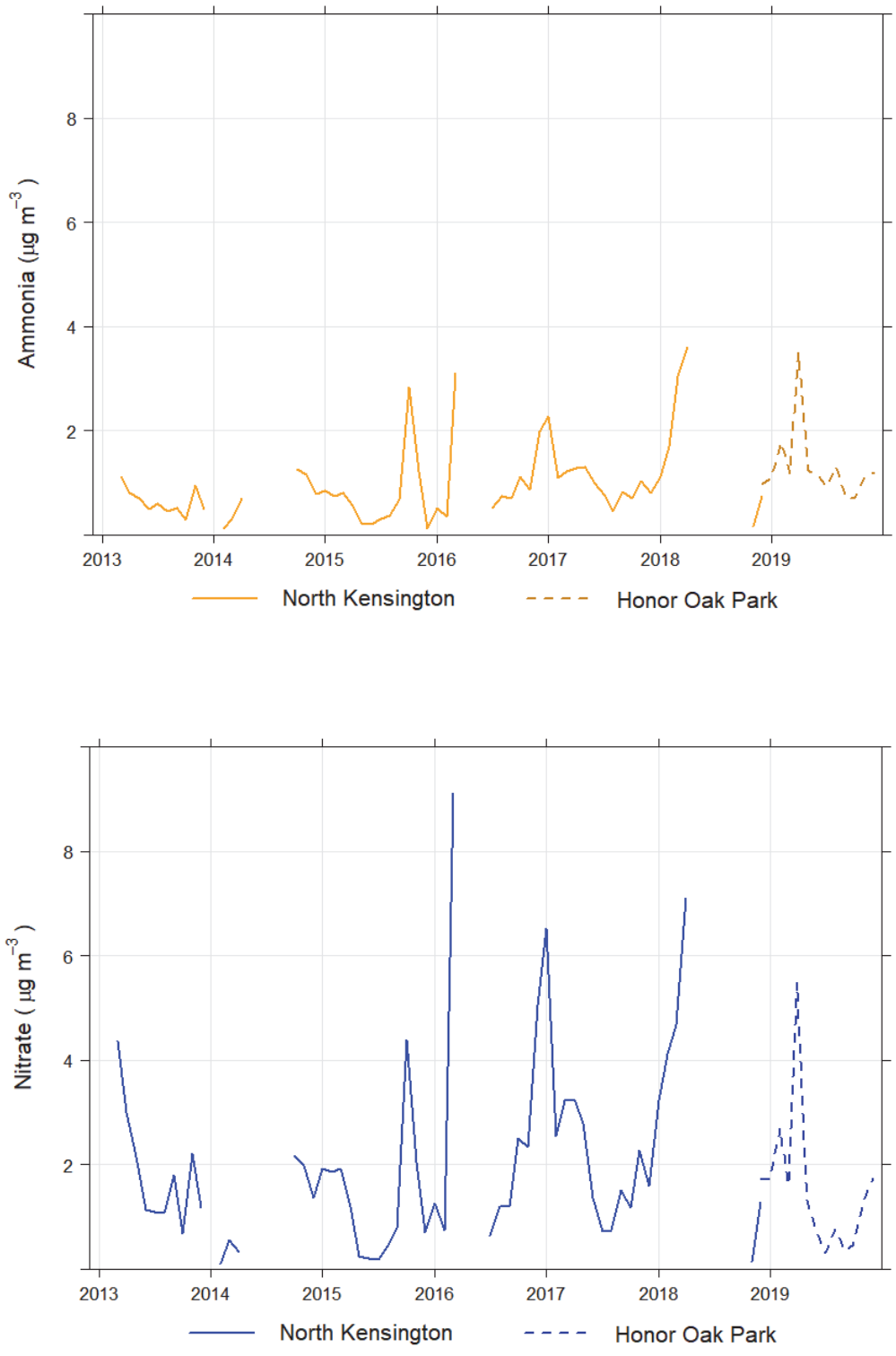

Figure 4-25 Long-term trends of Ammonia and Nitrate at the Urban Background site Honor Oak Park, previously North Kensington before 2019

4.7 DIURNAL, WEEKLY AND MONTHLY PROFILES

Diurnal, weekly and monthly profiles have been plotted in Figure 4-26 to Figure 4-31 for pollutants where hourly concentrations are available, using the Openair tools[10, 11, 12].

4.7.1 Profiles for anion and cation species

The correlation between NH_4^+, NO_3^- and SO_4^{2-} in Figure 4-26 and Figure 4-27 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 4-28 and Figure 4-29 show the profiles for Cl^-, Mg^{2+} and Na^+ concentrations at Honor Oak Park 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 4-30 and Figure 4-31 show values characteristic of traffic contribution, possibly re-suspension of crustal material from road surfaces.

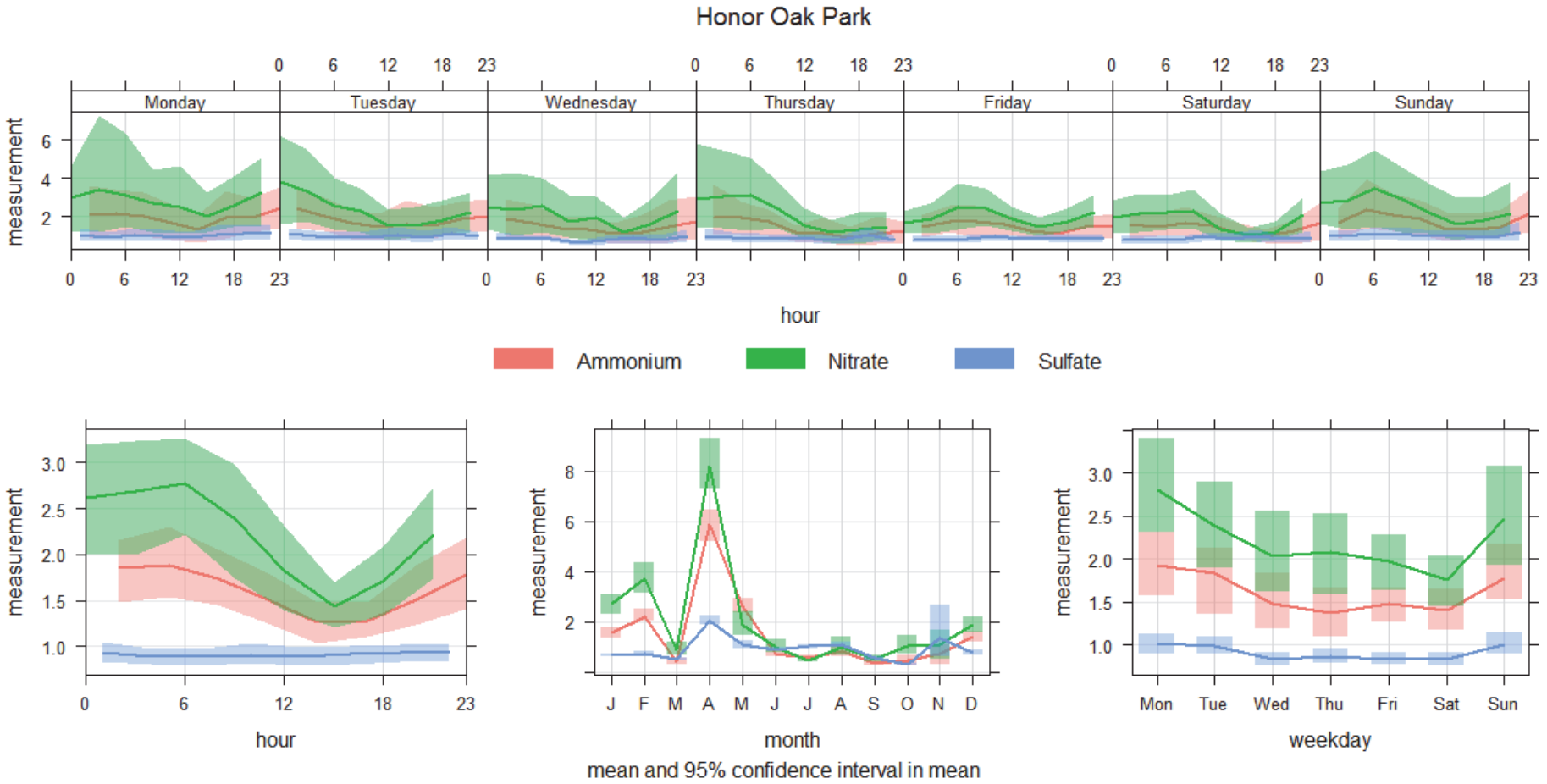

Figure 4-26 Diurnal, weekly and monthly profiles for and NH_4^+, NO_3^- and SO_4^{2-} during 2019 at Honor Oak Park. These graphs show the mean and 95% confidence interval (µg m^{-3})

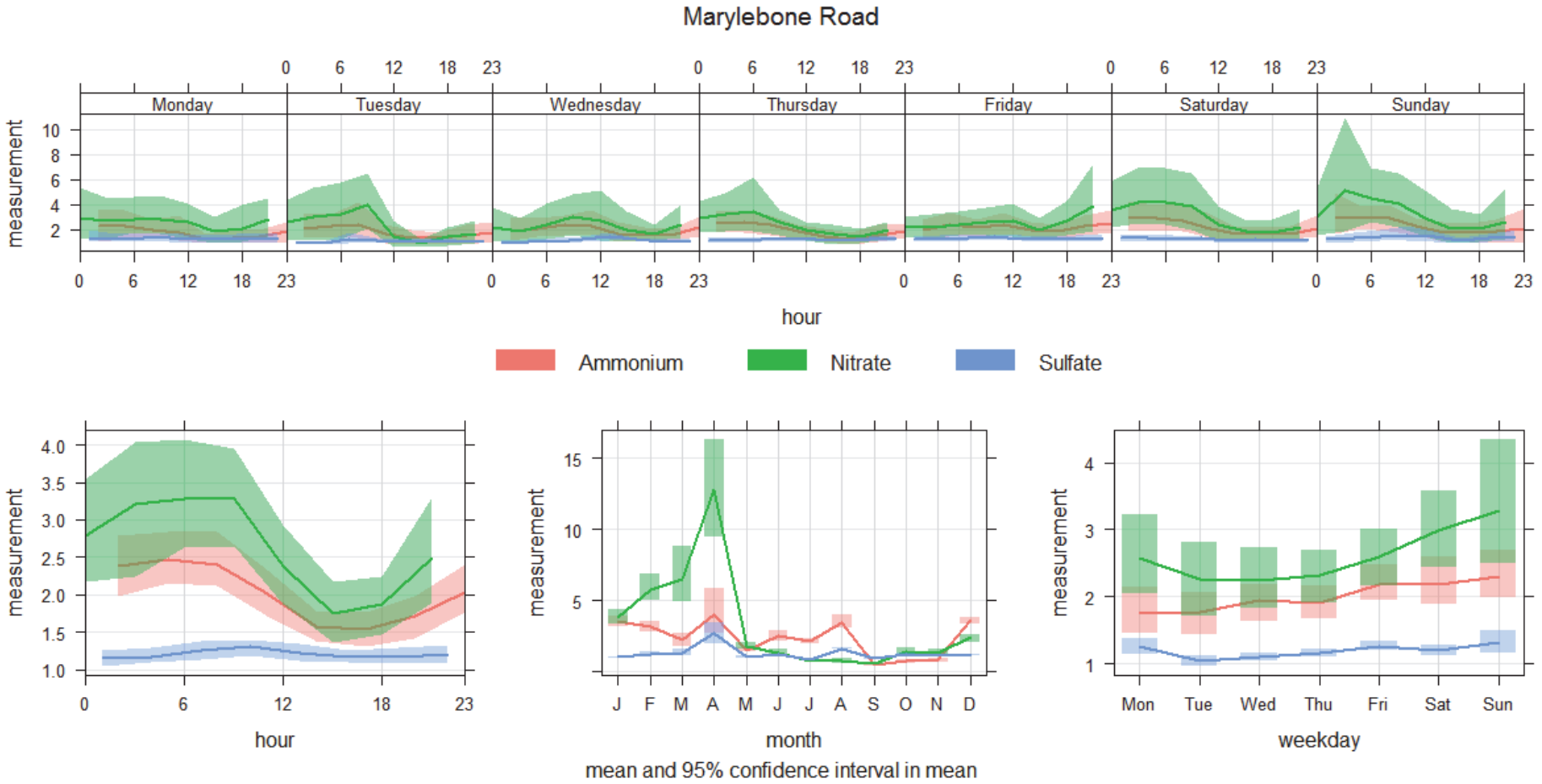

Figure 4-27 Diurnal, weekly and monthly profiles for and NH_4^+, NO_3^- and SO_4^{2-} during 2019 at Marylebone Road. These graphs show the mean and 95% confidence interval (µg m^{-3})

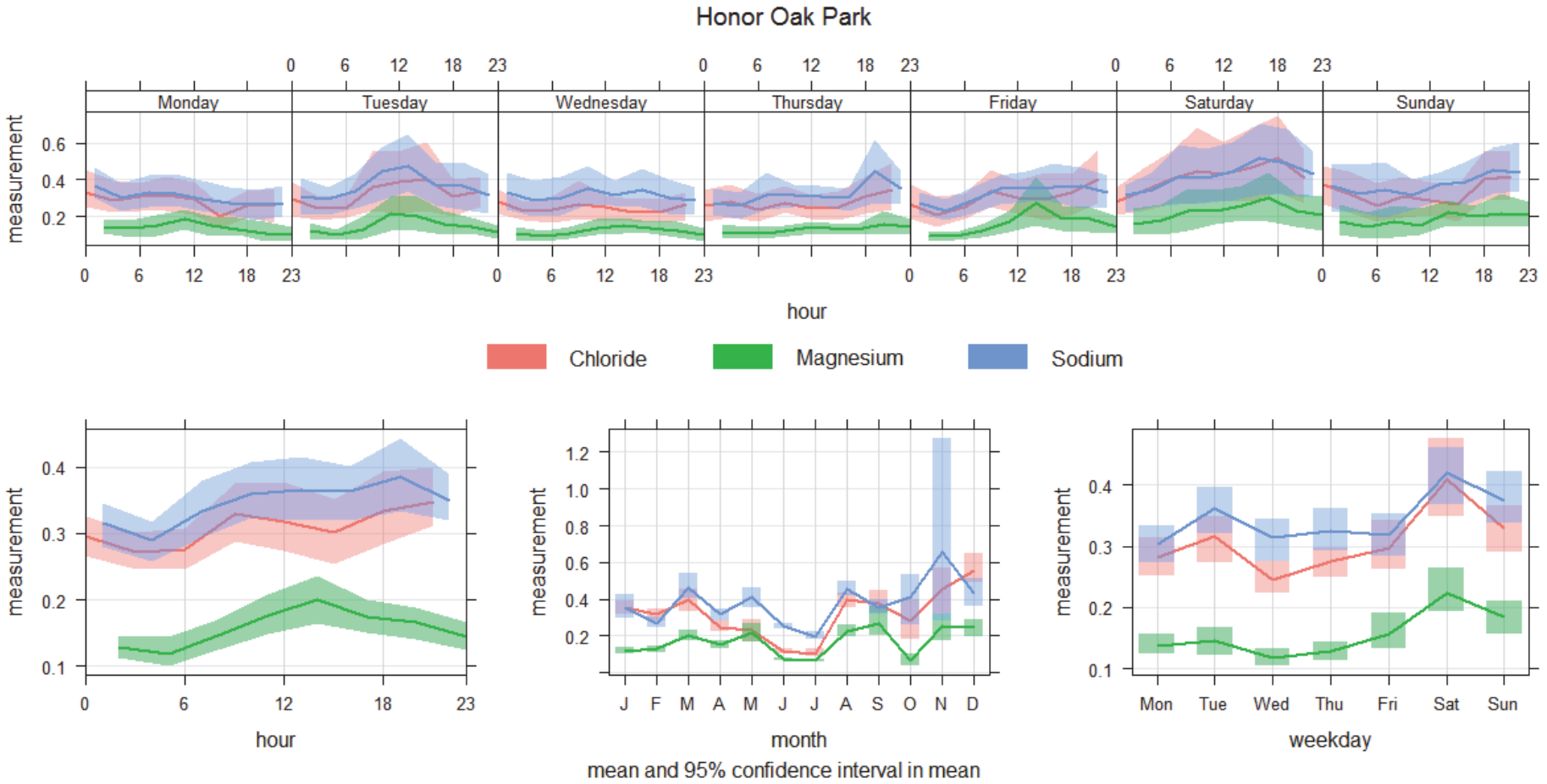

Figure 4-28 Diurnal, weekly and monthly profiles for Cl^-, Mg^{2+} and Na^+ concentrations during 2019 at Honor Oak Park. These graphs show the mean and 95% confidence interval (µg m^{-3})

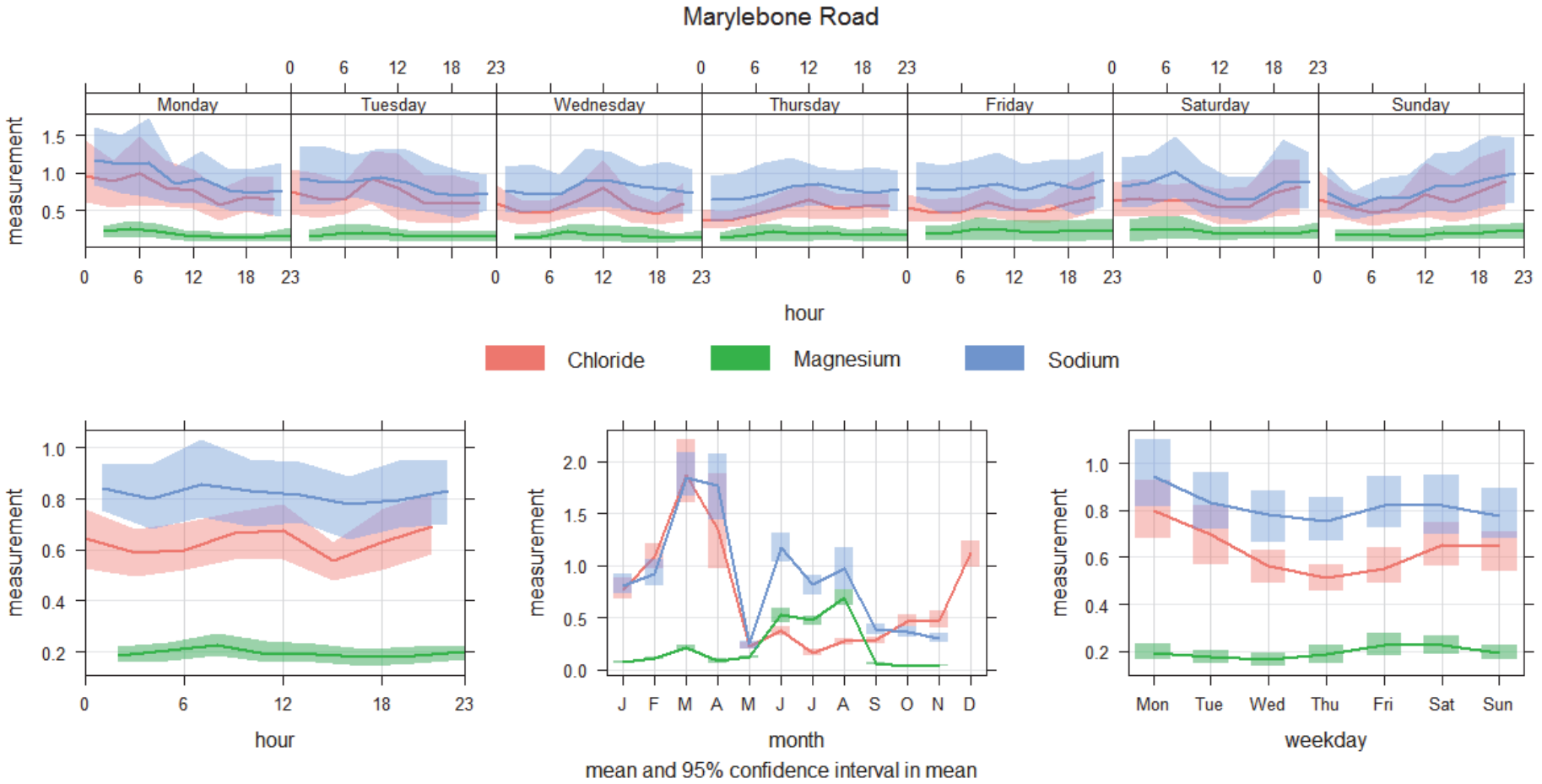

Figure 4-29 Diurnal, weekly and monthly profiles for Cl^-, Mg^{2+} and Na^+ concentrations during 2019 at Marylebone Road. These graphs show the mean and 95% confidence interval (µg m^{-3})

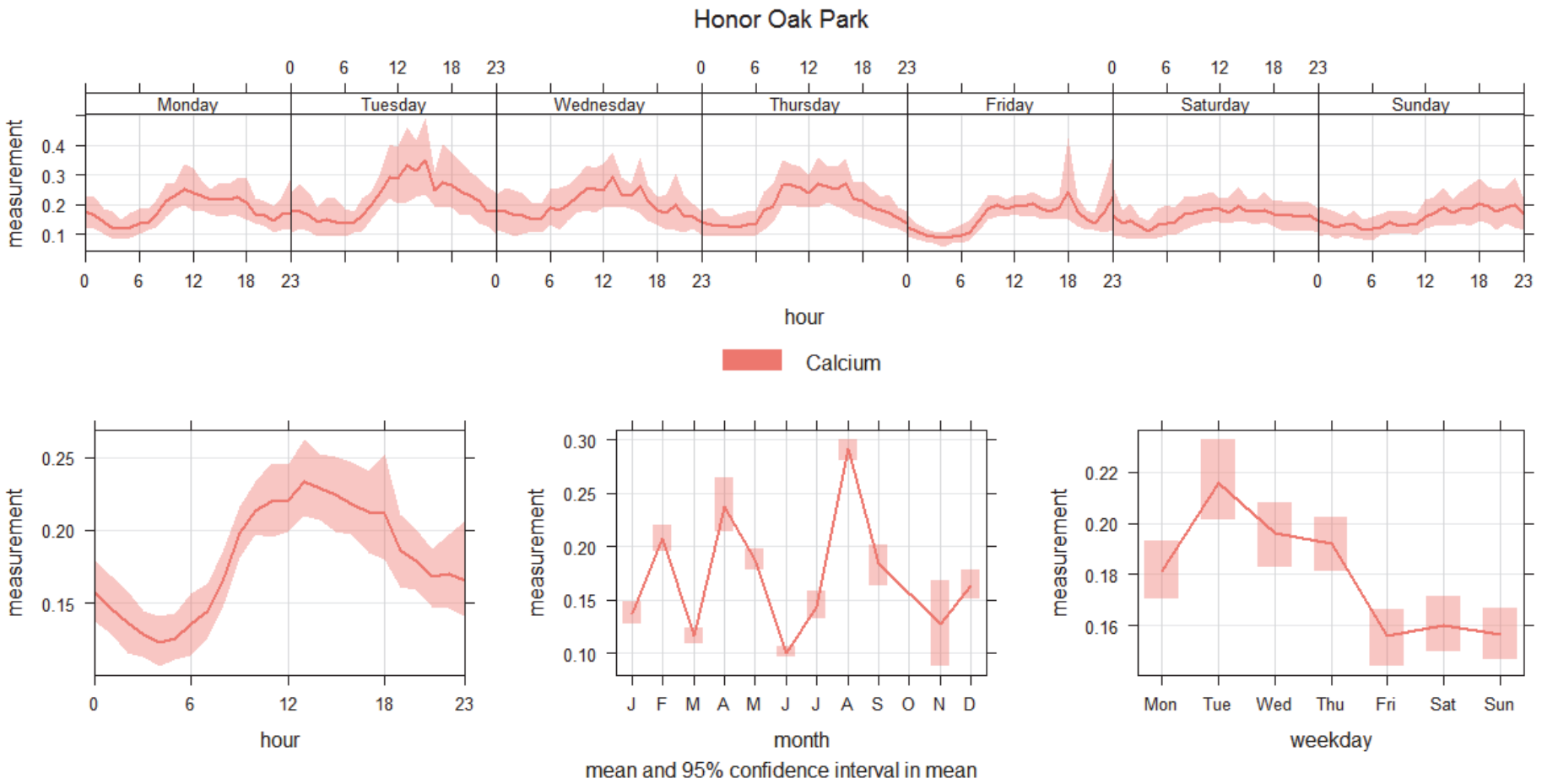

Figure 4-30 Diurnal, weekly and monthly profiles for Ca^{2+} during 2019 at Honor Oak Park. These graphs show the mean and 95% confidence interval (µg m^{-3})

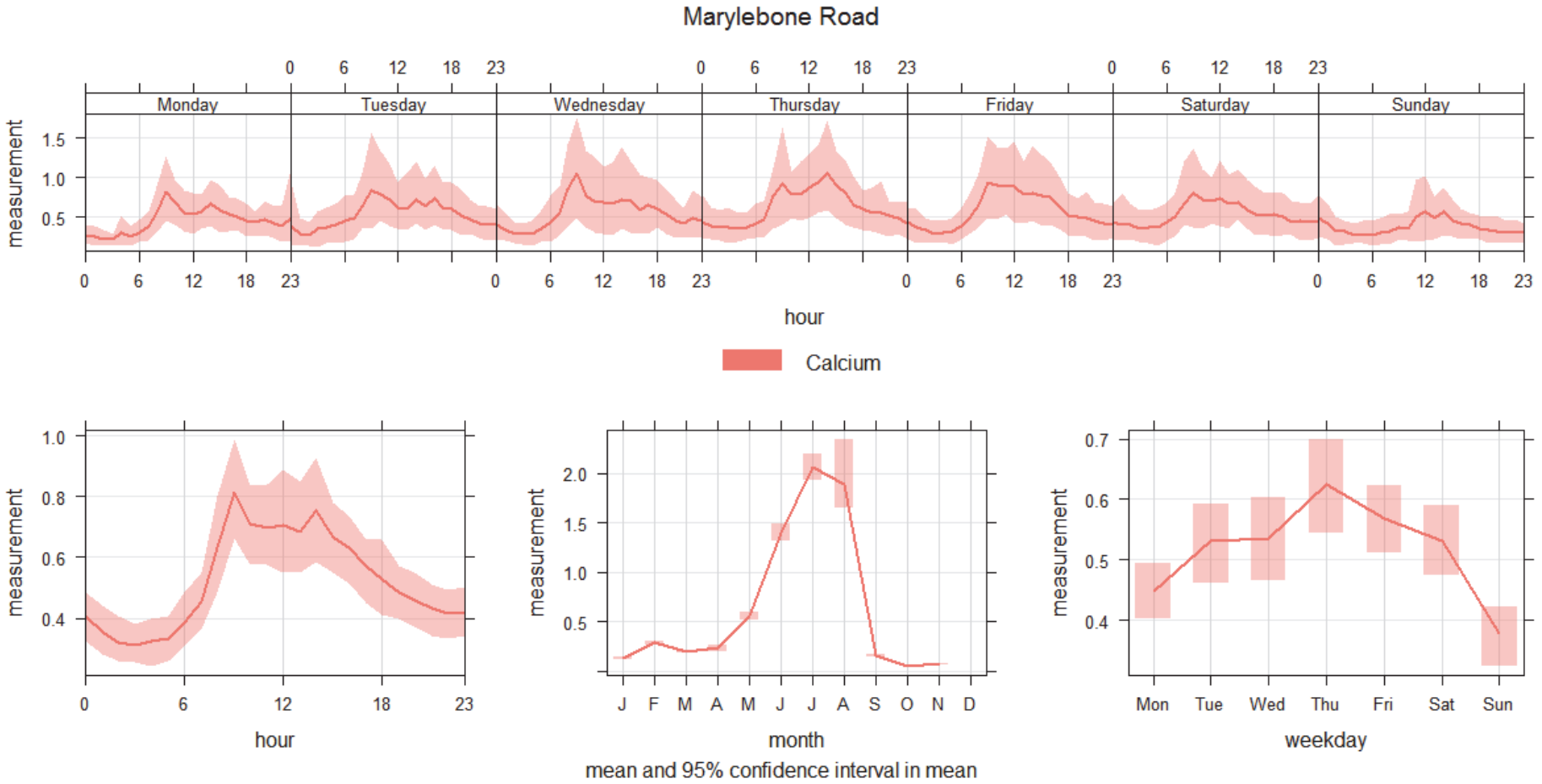

Figure 4-31 Diurnal, weekly and monthly profiles for Ca^{2+} during 2019 at Honor Oak Park (top) and Marylebone Road (bottom). These graphs show the mean and 95% confidence interval (µg m^{-3})

4.7.2 Profiles for particle number concentrations

The diurnal, weekly and monthly profiles for number concentrations in 2019 are shown for the Honor Oak Park and Marylebone Road sites in Figure 4-32 and

Figure 4-33 respectively. At these urban sites they show a strong correlation with human activity. At Marylebone Road there are higher concentrations during the working week and less at weekends. At Honor Oak Park, however, this effect is less pronounced presumably due leisure activities at the Sports Centre causing increased traffic in the evening and at the weekend.

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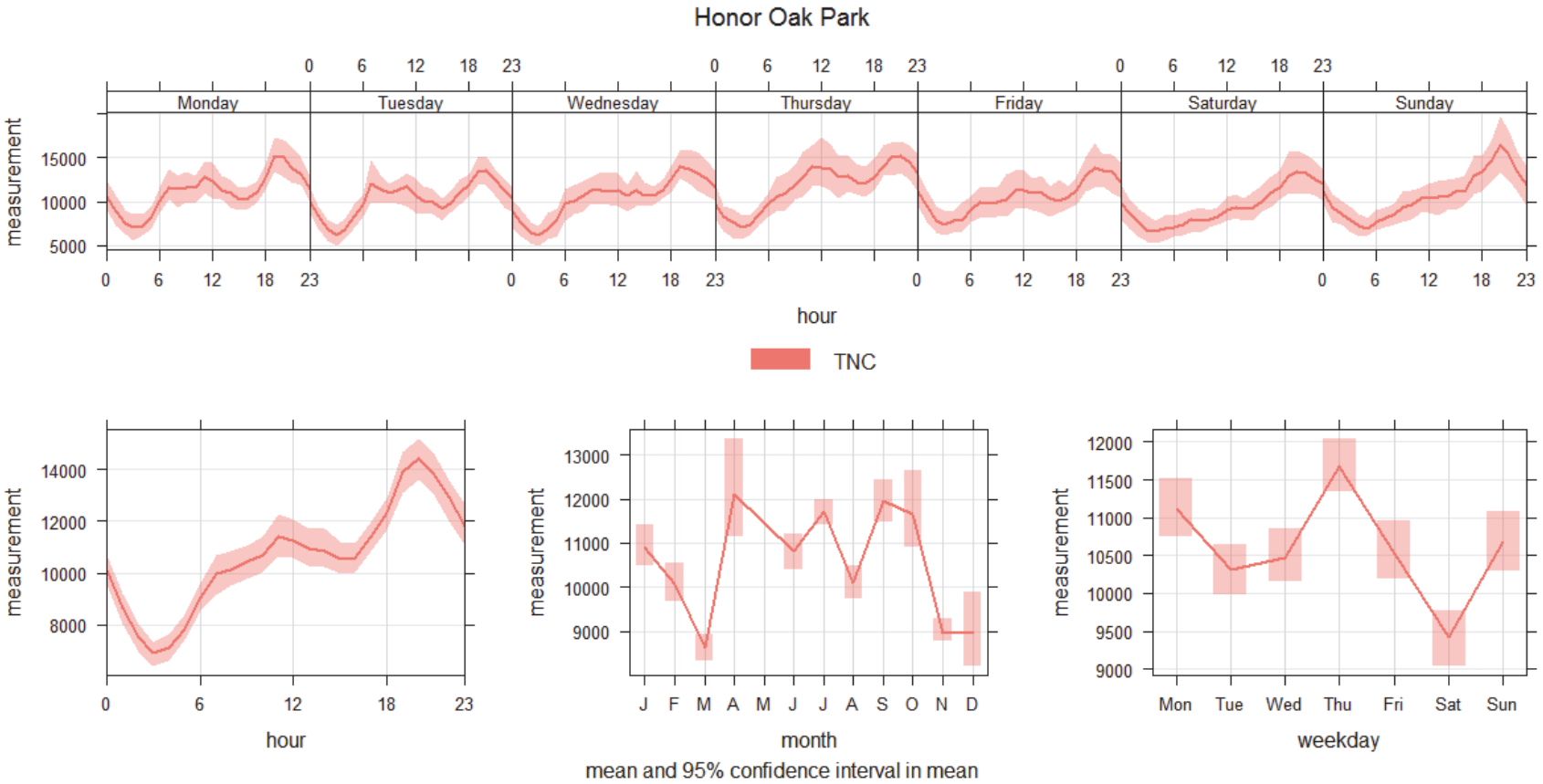

Figure 4-32 Temporal variations of number concentrations in 2019 at Honor Oak Park. These graphs show the mean and 95% confidence interval (cm^{-3})

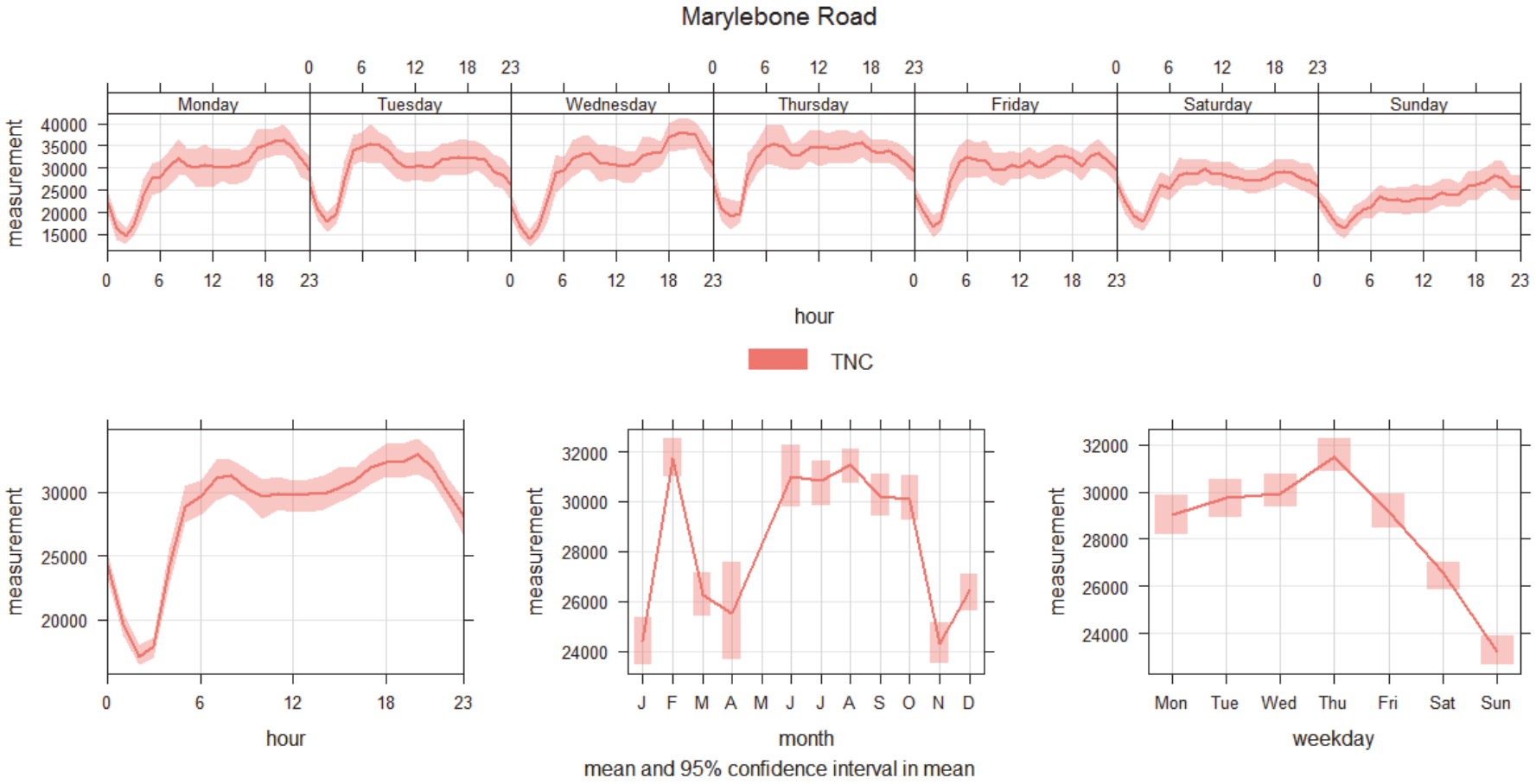

Figure 4-33 Temporal variations of number concentrations in 2019 at Marylebone Road. These graphs show the mean and 95% confidence interval (cm^{-3})

5 REFERENCES

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