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AIRBORNE PARTICLE CONCENTRATIONS, PARTICLE NUMBERS AND BLACK CARBON IN THE UNITED KINGDOM - ANNUAL REPORT 2020

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Airborne Particle Concentrations, Particle Numbers and Black Carbon in the United Kingdom - Annual report 2020

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EXECUTIVE SUMMARY

This report was prepared by the National Physical Laboratory (NPL) and the Environmental Research Group (ERG) at Imperial College London (ICL) as part of the UK Airborne Particle Concentrations, Numbers and Black Carbon contract. The contract is managed by the Environment Agency (EA) 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 was previously based at King's College London (KCL) and moved to ICL during 2020.

This annual report for 2020 contains:

- A summary of the network structure, its operation and quality procedures
- Descriptions of the instruments used on the Network
- The data capture recorded for each instrument
- Time series plots of all ratified Network data in 2020.

And, where applicable:

- Plots of the diurnal, weekly and monthly trends in ratified network data in 2020
- Plots of the long-term trends in ratified Network data
- Comparisons between pollutants measured by the Network

The Network operated a selection of instruments across the UK at 15 monitoring sites with a mixture of site classifications: rural background, urban background, and urban roadside. Seven of the sites were in England, four in Northern Ireland, three in Scotland and one in Wales.

In 2020, the Network measured:

- Hourly particle number concentrations using a Condensation Particle Counter (CPC) at three sites
- Hourly particle size distributions using a Scanning Mobility Particle Sizer (SMPS) at three sites
- Hourly concentrations of chloride, nitrate, sulphate, sodium, ammonium, potassium, magnesium, and calcium ions in $PM_{2.5}$ using an Ambient Ion Monitor (AIM) in combination with an ion chromatography system at London Marylebone Road and London Honor Oak Park. These measurements were stopped on 25 March 2020.
- Hourly aerosol mass and chemical speciation (ammonium, nitrate and sulphate ions and organic aerosols) in $PM_{2.5}$ at London Honor Oak Park, and since July 2020, in PM_1 at London Marylebone Road.
- Weekly measurements of organic carbon and elemental carbon (OC/EC) in $PM_{2.5}$ at Auchencorth Moss (for the whole of 2020) and Chilbolton Observatory (until June 2020). Daily $PM_{2.5}$ measurements of OC/EC at Chilbolton Observatory (from June 2020), London Marylebone Road and London Honor Oak Park (for the whole of 2020). $PM_{2.5}$ was collected on filters and analysed for OC/EC in a laboratory using a thermal/optical carbon analyser
- Hourly concentrations of black carbon (BC) and 'UV particulate matter' (UVPM) in $PM_{2.5}$ were measured by an Aethalometer at 14 sites.

The impact of the Covid-19 pandemic on the operation of the Network was limited. There were however some delays for Equipment Support Units responding to equipment breakdowns and carrying out routine service visits due to travel restrictions. Local Site Operator visits to sites were also reduced where possible. There were no delays to the laboratory analysis of OC/EC that had any effect on data capture or the annual reporting of data.

Fully ratified Network data can be downloaded from the Defra UK-AIR website[1].

This report also contains the results of a comparison campaign between three co-located instruments in August 2020: an ambient ion monitor, an aerosol chemical specification monitor and an X-ray fluorescence spectrometer.

Some notable features from the network data in 2020 are:

- Annual average particle number concentrations at London Marylebone Road fell noticeably from 2019 to 2020 to levels similar to those measured in 2015 and 2016. No significant change in annual average particle number concentrations from 2019 to 2020 was observed at London Honor Oak Park or Chilbolton.

- The steady decrease in the annual average EC mass concentrations at Marylebone Road observed since 2008 continued in 2020. A large decrease in OC mass concentration from 2019 to 2020 was observed at the same site. Much smaller changes in annual average EC and OC mass concentrations from 2019 to 2020 were observed at Chilbolton.

- Annual average mass concentrations from all seven Aethalometer channels (950 nm, 880 nm, 660 nm, 590 nm, 520 nm, 470 nm, and 370 nm) are reported for the first time since the AE33 model Aethalometers were introduced to the Network in November 2019.

- The significant downward trend in measured black carbon mass concentrations observed at all the long-running sites in the network apart from Strabane since 2009 continued into 2020. The relative decrease at London Marylebone Road remains much larger than that at other sites.

The annual average data capture across all network sites was:

- 79 % for particle number concentration measurements
- 90 % for particle size distribution measurements
- 65 % for anion and cation measurements
- 53 % for aerosol mass and chemical composition measurements
- 89 % for organic carbon and elemental carbon measurements
- 92 % for black carbon measurements

It should be noted that anion and cation measurements were stopped in March 2020, giving a time coverage of 23%. The aerosol mass and chemical composition measurements started in mid-July 2020 at London Marylebone Road, giving a time coverage of 46%.

1 INTRODUCTION

The UK Airborne Particle Concentrations and Numbers Network, and the UK Black Carbon Network currently operate 15 air pollution monitoring sites in total. 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.

These sites provide data on airborne particles by using instruments that measure: particle number concentrations, particle size distributions; organic and elemental carbon, black carbon, and ultraviolet particulate matter (UVPM); anions and cations; and aerosol mass and chemical speciation.

Prior to 2020, this data was reported in two separate annual reports, one for the UK Particle Concentrations and Numbers Network and one for the UK Black Carbon Network.

The UK Particle Concentrations and Numbers Network began operation in November 2001. Since then, the number and location of sites, and monitoring methodologies have transitioned through several iterations. The National Physical Laboratory (NPL), supported by the Environmental Research Group (ERG) at King's College London (now moved to Imperial College London), operated the network contract from 2005. As a standalone Network, it comprised 4 sites (London Marylebone Road, London Honor Oak Park, Chilbolton Observatory and Auchencorth Moss). Multiple instruments operated at each site, with the purpose of monitoring the UK's compliance with objectives set out in the EU Ambient Air Quality Directive[2] and provided data to improve understanding of airborne particulate matter, with a focus on $PM_{2.5}$.

The UK Black Carbon Network commenced operation in September 2006. The purpose of the network was to continue a historical black smoke dataset (which dates back to the 1920s) and monitor black carbon concentrations. NPL, supported by ERG, was awarded the contract to restructure and run the UK Black Smoke Network in September 2006. As a standalone Network, it comprised 14 sites: all the sites in Table 1 with the exception of London Honor Oak Park.

As these two networks were closely linked, they are now reported in one annual report to provide administrative cost-savings to the Environment Agency (EA) and Defra.

This report presents a summary of the 2020 data, key findings from the data, a comparison with previous years and, where relevant, a comparison with data from other networks.

2 NETWORK INFRASTRUCTURE AND OPERATION

2.1 NETWORK OVERVIEW (FOR 2020)

The network in 2020 was structured in broadly the same way as the previous year. Note that this is however the first year that a combined annual report has been produced – as described in section 0, separate reports were previously produced for the UK Particle Concentrations and Numbers Network and the UK Black Carbon Network.

The main changes to the network in 2020 were:

- The Ambient Ion Monitor (AIM) instruments at London Marylebone Road and London Honor Oak Park stopped analysis in March 2020 and were removed from the Network following a comparison campaign in August 2020. The results from this comparison are described in section 4.3.4
- The Leckel sampler at Chilbolton Observatory changed from weekly to daily sampling in June 2020
- The new aerosol chemical specification monitor (ACSM) sampling PM_1 was installed at Marylebone Road in July 2020.

Also of note are that:

- The CPC at the Birmingham Ladywood site was not operational throughout the whole of 2020 due to the need to relocate the instrument – discussions are ongoing to agree the best location for the instrument.
- The operation of the network was affected in 2020 by the Covid-19 pandemic.
    - The main effect of the pandemic was delays for Equipment Support Units (ESUs) responding to equipment breakdowns and carrying out the routine service visits. In most cases ESU are not local to sites, so travel and social distancing restrictions delayed work.
    - LSO (Local Site Operator) visits were reduced where possible, and mode of transport changed to private-hire vehicles (affecting sustainability data). In most cases the bi-weekly visits were maintained, but *ad hoc* visits to diagnose and fix breakdowns or change Aethalometer tapes were delayed. Due to the transport of consumables and LSO time required by the AIMs, it was decided to stop analysis earlier than planned.
    - NPL staff had limited access to the NPL site so were able to continue dispatching and receiving OC/EC filters and other consumables for equipment. The OC/EC lab analysis did experience some delays; however this had no overall effect on the data capture or annual reporting of data.

NPL has continued its role as the primary contractor, Central Management and Control Unit (CMCU) and Quality Assurance and Quality Control Unit (QA/QC), with significant support from the Environmental Research Group (ERG) at King's College London (now at Imperial College London). More details of the specific activities of each organisation are given in section 2.2.2.

2.2 NETWORK STRUCTURE AND OPERATION

2.2.1 Network sites

The measurement programme for during 2020 is shown in Table 1. Site locations are shown in Figure 1. Site details are available through the UK AIR website.[1]

The four sites that comprise the Particle Numbers and Concentrations Network (Auchencorth Moss, Chilbolton Observatory, London Marylebone Road and London Honor Oak Park) are located to provide $PM_{2.5}$ Organic Carbon and Elemental Carbon mass concentration data to assist in requirements of the 2008 Air Quality Directive[2] at two UK rural sites and to maximise the benefit of the measurements made, both in terms of drawing conclusions about the concentrations and chemical composition of particles in ambient air at these locations and understanding more fully the key pollutant sources.

The other eleven sites are in the Black Carbon network. These are located to target the measurement of traffic emissions of Black Carbon in urban areas, and of solid fuel and biomass emissions in Northern Ireland & Cardiff. Urban and traffic increments are targeted by having a rural background, an urban background, and a roadside / kerbside siting combination across each conurbation. Note that Chilbolton Observatory site is used as a Rural Background site for both Birmingham and London.

Table 1 - Network structure in 2020. The colour key indicates the emissions sources representative of each site (as previously defined for the Black Carbon sites): Green = Glasgow urban area; Red = Birmingham urban area; Blue = London Urban area; Orange = solid fuel use / domestic emissions.

Site Name	Site Classification	Hourly $PM_{2.5}$ ions	Hourly $PM_{2.5}$ or PM_1 aerosol mass and speciation	Daily $PM_{2.5}$ OC/EC	Weekly $PM_{2.5}$ OC/EC	Hourly particle number concentration	Hourly particle size distribution	Hourly BC and UVPM	Key
Glasgow High Street	Urban roadside							X	1
Glasgow Townhead	Urban background							X	2
Auchencorth Moss	Rural background				X			X	3
Birmingham A4540 Roadside	Urban roadside							X	4
Birmingham Ladywood	Urban background							X	5
Chilbolton Observatory	Rural background			X [2]	X [2]	X	X	X	6
London North Kensington	Urban background							X	7
London Marylebone Road	Urban roadside	X [1]	X [3]	X		X	X	X	8
London Honor Oak Park	Urban background	X [1]	X [4]	X		X	X		9
Detling	Rural background							X	10
Belfast Centre	Urban background							X	11
Kilmakee Leisure Centre (Dunmurry)	Urban background							X	12
Strabane 2	Urban background							X	13
Ballymena Ballykeel	Urban background							X	14
Cardiff Centre	Urban background							X	15

Notes
[1] In March 2020, the AIMs at London Marylebone Road and London Honor Oak Park were switched off.
[2] In June 2020, the Leckel at Chilbolton Observatory was changed from weekly to daily sampling.
[3] In July 2020, a new ACSM (sampling PM_1) was installed at London Marylebone Road.
[4] The London Honor Oak Park ACSM samples $PM_{2.5}$

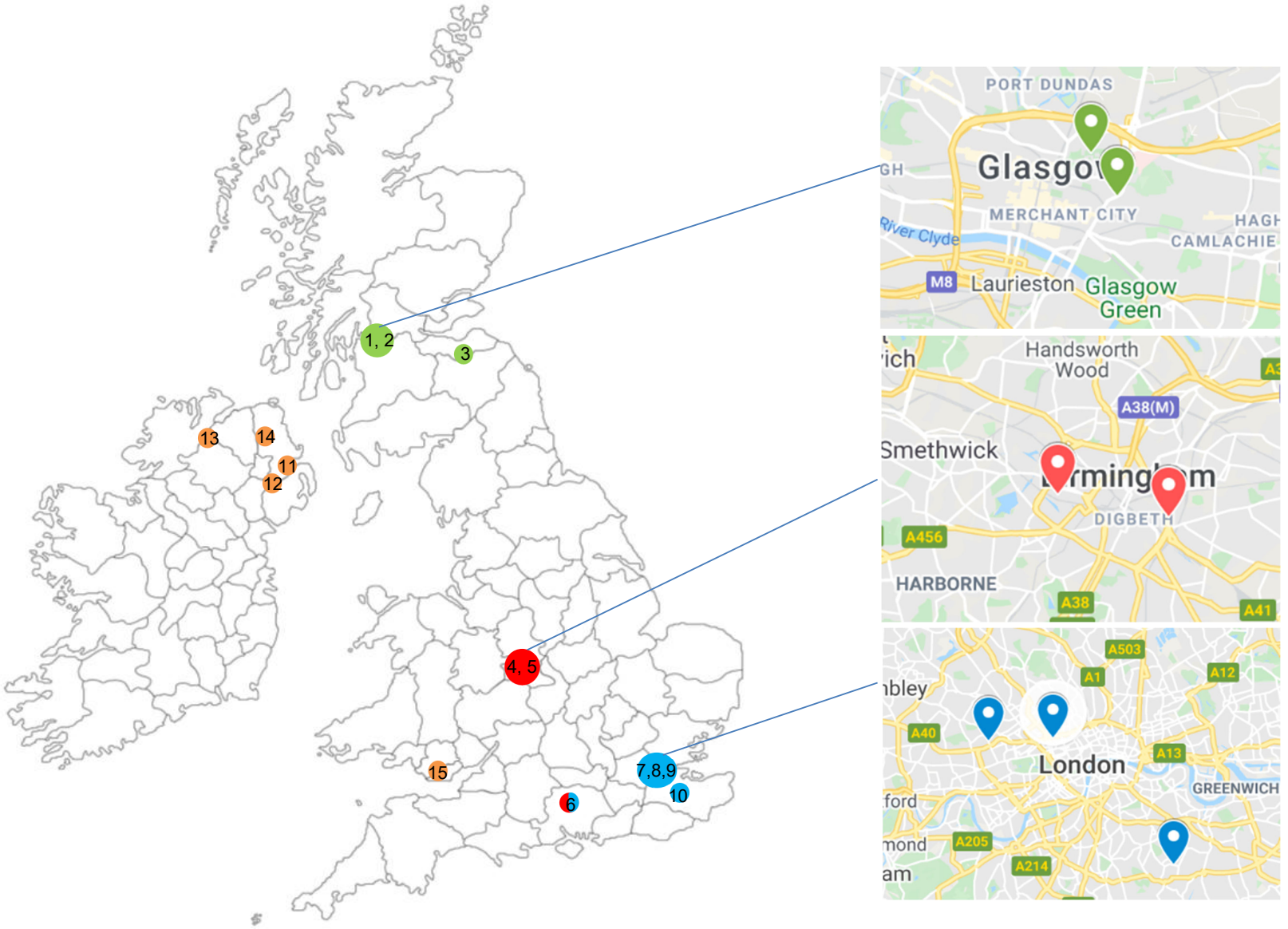


Figure 1 - Network sites in 2020. The colour key indicates the emissions sources representative of each site (as previously defined for the Black Carbon sites): Green = Glasgow urban; Red = Birmingham Urban; Blue = London Urban; Orange = solid fuel use / domestic emissions.

2.2.2 Network operation

The day-to-day operation of the Network is set up to mirror that of the Automatic Urban and Rural Network (AURN), to include a Central Management and Control Unit (CMCU) and a Quality Assurance and Quality Control Unit (QA/QC). NPL has continued its role as CMCU and QA/QC, with significant support from ERG.

CMCU activities include management of equipment, consumables, and health and safety; management of subcontractors such as LSOs and the ESU; collection and storage of data; reporting; and providing technical advice to the EA.

QA/QC activities include ensuring adherence to the appropriate technical standards; training and auditing LSOs; managing equipment services and calibrations; and data ratification and submission to the DDU (Data Dissemination Unit).

For CPCs, SMPSs, AIMs and Aethalometers, ERG is responsible for collecting and storing the data; ERG also manage the ESU emergency callouts for the Partisols and the scheduled services and calibration for Aethalometers.

ERG have continued to undertake the CMCU and QAQC activities for the ACSM equipment with support from NPL. As the CMCU for the ACSMs, ERG manage the equipment; perform LSO and ESU activities, including health and safety; collection and storage of data; provide the parts and consumables; co-author the quarterly and annual reports; and provide expert technical advice. For QA/QC activities, ERG take responsibility for following the appropriate technical standards; training LSOs and updating LSO and quality manuals; managing instrument services and calibrations; participating in intercomparisons; and attending the annual quality circle meeting and annual ratification of data.

NPL have continued to undertake OC/EC analyses in-house, including associated QA/QC activities.

Further details of the operation of the instruments on the Network are given in section 2.4 and section 3.

2.3 DATA CAPTURE

Annual data capture is calculated as the percentage of the time during which we intended to perform measurements (excluding downtime for planned calibrations) for which the measurements were valid.

The tables below show the annual data capture for 2020 for each instrument at each site. In the cases where an instrument measures more than one analyte, an average data capture has been calculated for each site. All data are stated to the nearest whole percentage.

2.3.1 Particle number concentration

The main cause of data loss was a CPC drier fault at London Honor Oak Park; a contaminated CPC drier and CPC fault at London Marylebone Road; and a butanol leak due to a cracked inlet in the CPC at Chilbolton. The CPCs and drier systems were fully serviced at NPL in February 2021 and a more regular on-site maintenance of the CPC drier systems was proposed to mitigate future drier failures.

Table 2 - Data capture for particle number concentration measurements

Site Name	Data capture [%]
Chilbolton Observatory	84
London Marylebone Road	63
London Honor Oak Park	91
Average	**79**

2.3.2 Particle size distribution

The main cause of data loss was due to a serious pump fault in the CPC component of the SMPS at London Marylebone Road. This was sent to the instrument manufacturer for repair..

Table 3 - Data capture for particle size distribution measurements

Site Name	Data capture [%]
Chilbolton Observatory	92
London Marylebone Road	86
London Honor Oak Park	92
Average	**90**

2.3.3 Anions and cations

In 2020, the AIM (Ambient Ion Monitor) at both sites only ran from 1 January to 25 March (i.e. an annual time coverage of 23%). The main causes of data loss during that time were a degraded column at London Marylebone Road that would have been replaced at the next service in April and the waiting time for major replacement parts to be delivered following a breakdown at London Honor Oak Park, which is more common due to the age of the equipment.

Table 4 - Data capture for anion and cation measurements

Site Name	Data capture [%]
London Marylebone Road	69
London Honor Oak Park	61
Average	**65**

2.3.4 Aerosol mass and chemical composition

The ACSM at London Honor Oak Park ran for the whole year, and the ACSM at London Marylebone Road was installed in mid-July 2020. Following its installation, the Marylebone Road ACSM suffered several major breakdowns (mainly due to problems with the temperature control module and replacement parts) as shown by the low time coverage for this 6-month period.

Table 5 - Data capture for aerosol mass and chemical composition measurements

Site Name	Data capture [%]
London Marylebone Road	23
London Honor Oak Park	82
Average	**53**

2.3.5 Organic Carbon and Elemental Carbon

The common causes of data loss across the four samplers were due to filter exchange errors and instrument breakdowns arising from various part failures. The samplers are due to be replaced from 2021 having reached their life expectancy.

Table 6 - Data capture for OC/EC measurements

Site Name	Data capture [%]
Auchencorth Moss	89
Chilbolton Observatory	99
London Marylebone Road	80
London Honor Oak Park	87
Average	**89**

2.3.6 Black carbon

The main cause of data loss was electric fuse failure. Although this could be easily diagnosed (by a blank screen), the replacement of fuses were, in most cases, delayed due to the COVID-19 travel restrictions for the ESU, especially those in Northern Ireland. The London Marylebone Road Aethalometer had a leak in the sampling line in January and needed to undertake routine service stability tests in June. At the Ballymena site there was no data in January and February due to a memory card failure.

Table 7 - Data capture for black carbon measurements

Site Name	Data capture [%]
Auchencorth Moss	93
Ballymena Ballykeel	82
Belfast Centre	86
Birmingham A4540 Roadside	95
Birmingham Ladywood	100
Cardiff Centre	99
Chilbolton Observatory	99
Detling	91
Glasgow High Street	98
Glasgow Townhead	98
Kilmakee Leisure Centre	95
London Marylebone Road	86
London N. Kensington	91
Strabane 2	81
Average	**92**

2.4 INSTRUMENTATION

2.4.1 Particle number concentration

Particle number concentrations are measured using Condensation Particle Counters (CPC), TSI model 3772-CEN, which were installed at the sites in June 2017, replacing the older TSI 3022a models.

The CPC instrument works by passing the continuous air sample through a heated tube saturated with butanol, and then cooling the airstream to set up supersaturated conditions. The butanol vapour then condenses on particles down to very small sizes, 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.

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 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 of a TSI Nafion drier system for the stand-alone CPC and a separate NPL designed Nafion drier system for the SMPS were employed.

Figure 2 shows the CPC and drying unit equipment at a typical site.

Figure 2 - CPC and drying unit equipment at a typical site

2.4.2 Particle size distribution

Particle size distributions are measured using a Scanning Mobility Particle Sizer (SMPS). This consists of a CPC (TSI model 3775) combined with an electrostatic classifier (TSI model 3080).

The electrostatic classifier consists of a charge neutraliser (incorporating an ^{85}Kr 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.

When the 3772-CEN CPC system was installed in 2017 the SMPS system was originally dried through the TSI CPC drier. This unfortunately caused flow issues in the CPC system and led to breakdowns and reduced data capture. Therefore, an NPL SMPS drier system was installed in January 2018 to separate the CPC and SMPS systems and fix the flow issue.

Figure 3 shows the SMPS and NPL drying unit equipment at a typical site.

Figure 3 - SMPS and NPL drying unit equipment at a typical site

2.4.3 Anions and cations

The AIM (Ambient Ion Monitor) manufactured by URG Corp., model 9000-B (Figure 4), provides time-resolved direct measurements of anions (Cl^-, NO_3^- and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}).

The sampler used 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 methanesulphonic 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. In this set up, particulate matter with diameters less than 2.5 μm ($PM_{2.5}$) 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. 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 ICSs.

The instrument samples for 55 minutes during each hour. The two ICSs then analyse the collected sample. The analysis takes 15 minutes. It is a two-stage instrument, analysing the previous sample whilst collecting the next sample. Hence the instrument allows the production of hourly averages for all relevant anions and cations. The two instruments were originally installed with a PM_{10} size selective monitoring head for consistency with the previous anions filter-based sampling equipment. At London Honor Oak Park and London Marylebone Road, the size selective heads were changed to $PM_{2.5}$ in November 2018 and January 2019, respectively.

Figure 4 - URG AIM 9000B Ambient Ion Monitor with Ion Chromatography Systems

2.4.4 Aerosol mass and chemical composition

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, sulphate, chloride, and organics. It is designed for continuous monitoring of aerosol composition with long-term (weeks) unattended operation.

The instrument operates by sampling air into a high vacuum system through a size-selective particle aerodynamic lens at either PM_1 or $PM_{2.5}$. The particle lens focuses particles 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 5 shows a schematic diagram of the set up.

The ACSM instrument was installed at London North Kensington in 2013 with a PM_1 aerodynamic lens. It was moved to London Honor Oak Park in November 2018 and the aerodynamic lens changed to $PM_{2.5}$. The ACSM instrument was installed at London Marylebone Road in July 2020 with a PM_1 aerodynamic lens.

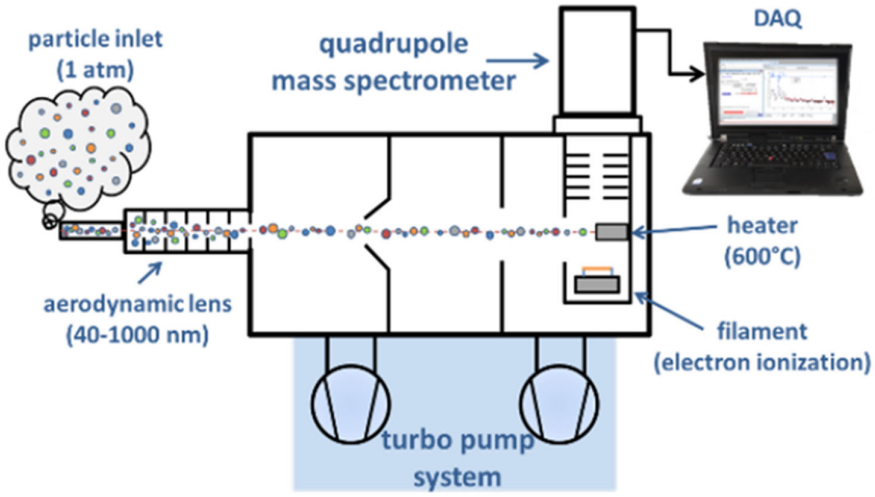


Figure 5 - ARI Aerosol Speciation Chemical Monitor schematic.
(DAQ = Data acquisition (control)).

2.4.5 Organic Carbon and Elemental Carbon

OC (organic carbon) and EC (elemental carbon) were collected on filters at four sites: Auchencorth Moss and Chilbolton Observatory (rural background); London Honor Oak Park (urban background); and London Marylebone Road (urban roadside). Ultrapure quartz filters (Pallflex Tissuquartz 2500QAT-UP) are used for the sampling.

Daily $PM_{2.5}$ is sampled using a Thermo Partisol 2025 sequential air sampler (Figure 6) at London Marylebone Road and London Honor Oak Park. The original PM_{10} sampling heads were changed to $PM_{2.5}$ heads at Honor Oak Park and Marylebone road in February 2019 and October 2019, respectively. At Chilbolton, the Partisol (daily, PM_{10}) was removed in October 2019.

Weekly measurements of $PM_{2.5}$ continued to be made at Auchencorth Moss throughout 2020 and at Chilbolton, up until June 2020, using a Leckel SEQ47/50 sequential sampler (Figure 6). The Chilbolton Leckel sampler (sampling $PM_{2.5}$) was changed from weekly to daily measurements in June 2020. This change from weekly to daily sampling was 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 by sampling for daily measurements of OC/EC components of $PM_{2.5}$.

Elemental carbon and organic carbon analysis was carried out using the Sunset Laboratory Inc. thermal/optical carbon analyser (Figure 7). In the laboratory, a 1.5 cm^2 punch is 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 analysis protocol used is termed EUSAAR2, as specified in EN 16909:2017[3]. The protocol also specifies that the transmittance correction must be used to determine concentrations for EC and OC. Data are reported as the mass of carbon atoms per unit volume of air. The temperatures are calibrated using the Sunset Laboratories calibration kit.

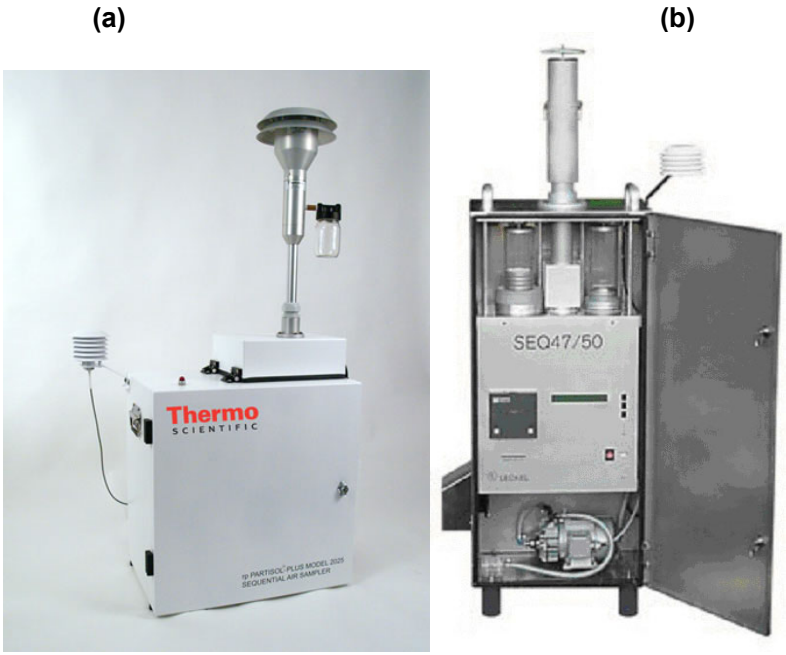


Figure 6 - (a) Thermo Partisol 2025 sampler (b) Leckel SEQ47/50 sampler

Figure 7 - Sunset Laboratory Inc. thermal/optical carbon analyser

2.4.6 Black Carbon and UV-absorbing particulate matter

Aethalometers quantify black carbon (BC) on filter samples based on the transmission of light through a sample. In November 2019, all sites were upgraded to the new Aethalometer model AE33 (see Figure 8).

Figure 8 Aethalometer model AE33

This 7-wavelength instrument operates at 950 nm, 880 nm, 660 nm, 590 nm, 470 nm, and 370 nm. The sample is collected onto a Teflon tape (M8060 type), and the optical attenuation is measured with time resolution of 1 min. Two spots with different sample flows together with the reference spot without the flow are used to calculate attenuation. The rate of change of the attenuation of light, together with flow, area and volume of the sample are mathematically converted to the compensated particle light absorption and a black carbon mass concentration. A mass absorption cross-section of 7.77 $m^2\ g^{-1}$ was used at 880 nm and 18.47 $m^2\ g^{-1}$ at 370 nm, as described in Drinovec *et al*.[4]. The equation used to determine the concentration of black carbon is:

Equation 1

$$BC = \frac{S * (\frac{\Delta ATN_1}{100})}{F * \sigma_{air} * C * (1 - k * ATN_1) * \Delta t}$$

Where:
S = spot area; ATN_1 = optical attenuation; F = flow; σ_{air} = mass absorption cross section; C = multiple scattering parameter (1.39); k = compensation parameter; t = time.

Results from channel 880 nm, give the quantitative concentration of 'black' carbon and those from 370 nm indicate the presence of aromatic organic compounds such as are found in wood smoke, biomass-burning smoke, and tobacco smoke. The ‘UV’ Particulate Matter (UVPM) is calculated as a difference between UV and BC channels.

At all sites, ambient air was 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 was made by a $PM_{2.5}$ cyclone placed close to the inlet of the Aethalometer. All the tubing before the cyclone is constructed from stainless steel. Sampling has been standardised across the network by using this size selective inlet before the Aethalometer, which was not possible with the black smoke method.

The Aethalometers were upgraded in November 2019, and since then both Aethalometers (model AE22 and AE33) have been sampling air in parallel from the same inlet at traffic and urban background sites in London. The aim of this campaign was to show continuity of data and quantify any differences in measurements. Preliminary results from this comparison campaign, however, suggest that concentrations measured by AE33 model are approximately 30% higher than from the AE22 model, and a follow-on comparison is currently being planned to investigate this further.

Thus, all results provided in this report should be treated with caution especially when comparing 2020 data from the AE33 model with previous years when AE22 model was used. A note to this effect was added to Black Carbon Network page of the UK AIR website[5] in the summer of 2021.

3 DATA QUALITY

3.1 QA/QC PROCEDURES

NPL operates under a Quality Management System registered for scientific research and development and the provision of internal services by Lloyd's Register Quality Assurance (LRQA) according to ISO 9001:2015[6]. NPL is accredited in accordance with International Standard ISO/IEC 17025:2017[7] for the general requirements for the competence of testing and calibration laboratories.

A summary of the general quality assurance and quality control (QA/QC) procedures used during the measurement and ratification process is given below:

- A Technical lead is appointed for each instrument type to manage data collection and ratification, and is supported by a deputy and expert consultants.
- Local Site Operators (LSOs) are trained and audited on an ongoing basis to carry out routine maintenance and report issues. All LSO maintenance activities are recorded.
- Each type of equipment has an appointed Equipment Support Unit (ESU) who is responsible for routine servicing and emergency repairs.
- An annual audit of all sites, LSOs, and instruments (including flow checks) is conducted by an independent NPL audit team.
- Equipment calibrations and calibration checks are carried out at regular intervals throughout the year.
- Data collection is done manually for Leckel and Partisol samplers by NPL and automated by the MONNET system at ERG for all other instruments. All data is stored securely and backed up.
- The Quarterly Network Report includes data capture values from the verified data of the previous quarter.
- Automatic and manual data validation is followed by rigorous ratification procedures.
- Data quality circle meetings are held at least annually to review and validate the data. Other measurements made in this monitoring programme and in other EA monitoring programmes are also used to check the validity of the measurements.

The key additional measurement-specific QA/QC procedures are summarised below:

3.1.1 Particle number concentration

- The manufacturer's software is set up to automatically repeat measurements every 15 minutes, providing verified numerical data.
- NPL is accredited by UKAS to ISO 17025 to perform the primary calibration of CPCs and is the only institute in UK with this accreditation. The primary calibration of CPC instruments is by comparison with a Faraday Cup Electrometer (FCE) - the reference FCE and the test CPC simultaneously measure the number concentration of a test sample being produced by a well characterised aerosol generator. The concentrations obtained are corrected for any multiple charges on the test particles. The calibration and flow factors are then applied during ratification to give the best estimate of the number concentrations.

3.1.2 Particle size distribution

- The LSO confirms that the radioactive source is present and makes a radiation measurement monthly.
- The manufacturer's software is set up to automatically repeat measurements every 15 minutes, providing verified numerical data.
- The CPC part of the SMPS is calibrated at NPL (see section 3.1.1).
- For the SMPS calibration process carried out by NPL, aerosols containing traceable (NIST-certified) polystyrene latex nanospheres of different sizes are used to check the sizing accuracy. These are generated using a nebuliser and diffusion dryer.
- A further validation of the SMPS size distribution is performed by comparing the response of all network SMPSs to several common broad sized distributions of soot nanoparticles.

3.1.3 Anions and cations

- The instrument control and data software are remotely checked by the LSO daily to ensure the equipment and software are operating and identifying peaks correctly.
- NPL tracks peak widths and resolution to monitor chromatography column degradation. The columns are changed as required to ensure data quality.
- Monthly, or as required, the liquid diffusion denuder, saturation chamber and separator are exchanged for clean ones to ensure instrument efficiency.
- Bi-annually, NPL prepares the calibration standards for the Ion Chromatography Systems (ICSs) using traceable certified reference materials, in line with NPL's UKAS accredited in-house procedure. Quarterly, the NPL technical lead attends each site to calibrate the ICSs, or more often if there is a breakdown. The calibration data is entered into the instrument software for real-time calculation of ion concentration.
- An internal standard of lithium bromide (LiBr) is used for on-going calibration. The LiBr solution is prepared by the LSO. Measurements are rejected if the measured Li^+ and Br^- concentrations deviate by more than ±15% of the known concentration.

3.1.4 Aerosol mass and chemical composition

- LSO attends the instruments bi-monthly to perform sensibility checks on the instrument and software. These checks include flow rate checks, pinhole and inlet cleaning and instrument tuning using EU SOP procedures developed for the ACSM (ACTRIS).
- Calibrations are performed quarterly or bi-annually by trained technical users. Particles of ammonium sulphate and ammonium nitrate are generated from solution and then size-selected by passing through the SMPS Differential Mobility Analyser (DMA). Particles are then counted by the CPC to produce a particle stream of known concentration before entering the ACSM. The stream is diluted with particle free air to produce the calibration curve.
- Ratification is performed by the proprietary software. Data are scaled and corrected for pressure, flow and temperature using EU SOP procedures developed for the ACSM (ACTRIS). Sensibility checks are performed by mass closure comparison to co-located PM mass measurements.

3.1.5 Organic carbon and elemental carbon

- Sampled filters received at the NPL laboratory are recorded, handled, stored, and analysed following NPL's UKAS accredited in-house procedure for OC/EC samples.
- NPL's analysis procedure describes a method for the accurate measurement of the collected Total Carbon (TC) on ambient air monitoring filters, subdivided into EC and OC. As part of this procedure, field blank filters are analysed to evaluate the contamination due to the transport of the filters to the sites and back to the laboratory.

3.1.6 Black carbon and UV-absorbing particulate matter

- Measurements of black carbon, UVPM, flow, tape life and remaining five channels are remotely downloaded by the ERG system (MONNET). A range of checks are undertaken at this point to ensure measurements are within threshold value range; the flow data is also checked to ensure it is 5 L min^{-1} (±10 %).
- Issues raised during the manual data checking are noted in the database, this information is retained and passed to NPL to inform the ratification process. Occasionally, issues raised during data checking require an intervention from either the LSO or ESU. If this is the case a visit request is sent to either the LSO or ESU.
- The validated 1-minute measurements are averaged to 15-minute means in line with measurements made using gaseous and particulate monitors on the AURN. A valid 15-minute measurement is only calculated where at least ten 1-minute measurements exist in that 15-minute period. Hourly averages are calculated if there are at least three valid 15-minute averages in that period.

3.2 MEASUREMENT UNCERTAINTY

3.2.1 Particle number concentration

The expanded uncertainty of these measurements is 5%, in accordance with NPL's Calibration and Measurement Capabilities, which have been agreed internationally by the Gas Analysis Working Group of CCQM, in support of the Mutual Recognition Arrangement of the CIPM. This value is based on the results of the EURAMET comparison 1282 "Comparison of Condensation Particle Counters"[8].

3.2.2 Particle size distribution

The expanded uncertainty of these measurements is 4.1%. This value has been obtained from the uncertainty budget for the NPL "Calibration of Differential Mobility Analyser for Airborne Nanoparticle Size Selectivity" commercial calibration service. The main component of uncertainty in this measurement is due to uncertainty in the mobility diameter of polystyrene latex beads used in the calibration.

3.2.3 Anions and cations

The overall expanded uncertainty of the ambient concentrations for all the measured anion and cation species is estimated to be 10%[9].
This takes into account the uncertainty of the flow rate of the AIM sampler; the volume of solution collected; and the determination of the mass of each species, including the preparation of the calibration standards and the purity of the salts used to prepare the certified reference materials. It does not include the efficiency of the denuder and the particle extraction system, which are currently unknown.

3.2.4 Aerosol mass and chemical composition

Post processing, ACSM uncertainty is obtained by comparison of the sum of measured concentrations with a regulatory measurement of time-resolved mass concentration of particulate matter, by a Tapered Element Oscillating Microbalance Filter Dynamics Measurement System (TEOM FDMS), Beta gauge or Fine Dust Analysis System (FIDAS) aerosol spectrometer.

The correlation between measurements obtained by ACSM and particle mass measurements must take into account the uncertainties of each method, which necessarily entails a dispersion of points around the line. The uncertainty of the comparison between the different methods can be expressed as follows:

Equation 2

$$\sigma = \sqrt{\sigma_{ACSM}^2 + \sigma_{PM-AMS}^2}$$

According to the results of the European interlaboratory comparison campaign (ACTRIS) in 2013, the expanded uncertainties of ACSM concentration from hourly measurements are equal to 9 % for the sum of the five measured compounds in non-refractory sub-micron aerosols[10]. Uncertainties for individual species are 15 % for nitrate, 19% for organics, 28% for sulphate and 36 % for chloride.

3.2.5 Organic carbon and elemental carbon

As the methods for assessing the accuracy of the OC/EC split of total carbon (TC) are not yet established, the uncertainties on the OC and EC concentrations have not been assessed

The uncertainty in the measured TC concentrations are a combination of the analytical and sampling uncertainties. The expanded analytical uncertainty for TC has been found to be 6 % relative. EN 12341:2014[11] requires the consistency of the average volumetric flow for $PM_{2.5}$ and PM_{10} samplers to be ≤ 2 % over the sampling period. The uncertainty of the measurement of OC and EC is therefore dominated by the analytical uncertainty.

3.2.6 Black carbon UV-absorbing particulate matter

The Aethalometer measurement does not depend on any absolute calibration response signals of the detectors, but instead relies upon their ability to determine very small relative changes in optical transmission. Determining the zero noise of the system gives relevant information on the ability of the instrument to measure small changes in optical transmission. Results from the HEPA filter zero noise tests show that the stability of the optical / electrical system was approximately ± 0.11 µg m^{-3} for hourly means, compared to the network BC mean concentration of 0.86 µg m^{-3}. Converting this into a standard uncertainty represents an average contribution of 11 %.

The provisional overall expanded uncertainties in the measurements for the AE33 model Aethalometer for different averaging periods are given below. These data will be confirmed in due course after completing the comparison campaign with the AE22 model (see details in section 2.4.6).

Hourly	22.9%
Monthly	6.3%
Annual	6.4%

3.3 SCHEDULED INSTRUMENT SERVICE AND CALIBRATION

3.3.1 Condensation Particle Counter

NPL obtained ISO 17025 accreditation for CPC calibration in 2008. The network CPCs have been serviced and calibrated at NPL on an annual basis since that time.

3.3.2 Scanning Mobility Particle Sizer

Since January 2010, the SMPS instruments have been serviced and calibrated at NPL on an annual basis. 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.

3.3.3 Ambient Ion Monitor

The AIMs were serviced by the ESU, Enviro Technology Services during 2020. NPL continue to make the ion chromatography system calibration standards from traceable stock standard solutions and carry out quarterly calibrations. These activities took place until the instruments were decommissioned at the end of March 2020.

3.3.4 Aerosol Chemical Speciation Monitor

The ACSMs are supported by ERG staff who perform monthly flow checks and *ad hoc* instrument tuning, pinhole cleaning, and inlet cleaning. Repairs are carried out by the ERG operator following Aerodyne advice and procedures. The instruments are to be calibrated bi-annually using laboratory ammonium sulphate and ammonium nitrate standards.

3.3.5 Partisol and Leckel sequential Air Samplers

The Partisol 2025 samplers were serviced by the EA Ambient Air Monitoring (AAM) Team, during 2020. The Leckel SEQ47/50 samplers were serviced by Enviro Technology Services. These 6-monthly service procedures include replacing old or worn parts, temperature and flow calibrations, leak tests and pump refurbishment.

3.3.6 Elemental carbon and Organic carbon analyser

The Sunset Laboratory Inc. thermal/optical carbon analyser is usually serviced annually by a Sunset Laboratory Inc. employed engineer, as per the manufacturer’s guidelines. However, due to the Covid-19 pandemic and ongoing travel restrictions, the engineer was unable to travel to the UK in 2020. The service involves replacing worn parts and a full test and calibration. NPL run a daily calibration check prior to sample analysis using a laboratory blank filter and a filter spiked with a traceable standard solution. An interim temperature calibration was carried out by NPL in December 2020.

3.3.7 Aethalometer

The AE33 Aethalometer instruments were serviced by ACOEM UK Ltd during 2020. These 6-monthly service visits include replacing old or worn parts, cleaning cyclones/optics, flow calibrations, leak tests and tape mechanism check. Service visits are either scheduled or carried out during a callout visit.

4 NETWORK DATA

4.1 PARTICLE NUMBER CONCENTRATIONS

4.1.1 2020 time series

Time series of hourly particle number concentrations (between approximately 7 nm and 3 µm in diameter) measured at network sites during 2020 are shown in Figure 9.

4.1.2 2020 diurnal, weekly, and monthly profiles

The diurnal, weekly and monthly profiles for particle number concentrations in 2020 are shown for the London Honor Oak Park, London Marylebone Road and Chilbolton Observatory sites in Figure 10, Figure 11 and Figure 12 respectively. At all three sites there are higher concentrations during the working week and less at weekends. There is also a clear increase in particle number concentration at Honor Oak Park during the evening. This may be due to domestic wood-burning. The low particle number concentrations recorded at Marylebone Road in April and May could be a result of the Covid-19 lockdown, but it is difficult to draw any firm conclusion on this from the incomplete annual dataset.

4.1.3 Long-term trends

Figure 13 and Figure 14 show 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 in Figure 13 (the London sites) 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)[12].

UK wide legislation[13] enacted in June 2007 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)[14] from 4 December 2007, with all UK road vehicle fuel being “sulphur free” (less than 10 ppm sulphur) by 1 January 2009.

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. 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.

For the London Ultra Low Emission Zone (ULEZ) introduced in April 2019 (and due to expand in Oct 2021) however, the effects on annual particle concentrations for 2020 are currently difficult to determine, predominately due to the potential influence of the Covid-19 lockdown in 2020.

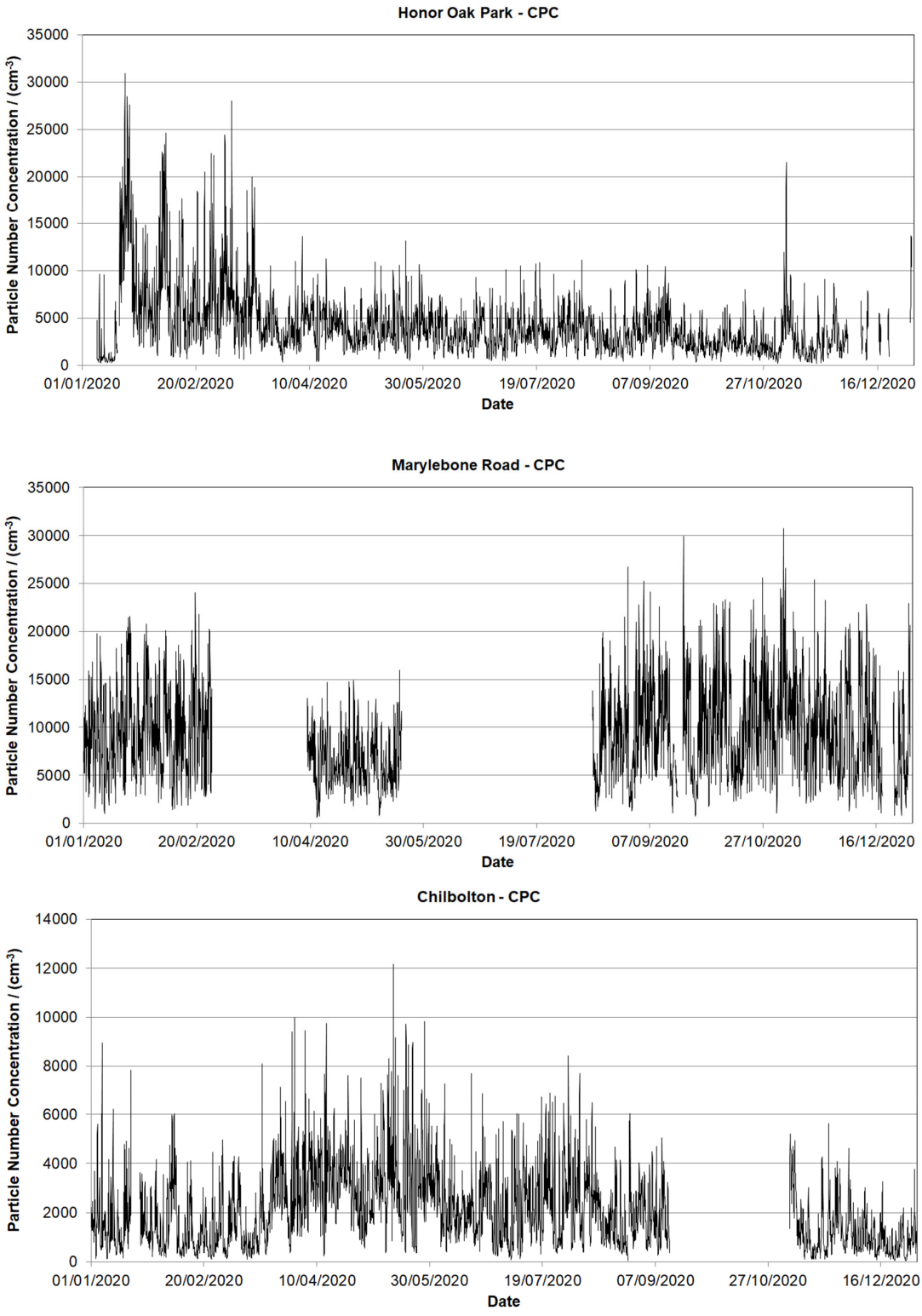


Figure 9 - Hourly particle number concentrations at London Honor Oak Park, London Marylebone Road and Chilbolton Observatory in 2020.

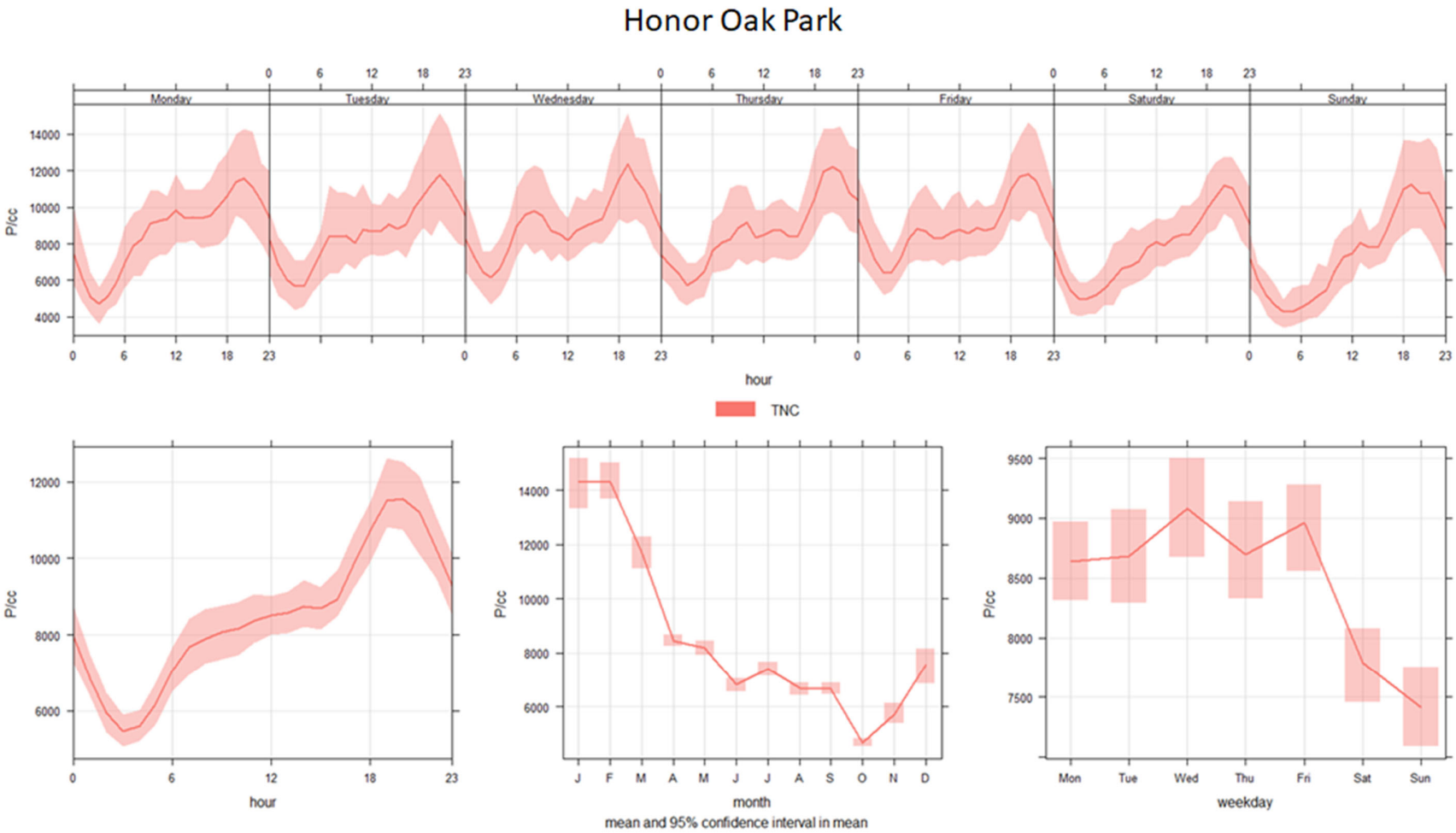


Figure 10 - Temporal variations of Total Number Concentrations (TNC) in 2020 at London Honor Oak Park. These graphs show the mean and 95% confidence interval (cm^{-3}).

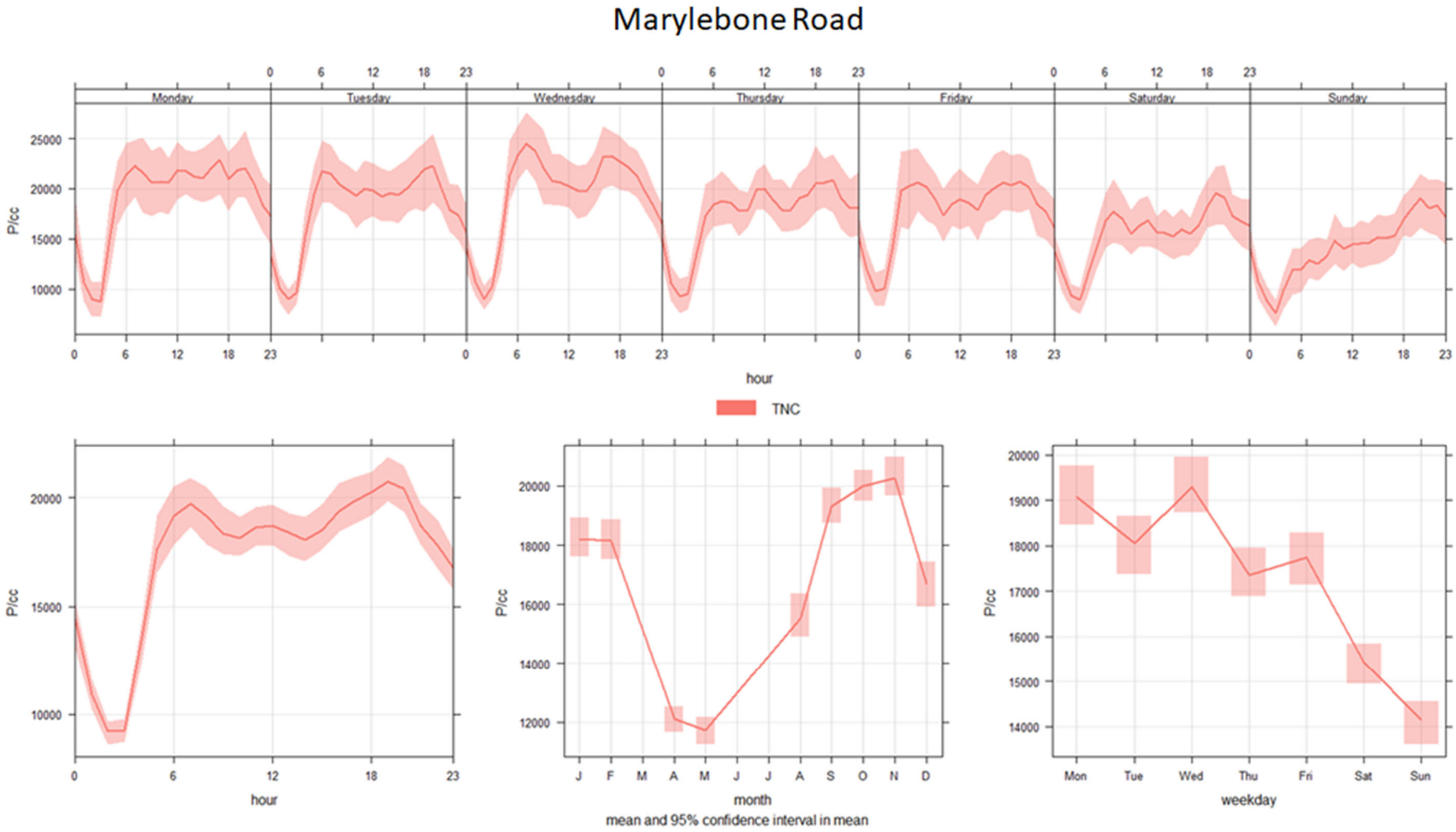


Figure 11 - Temporal variations of total number concentrations (TNC) in 2020 at London Marylebone Road. These graphs show the mean and 95% confidence interval (cm^{-3}).

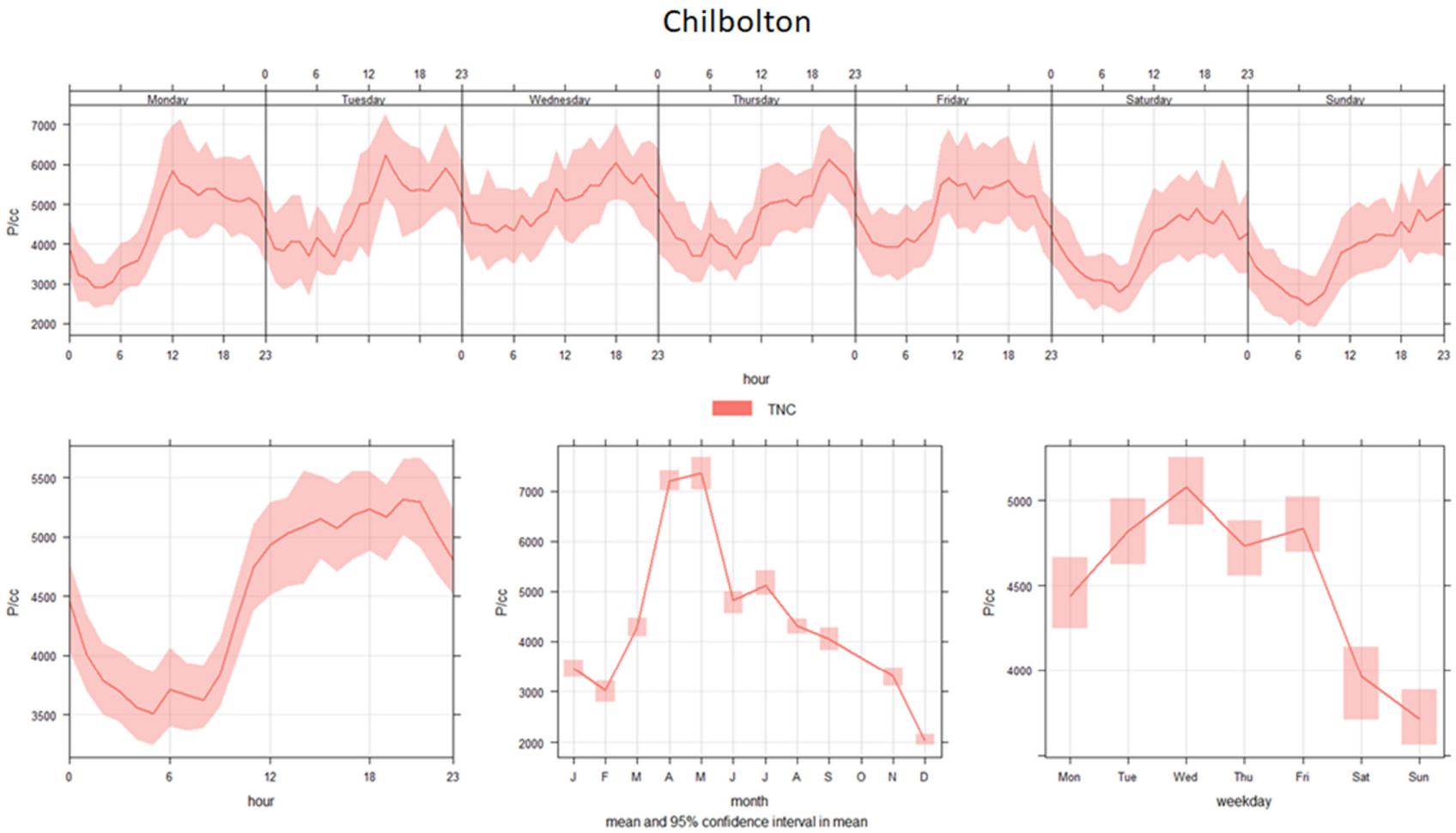


Figure 12 - Temporal variations of total number concentrations (TNC) in 2020 at Chilbolton Observatory. These graphs show the mean and 95% confidence interval (cm^{-3}).

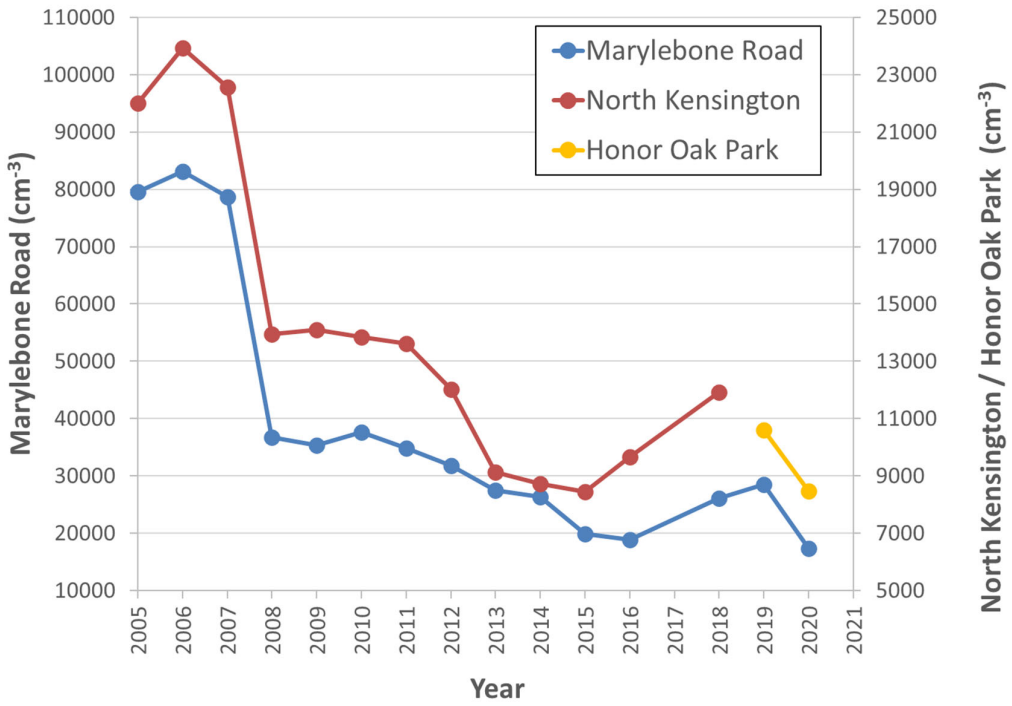


Figure 13 - Historical long-term particle number concentration annual trends at all London sites. The London N. Kensington site moved to London Honor Oak Park in mid-November 2018.

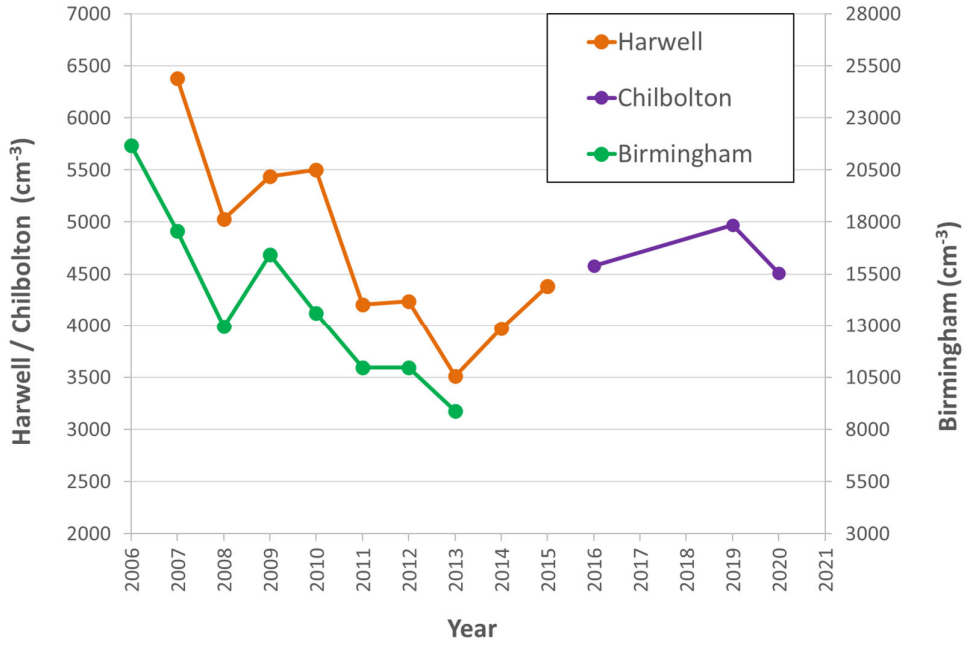


Figure 14 - Historical long-term particle number concentration annual trends at all non-London sites. The Harwell site moved to Chilbolton Observatory in 2016. Insufficient data was available from Chilbolton Observatory for reliable averages in 2017 and 2018.

4.2 PARTICLE SIZE DISTRIBUTIONS

The production of data from SMPS instruments is a complex process. 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 PSL spheres, the number concentration axis, and hence both the scale and shape of the size distribution, is much less amenable to direct evaluation.

4.2.1 2020 time series

Time series of monthly particle size distributions measured at network sites during 2020 are shown in Figure 15. The plots show both the variation in particle number concentration and the shape of the particle size distribution across 2020 at each site.

4.2.2 Long-term trends

Time series of annual particle size distributions measured at network sites from 2010 to 2020 are shown in Figure 16. The plots show both the variation in particle number concentration and particle size distribution.

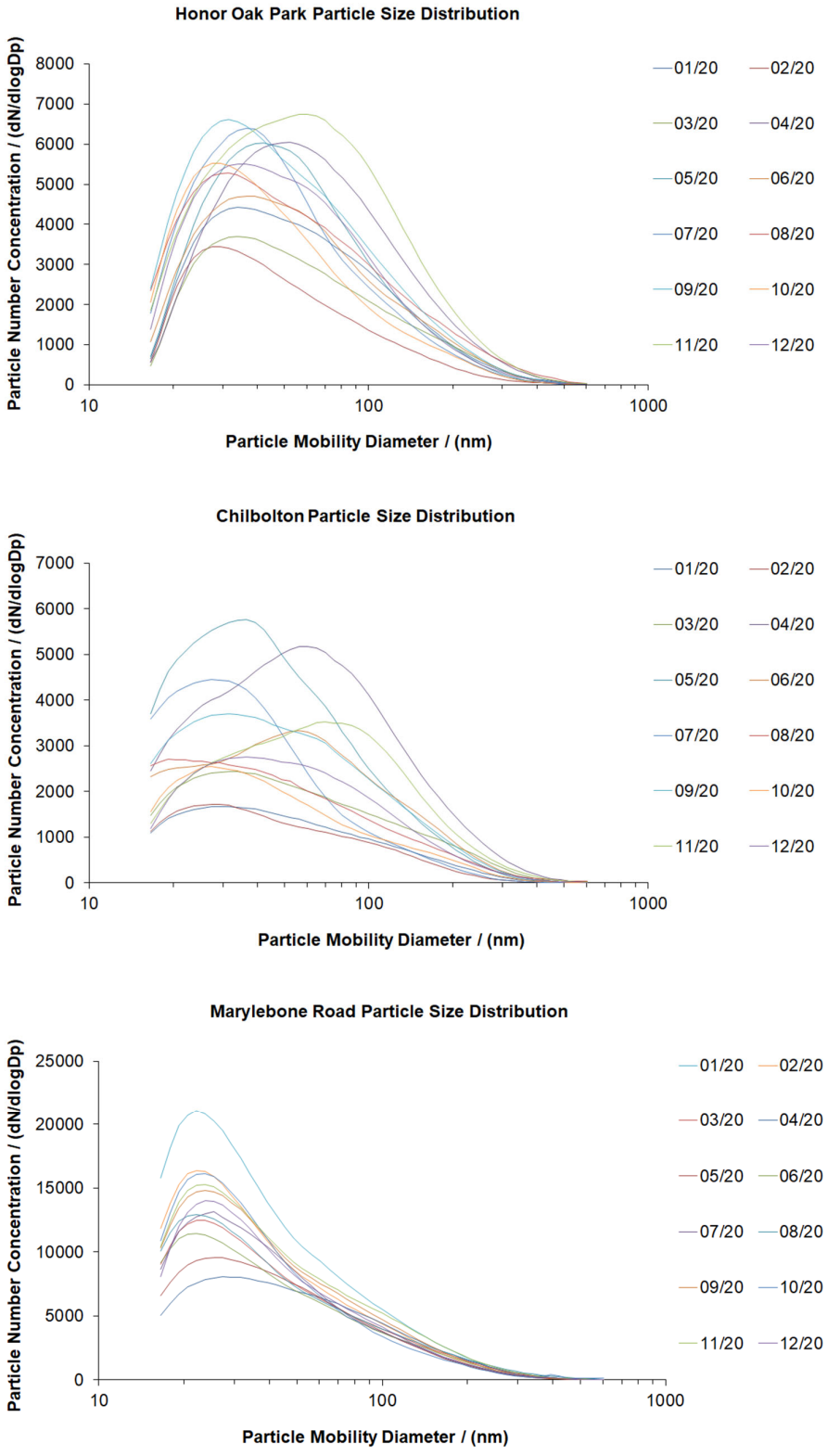


Figure 15 - Monthly averaged particle size distributions at the Network sites for each month during 2020

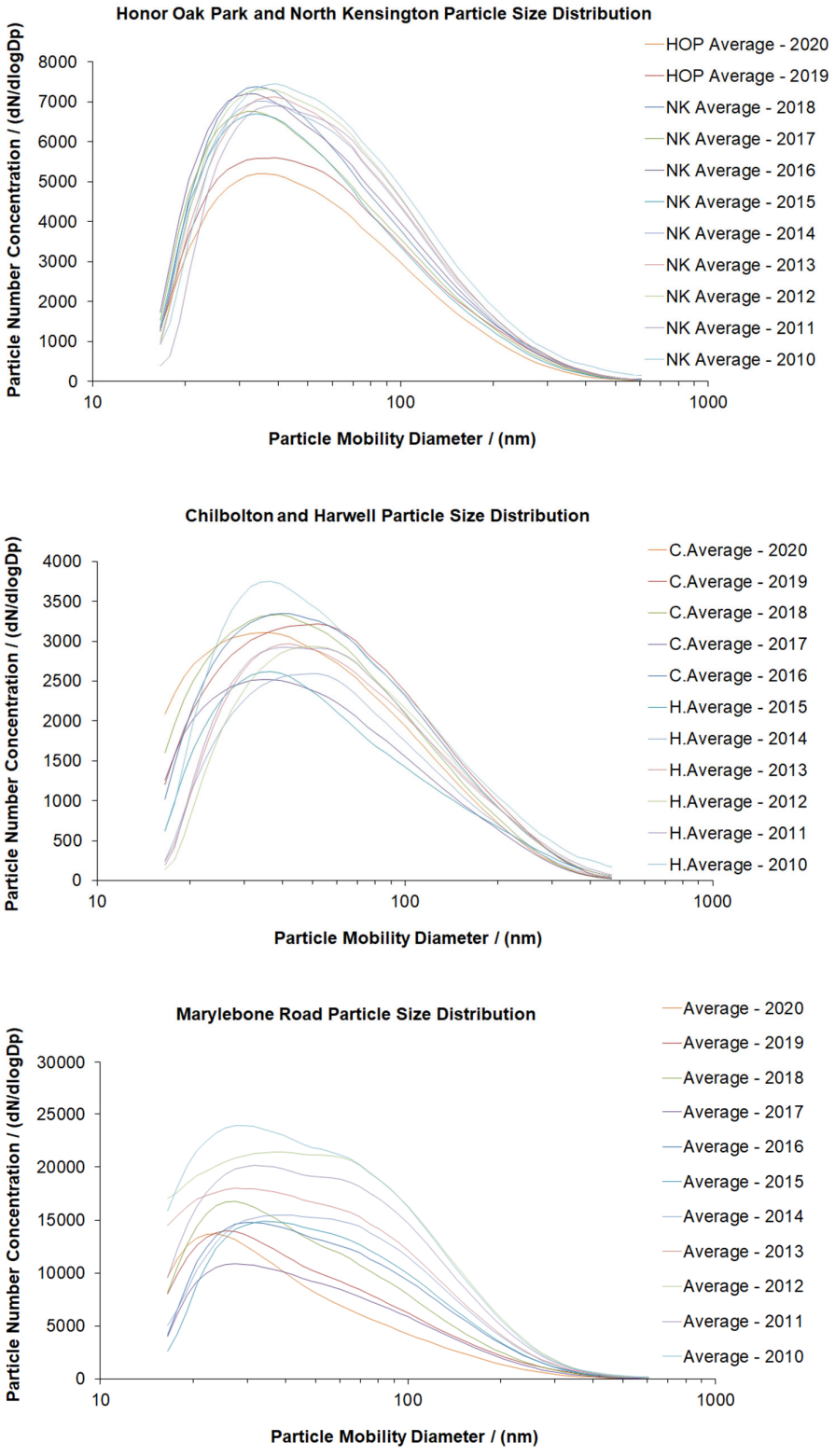


Figure 16 - Comparison of the 2010 to 2020 annual-averaged size distributions

4.3 ANION AND CATION MEASUREMENTS

4.3.1 2020 time series

Figure 17 to Figure 19 show the time series for anions and cations at London Marylebone Road and London Honor Oak Park in 2020.

4.3.2 2020 diurnal, weekly, and monthly profiles

Diurnal, weekly, and monthly profiles have been plotted in Figure 20 to Figure 25 for pollutants where hourly concentrations are available, using the Openair tools[15, 16].

It should be noted that the averages plotted for the diurnal and weekly profiles at both sites are derived from three months of data (January to March), so interpretation is limited and data from these three months are not intended to be representative of the whole year. A recent example of profiles derived using a full year of data can be found in the 2019 Particle Concentration and Numbers Annual Report[17].

At both sites, the correlation between ammonium, nitrate, and sulphate in Figure 20 and Figure 21 indicates the existence of both ammonium sulphate and ammonium nitrate. The lowest concentrations of nitrate and ammonium in the afternoon are attributed to the dissociation of ammonium nitrate at higher temperatures during the day.

Figure 22 and Figure 23 show the profiles for chloride, magnesium, and sodium concentrations at London Honor Oak Park and London Marylebone Road. There is some correlation between chloride and sodium, consistent with them having been derived from the same source, most likely sea salt.

Calcium profiles at both sites in Figure 24 and Figure 25 show values characteristic of traffic contribution, possibly re-suspension of crustal material from road surfaces.

4.3.3 Long-term trends

Prior to 2011, PM_{10} anion concentrations were measured using a manual, filter-based, method. Ratified data were not available in 2010 and 2011. In 2011, the method was changed to automatic instruments – URG AIM and Metrohm MARGA (Monitor of AeRosol and Gases in ambient Air).

In January 2016, the MARGA was moved from Harwell to Chilbolton Observatory. In November 2018, the URG AIM at London North Kensington was moved to London Honor Oak Park and the size selective head was changed from PM_{10} to $PM_{2.5}$. The change to $PM_{2.5}$ at London Marylebone Road occurred in January 2019. In March 2020 the AIMs at Marylebone Road and Honor Oak Park were stopped.

Figure 26 shows long-term trends of the annual averages for the anion species. Note that the data from the MARGA at Harwell/Chilbolton was provided by the MARGA network[1]. It should be noted that the 2020 annual average for Marylebone Road and Honor Oak Park is calculated using three months of data, January to March.

After the change to automatic instruments in 2011, and the move from Harwell to Chilbolton in 2016, some discontinuity can be observed. Overall, chloride has been at a steady level apart from a spike in 2008, nitrate has shown a slight downward trend; and sulphate has shown a distinct downward trend but has levelled off over the last four years.

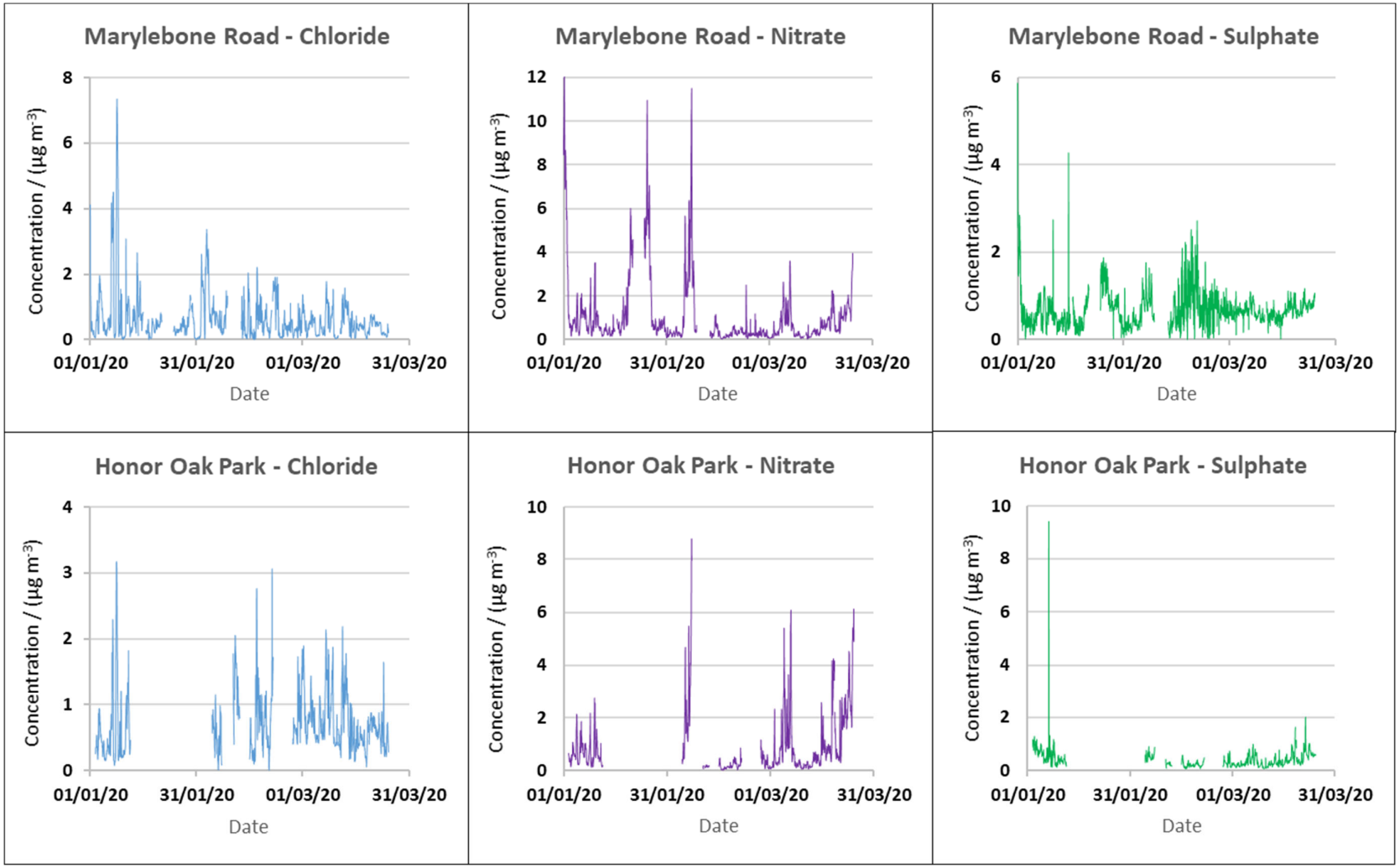


Figure 17 - Time series for Anion (Chloride, Nitrate and Sulphate) ion concentrations in $PM_{2.5}$ at London Marylebone Road and London Honor Oak Park in 2020 (removed 25 March)

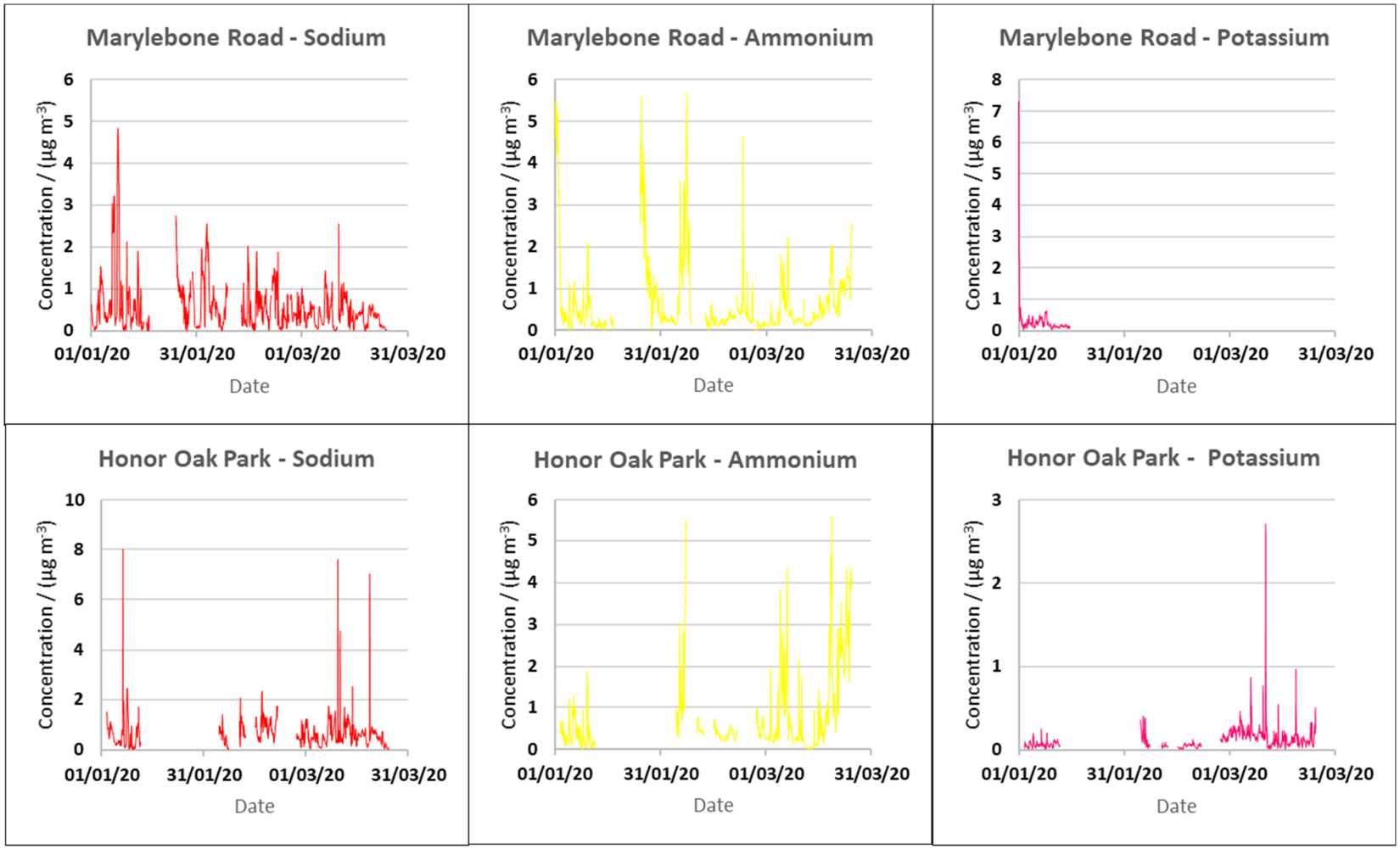


Figure 18 - Time series for Cation (Sodium, Ammonium and Potassium) ion concentrations in $PM_{2.5}$ at London Marylebone Road and London Honor Oak Park in 2020 (removed 25 March)

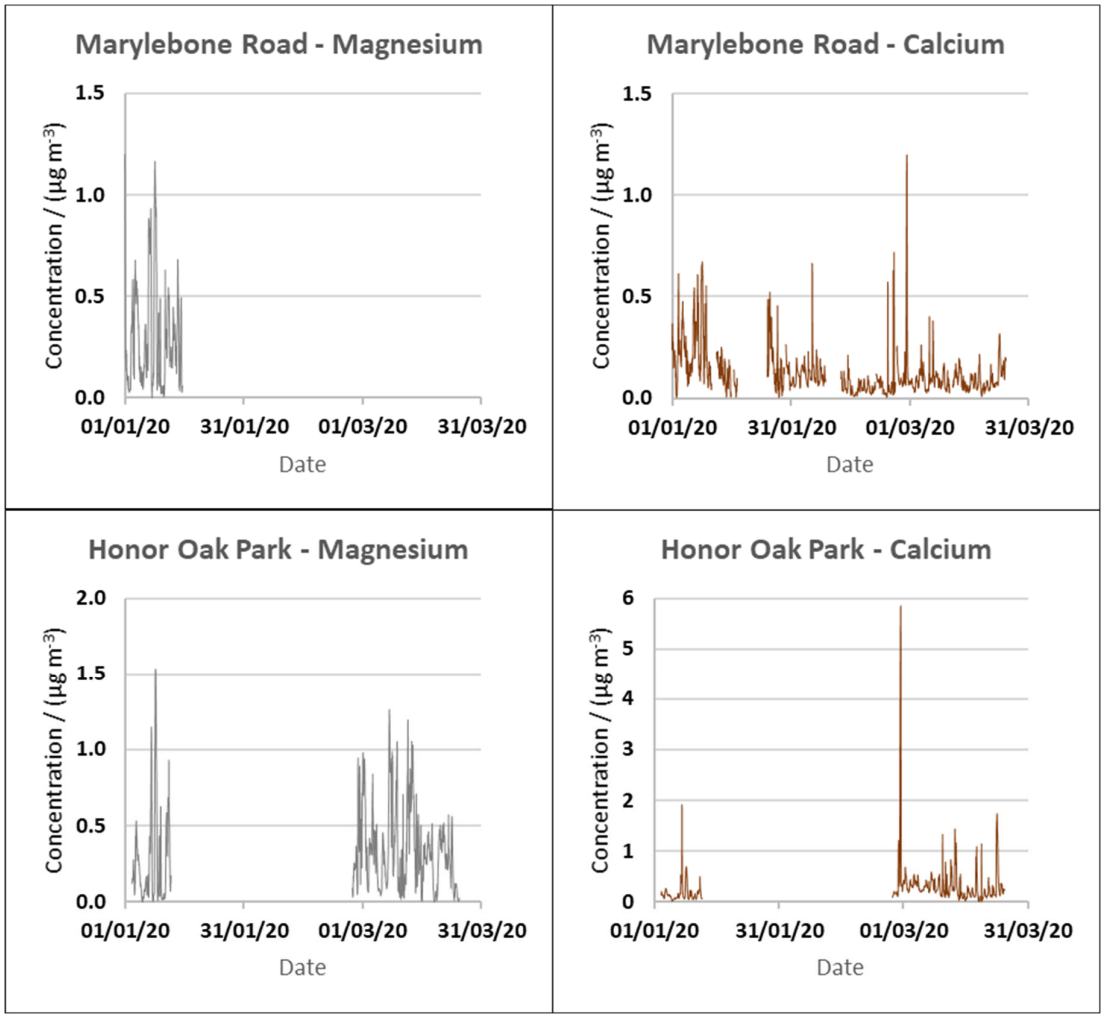


Figure 19 - Time series for Cation (Magnesium and Calcium) ion concentrations in $PM_{2.5}$ at London Marylebone Road and London Honor Oak Park in 2020 (removed 25 March)

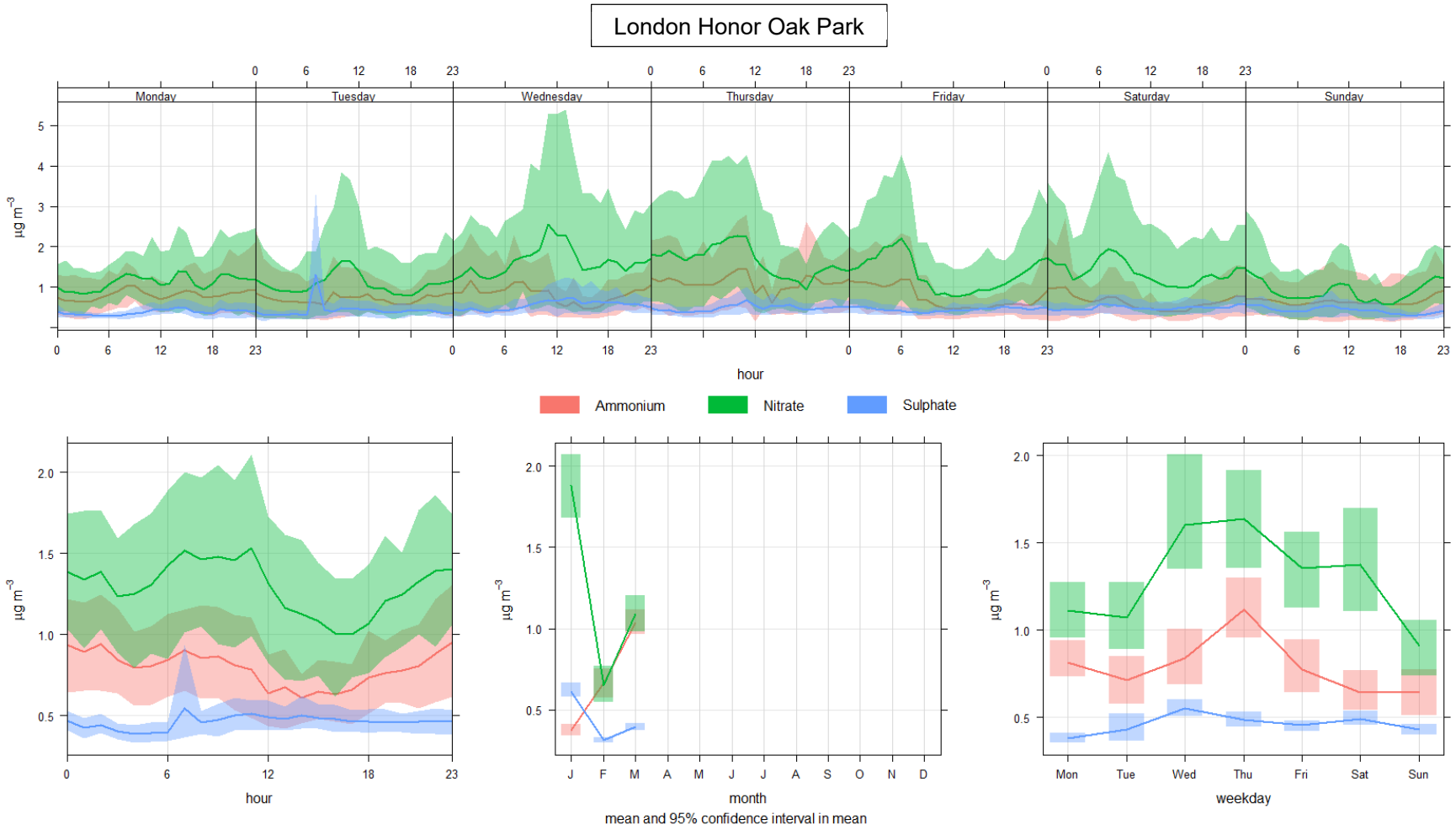


Figure 20 - Diurnal, weekly and monthly profiles for Ammonium, Nitrate, and Sulphate during 2020 at London Honor Oak Park. These graphs show the mean and 95% confidence interval (µg m^{-3}).

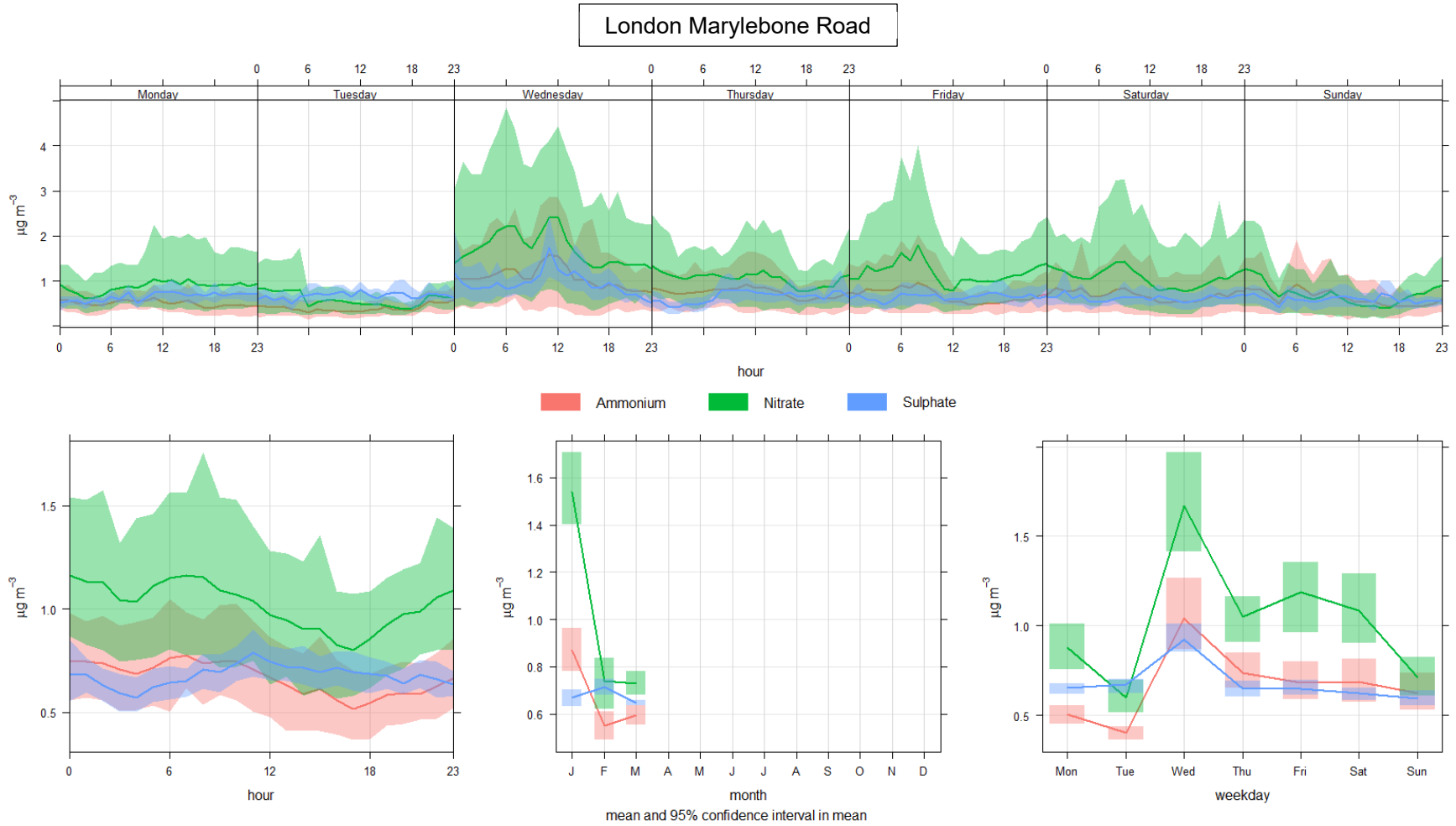


Figure 21 - Diurnal, weekly and monthly profiles for and Ammonium, Nitrate, and Sulphate during 2020 at London Marylebone Road. These graphs show the mean and 95% confidence interval (µg m^{-3}).

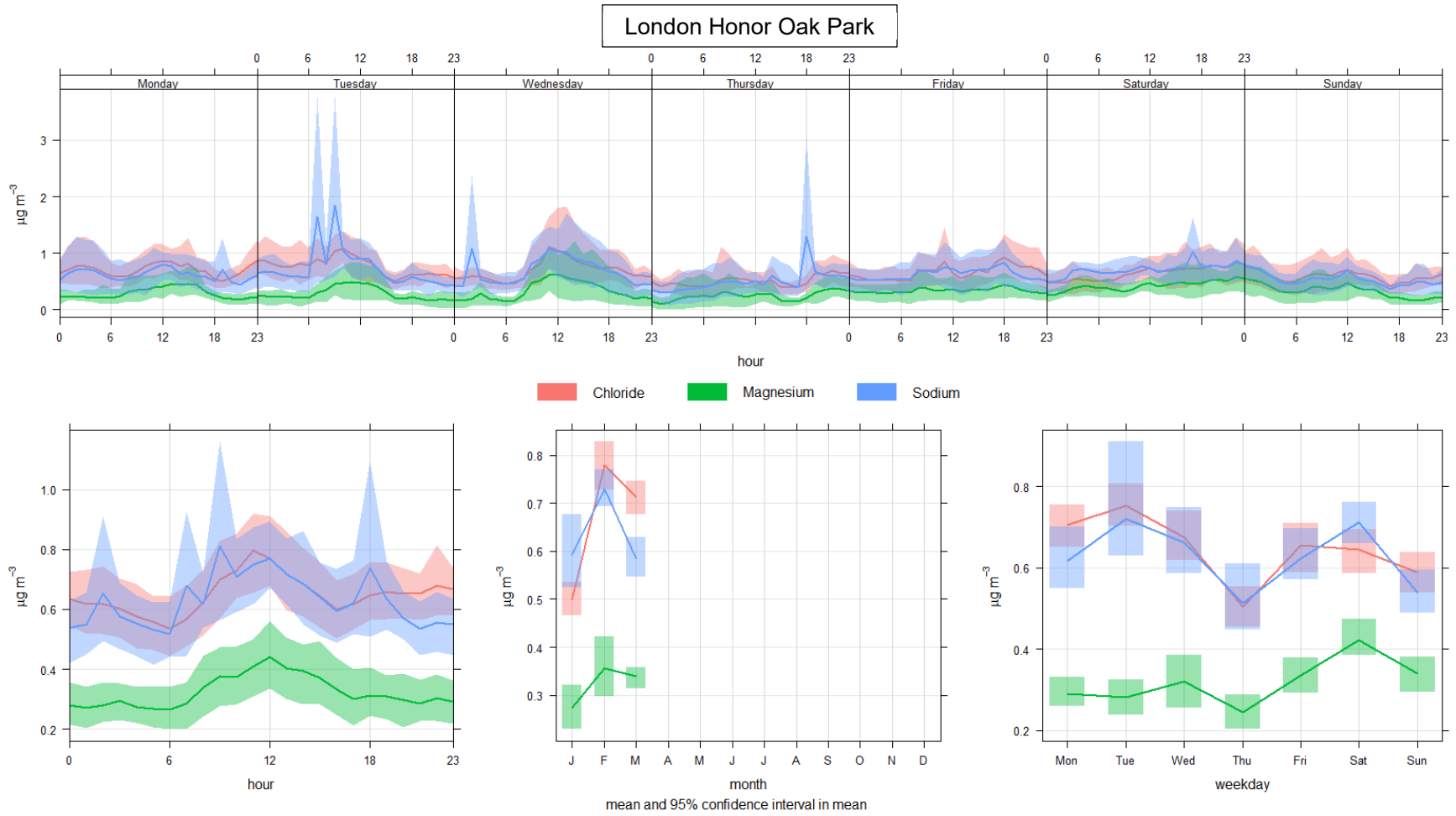


Figure 22 - Diurnal, weekly and monthly profiles for Chloride, Magnesium, and Sodium concentrations during 2020 at London Honor Oak Park

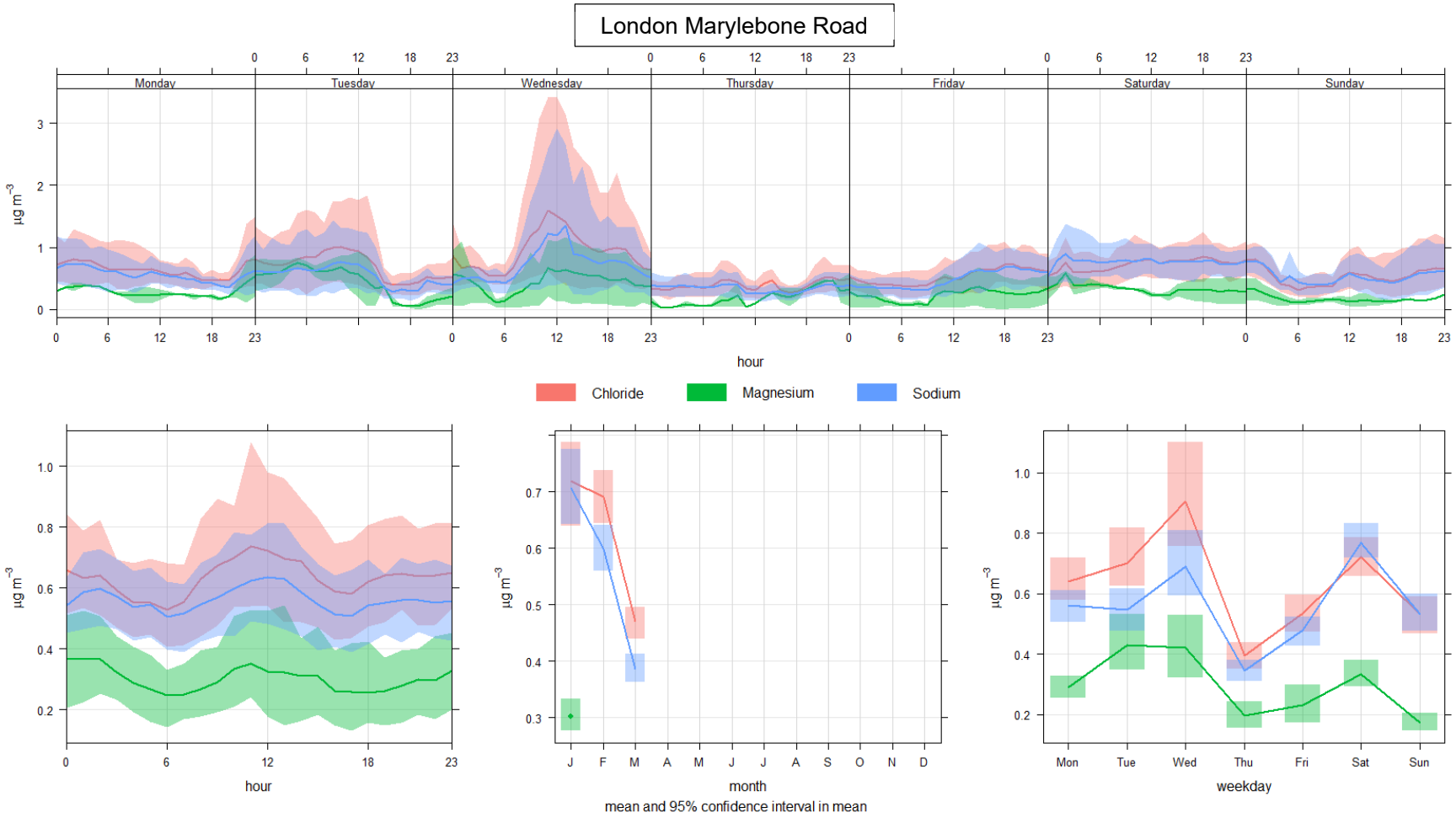


Figure 23 - Diurnal, weekly and monthly profiles for Chloride, Magnesium, and Sodium concentrations during 2020 at London Marylebone Road. These graphs show the mean and 95% confidence interval (µg m^{-3}).

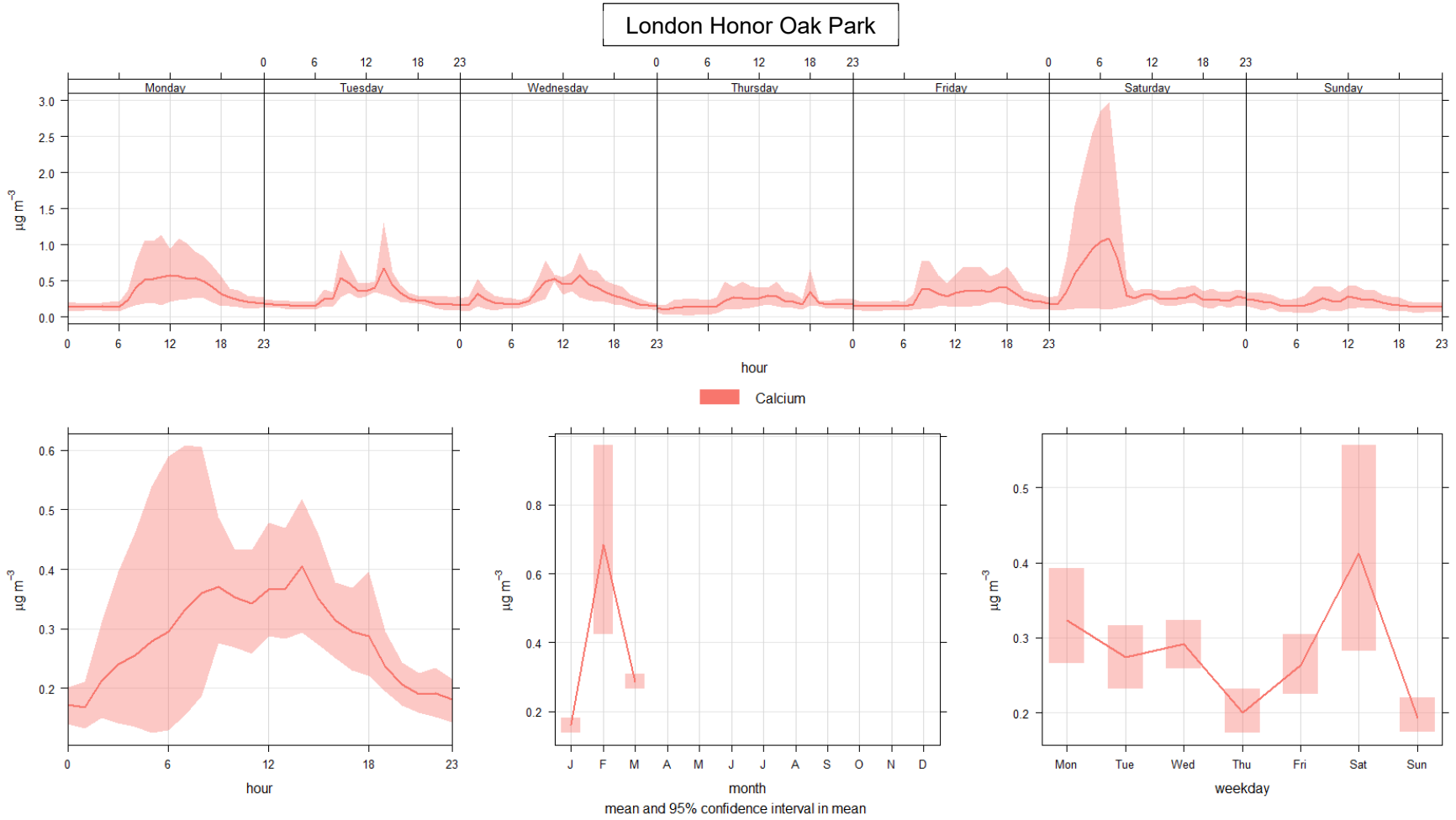


Figure 24 - Diurnal, weekly and monthly profiles for Calcium during 2020 at London Honor Oak Park. These graphs show the mean and 95% confidence interval (µg m^{-3}).

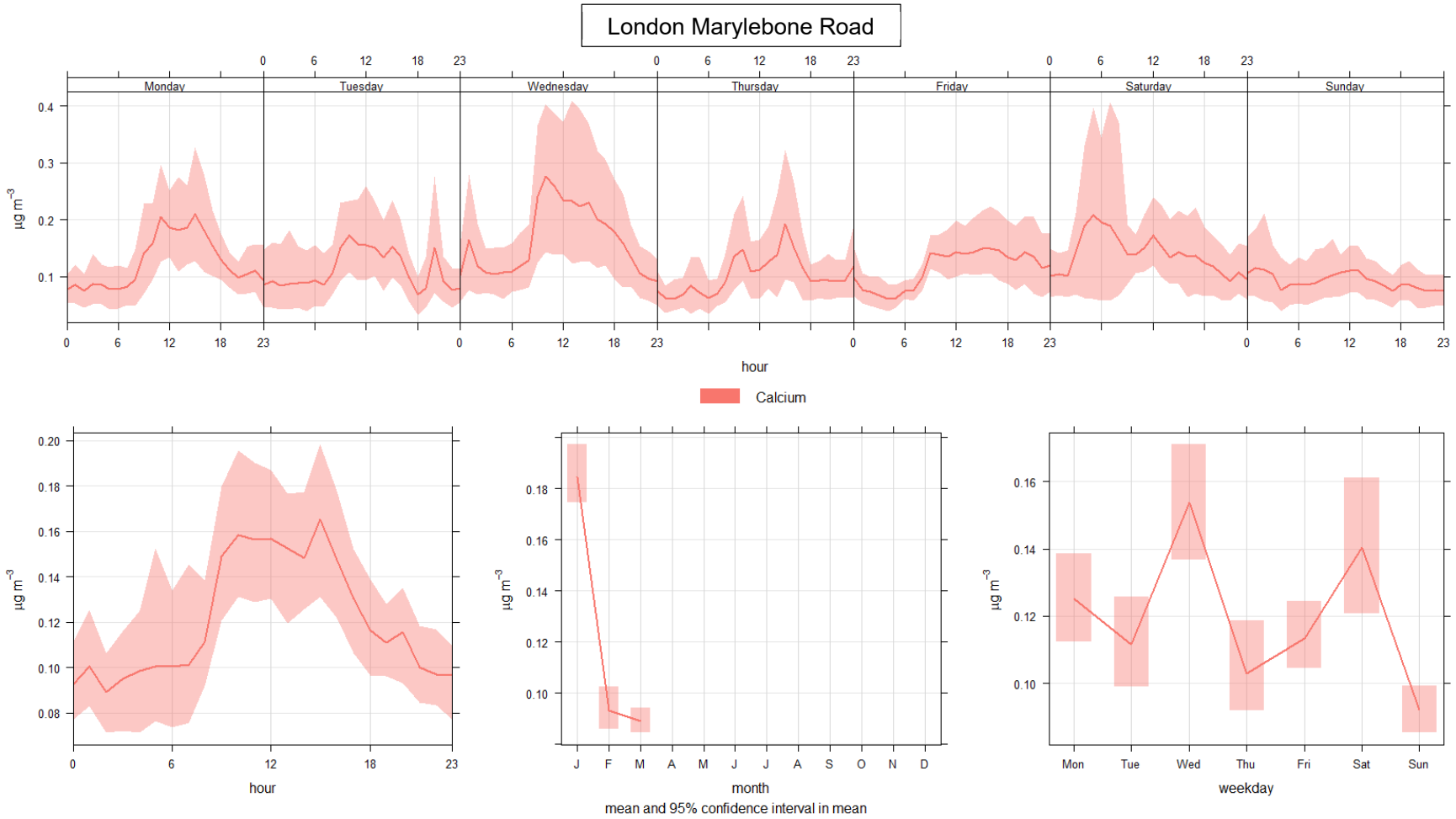


Figure 25 - Diurnal, weekly and monthly profiles for Calcium during 2019 at Marylebone Road. These graphs show the mean and 95% confidence interval (µg m^{-3}).

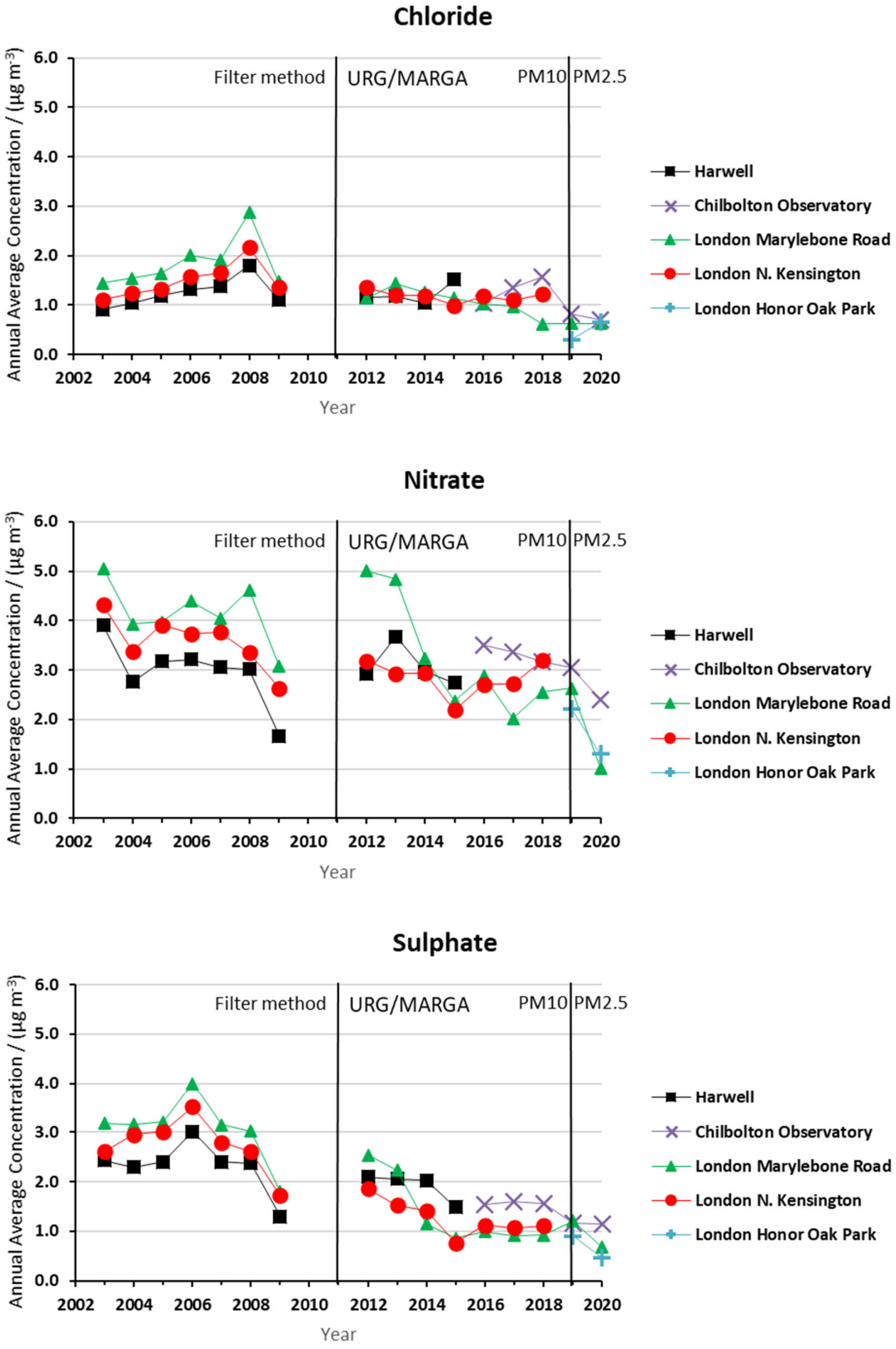


Figure 26 - Anion long-term annual trends (chloride, nitrate, and sulphate)

4.3.4 Comparison between AIM, ACSM and XRF

As the URG AIMs ($PM_{2.5}$) at London Marylebone Road and London Honor Oak Park had reached their life expectancy, in 2020 the decision was taken to replace these instruments with a combination of two separate instruments at each site – Aerosol Chemical Speciation Monitor (ACSM) and X-Ray Fluorescence spectrometer (XRF).

At the time the decision was taken, there was already an ARI ACSM ($PM_{2.5}$) included on the Particle Concentration and Numbers network at London Honor Oak Park, and an ACSM owned by ICL at London Marylebone Road. There were also ICL-owned XRFs at both sites (funding for the XRFs and support for this work was provided by the Natural Environment Research Council [grant number NE/T001909/2]). The EA purchased and ERG installed an ARI ACSM (PM_1) at Marylebone Road in July 2020. The ICL ACSM was removed from Marylebone Road in May 2021. In the future, as the ICL XRFs will be removed from the sites, the EA plan to replace them.

AIM analysis was halted on 25 March 2020 due to LSO and equipment safety concerns during the Covid-19 lockdown. In August 2020, when travel restrictions were eased, AIM analysis was resumed for one month at Honor Oak Park to provide $PM_{2.5}$ comparison data for the co-located AIM, ACSM and XRF.

AIM and ACSM instrument details are given in section 2.4. The ICL XRF at Honor Oak Park is a Cooper Environmental Services XACT 625i which alternates between $PM_{2.5}$ and PM_{10} every hour using a bespoke switching inlet valve, which was installed on 28 July 2020 (prior to this it was measuring just PM_{10}).

Overall, there are good to excellent linear relationships for all elements (R^2 = 0.81 to 0.93). The slopes of the linear regressions between equivalent elements and compounds are generally good (ranging from 0.76 to 1.44). The exception is calcium, which had a slope of 0.25, most likely due to interferences at the low ambient concentrations measured. These differences in magnitude are the result of different approaches to sample collection, analysis and calibration and are summarised in Table 8 and discussed in more detail in relation to each comparison in the following sections. This short study provides the evidence needed to confidently interpret the data across the instrument changes.

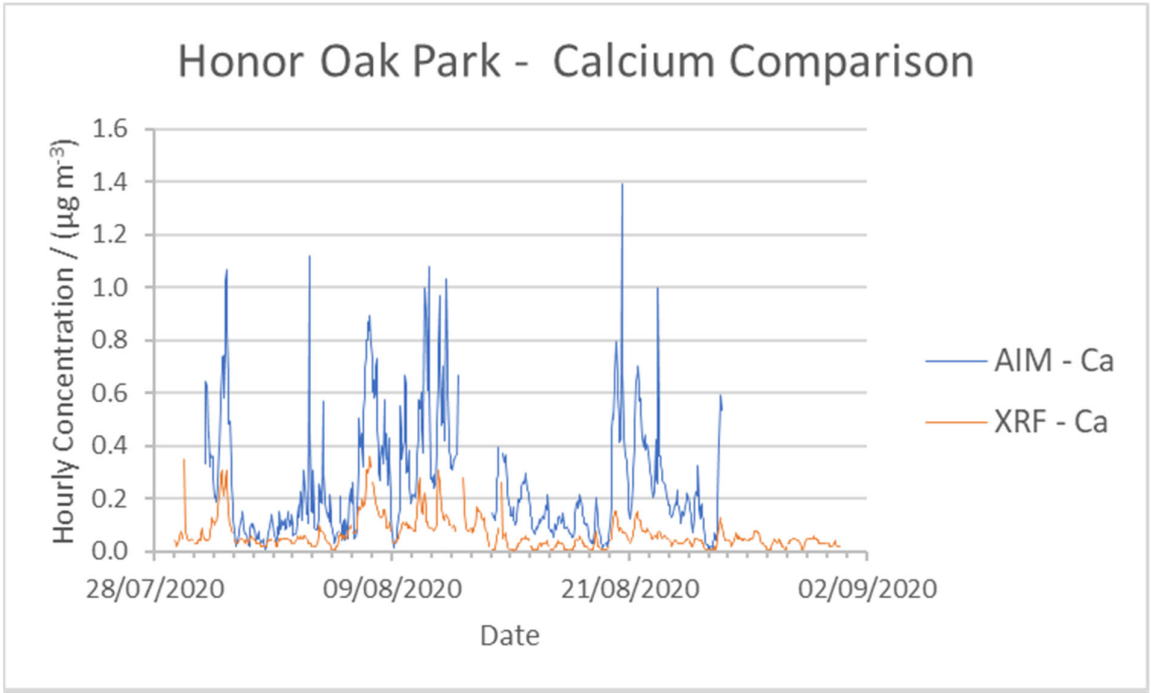
Figure 27 to Figure 32 show the hourly measured mass concentrations between 29 July and 31 August 2020 for analytes from each instrument, and the corresponding correlation plots.

Table 8 - Key differences between AIM, ARI ACSM and XACT XRF

	Size Selection	Collection	Analysis	Calibration
AIM	$PM_{2.5}$ cyclone	Particles into liquid following removal of interfering gases - potential for incomplete gaseous removal and only soluble components will be dissolved and analysed.	Ion Chromatography	IC calibrated using solutions at varying concentrations
ACSM	$PM_{2.5}$ aerodynamic lens. This does not provide as sharp a cut off as aerodynamic cyclone	Impaction onto vaporiser at 650°C - refractory aerosols (e.g. minerals, metals, soot) will not vaporise leading to bias for these sources	Mass spectrometer	Ammonium nitrate and ammonium sulphate aerosols at varying concentrations
XRF	$PM_{2.5}$ cyclone	Teflon tape. Sampling every other hour, interpolated to provide hourly measurements, resulting in increased uncertainty for hours not measured.	Energy Dispersive (ED) XRF	Thin film deposits

4.3.4.1 Calcium

Overall, there is good agreement between the AIM and XRF calcium concentrations. The differences that can be observed on the concentration plot and the scatter on the correlation plot (Figure 27) are accentuated because of the low concentrations of calcium compared to the other analytes. Mostly likely, any difference is caused by the incomplete solubility by the AIM; the interpolated XRF concentrations on alternate hours; and the slight difference in calibration materials between the two systems.



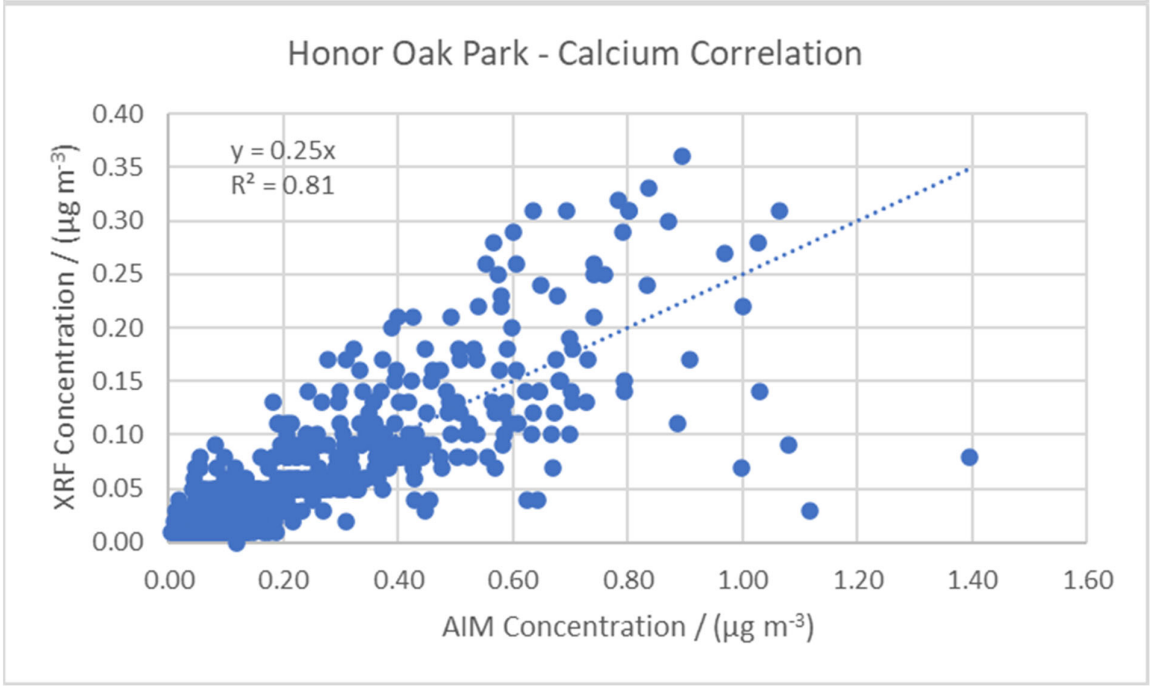


Figure 27 - Hourly concentration and correlation plots for calcium from the AIM and XRF

4.3.4.2 Chloride

Overall, there is very good agreement between the AIM and XRF chloride concentrations (Figure 28); R^2 0.89, slope 1.44. Mostly likely any difference is caused by incomplete solubility measured by the AIM; the interpolated XRF concentrations on alternate hours; and the slight difference calibration materials between the two systems.

There are several hours where the XRF reports zero values where the AIM reports positive values, which is causing a secondary trendline along the x-axis. This is likely due to an elevated baseline in the AIM instrument.

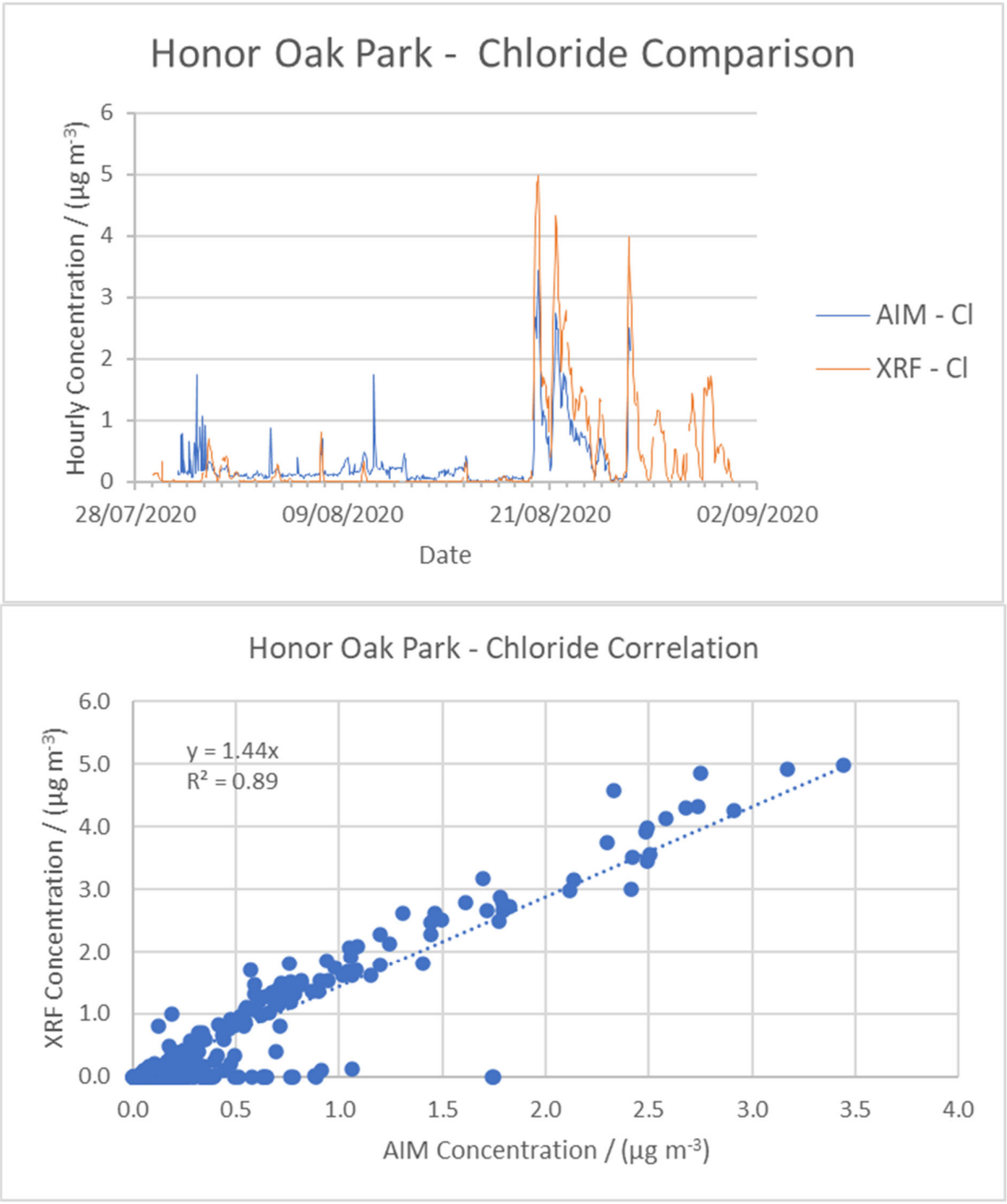


Figure 28 - Hourly concentration and correlation plots for chloride from the AIM and XRF

4.3.4.3 Ammonium

Overall, there is exceptional agreement between the AIM and ACSM ammonium concentrations (Figure 29). Mostly likely any difference is caused by the incomplete removal of interfering gases and incomplete solubility by the AIM; the differences in size selection approach (aerodynamic inlet vs. lens); and the slight differences calibration materials and approach between the two systems.

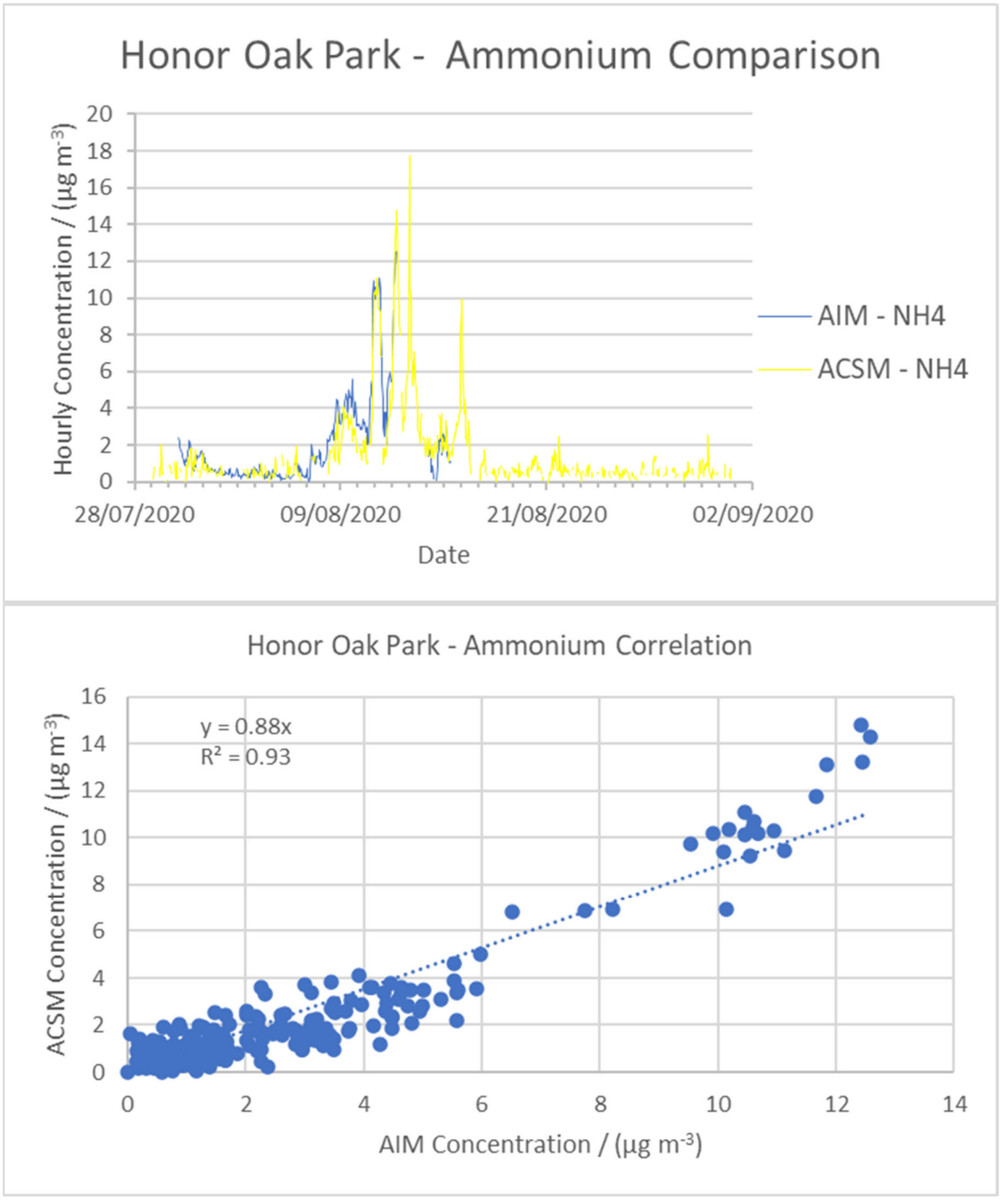


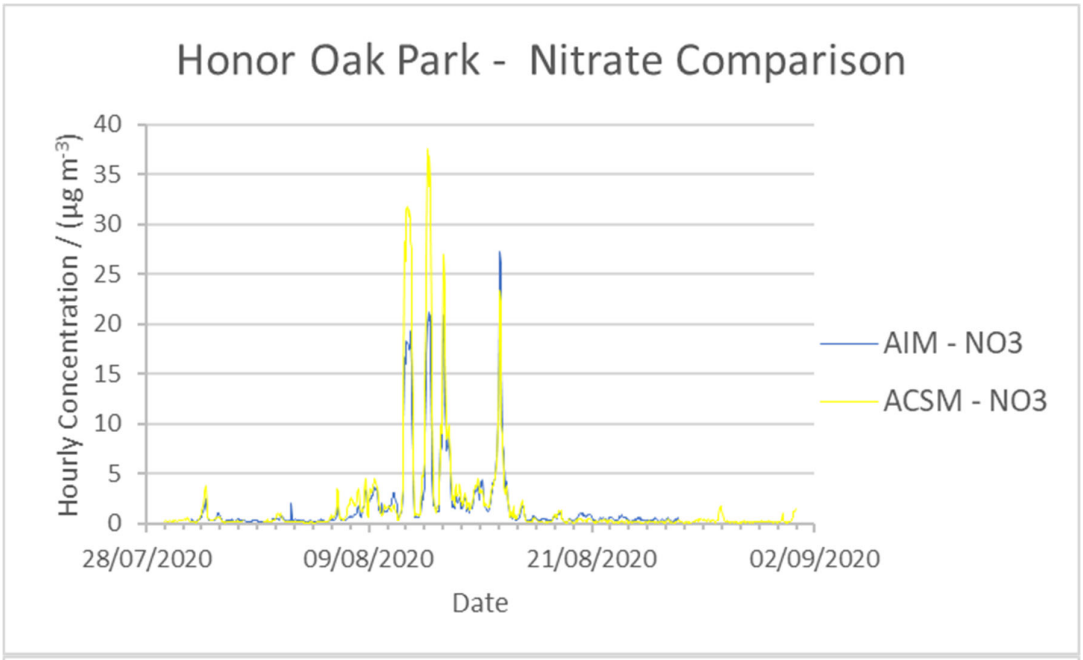
Figure 29 - Hourly concentration and correlation plots for Ammonium from the AIM and ACSM

4.3.4.4 Nitrate

Overall, there is exceptional agreement between the AIM and ACSM nitrate concentrations (Figure 30), apart from the 4 elevated periods.

The four points on the scatter plot which veer away from the general trend are on 16/08/20 (00:00 – 04:00), the only elevated peak where the AIM concentration is higher than ACSM.

Mostly likely the differences seen are caused by the incomplete removal of interfering gases and solubility by the AIM; the differences in size selection approach (aerodynamic inlet vs. lens); and the slight difference calibration materials between the two systems.



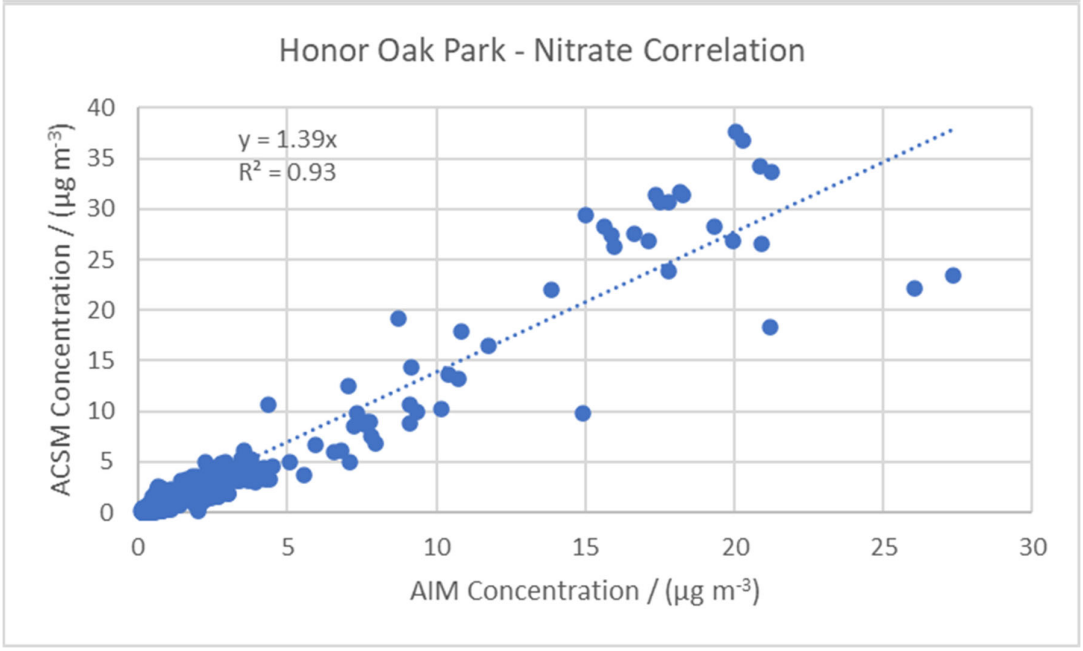


Figure 30 - Hourly concentration and correlation plots for Nitrate from the AIM and ACSM

4.3.4.5 Sulphate / Sulphur

Overall, there is good agreement between the AIM and ACSM sulphate, and XRF sulphur concentrations (Figure 31). Mostly likely any difference is caused by the incomplete removal of interfering gases by the AIM; the differences in size selection approach (aerodynamic inlet vs. lens); and the slight difference in calibration materials between the two systems.

There is good correlation between sulphate and sulphur in both cases (Figure 32), but as expected there is an offset of the concentrations as sulphur (S) is only one component of the sulphate ion (SO_4^{2-}). These slopes of approximately 0.3 in these comparisons are consistent with S making up 33% of sulphate by mass. The AIM baseline is elevated above the ACSM and XRF baselines as is visible in both scatter plots. The choice of baseline is driven by short periods towards the end of the colocation were the AIM baseline drops to agree with the XRF and ACSM.

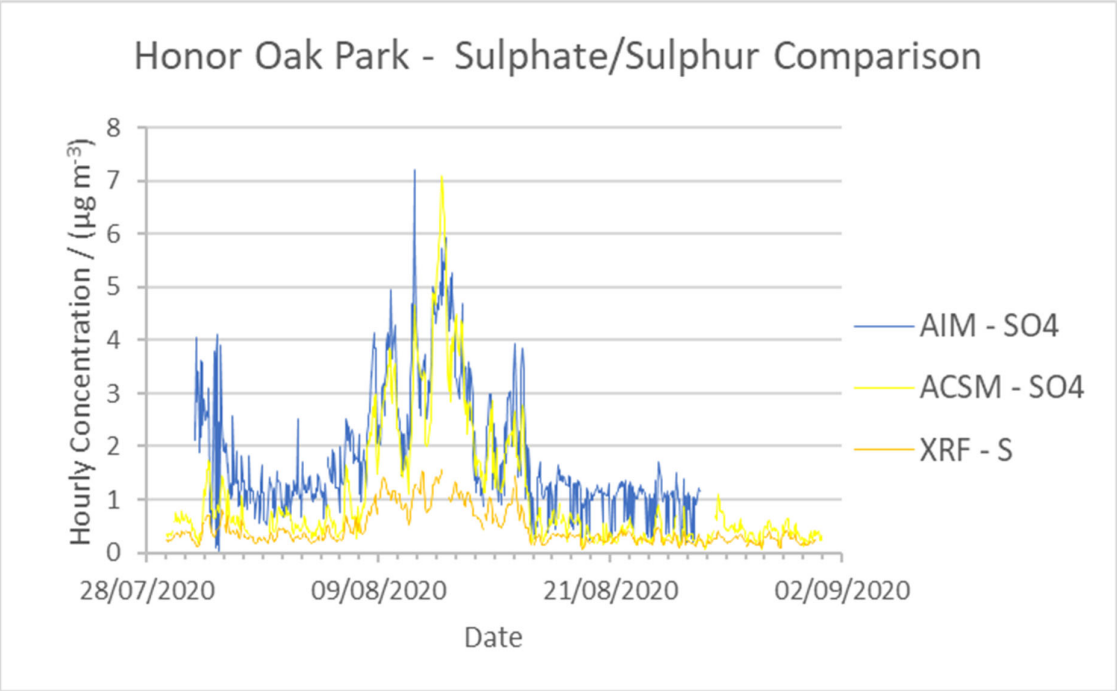


Figure 31 - Hourly concentration plots for Sulphate from the AIM and ACSM, and Sulphur from the XRF

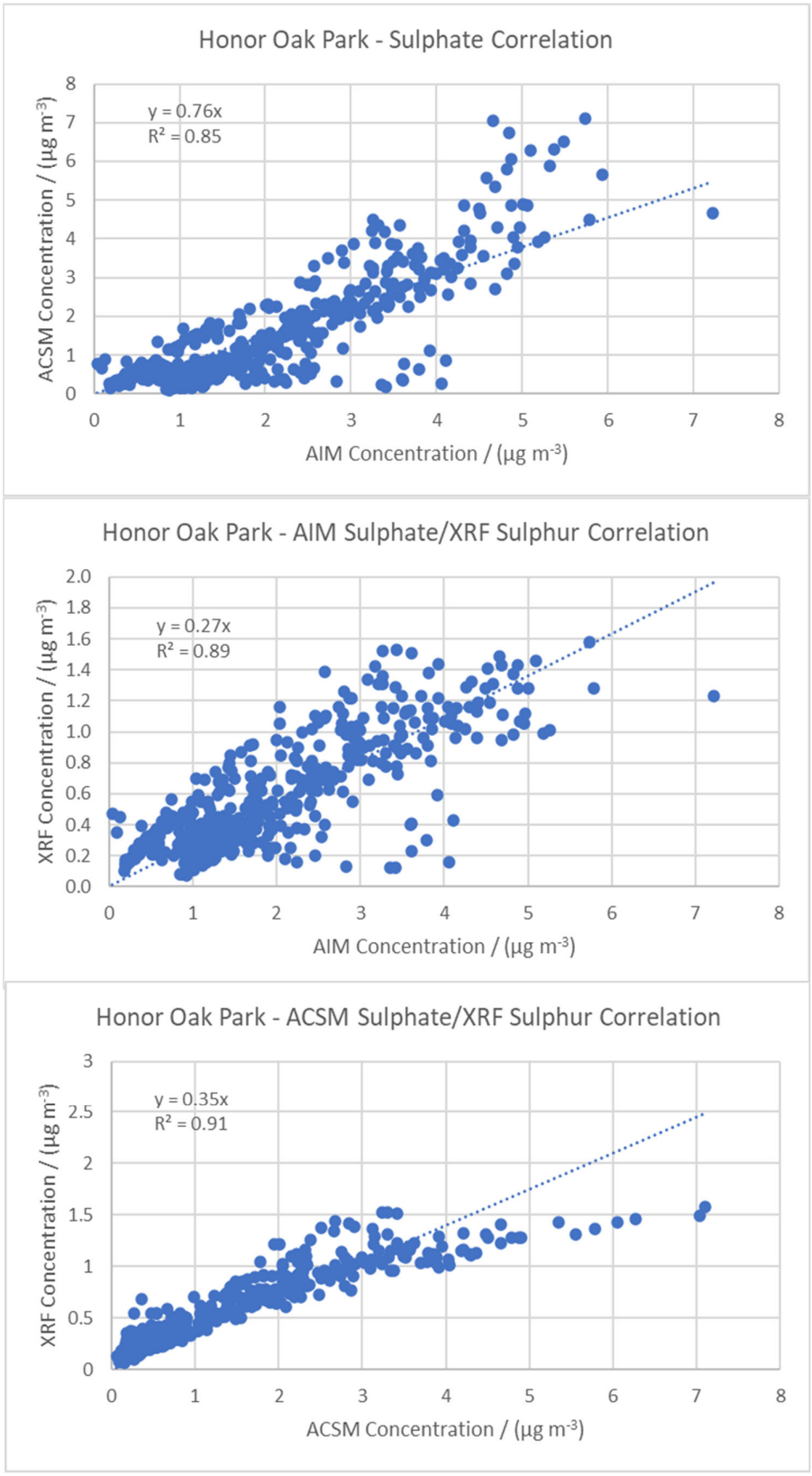


Figure 32 - Correlation plots for Sulphate from the AIM and ACSM, and Sulphur from the XRF

4.4 AEROSOL MASS AND CHEMICAL COMPOSITION

4.4.1 2020 time series

An ACSM instrument was installed at London North Kensington in 2013 with a PM_1 size-selective head. It was moved to London Honor Oak Park and has operated there since November 2018. Since November 2018, the instrument has measured the hourly concentrations of organics, nitrate, sulphate, and ammonia in the $PM_{2.5}$ size fraction. Figure 33 shows the time series for these components at Honor Oak Park during 2020.

The new ACSM instrument with a PM_1 size-selective head was installed at London Marylebone Road in mid-July 2020. After some initial teething problems, as described in section 2.3.4, there was only approximately three months of data, so this has not been included in this report.

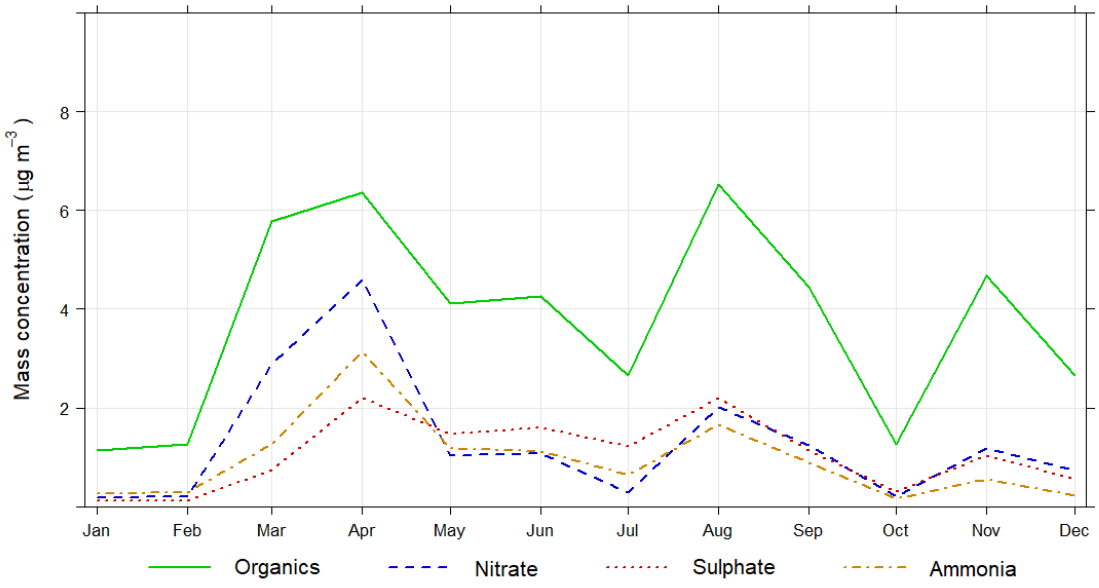


Figure 33 - Monthly average mass concentrations for 2020 ACSM data at London Honor Oak Park

4.4.2 Long-term trends

Figure 34 and Figure 35 show the long-term annual trends (using monthly averages) of the four components measured using the ACSM instrument at London North Kensington / London Honor Oak Park. Not enough data has yet been collected using these instruments to discern any meaningful seasonal or annual trends.

Figure 34 - Long-term mass concentration trends of organics and sulphate at the Urban Background site London Honor Oak Park (London North Kensington before 2019)

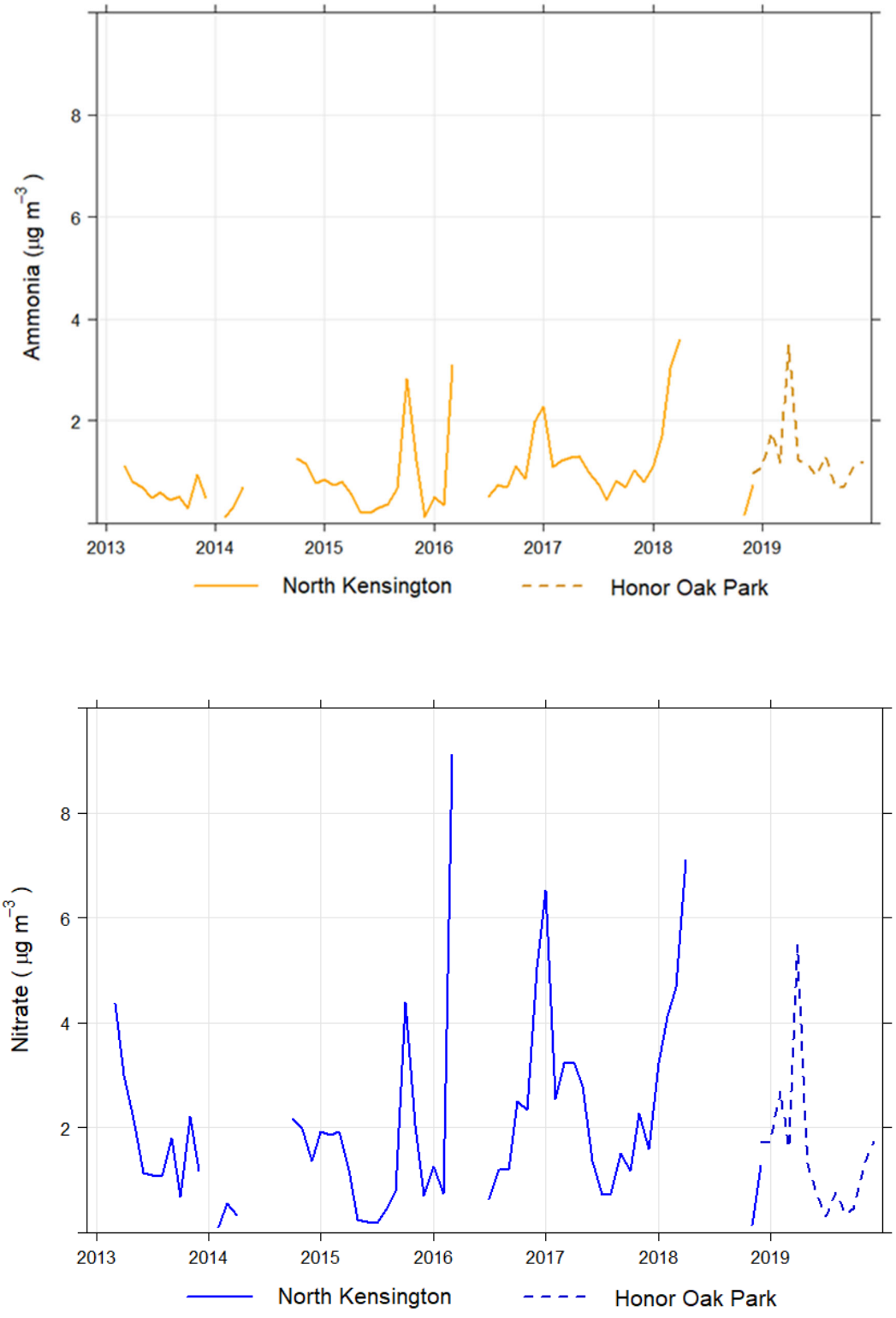


Figure 35 - Long-term mass concentration trends of ammonia and nitrate at the Urban Background site London Honor Oak Park (London North Kensington before 2019)

4.5 ORGANIC CARBON AND ELEMENTAL CARBON

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.

$PM_{2.5}$ sampling at Chilbolton Observatory and Auchencorth Moss is done to comply with a statutory requirement under the European Air Quality Directive[2], 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 since 4 February 2016. The sampler at Auchencorth Moss has been operational since 17 November 2011.

4.5.1 2020 time series

The time series of OC, EC and TC (Total Carbon – the sum of OC and EC) are displayed in Figure 36, Figure 37, Figure 38 and Figure 39 for all the sites.

4.5.2 Long-term trends

Figure 40 and Figure 41 show the time series for the weekly measurements since the installation of the Leckel samplers. The data from Chilbolton Observatory (February 2016 - June 2020) is plotted continuously with the data from the former Harwell site.

Figure 42 shows the long-term trends in annual average mass concentrations for OC, EC, and TC measurements for the daily sampling of the Partisols at the two London sites (London Marylebone Road and London Honor Oak Park).

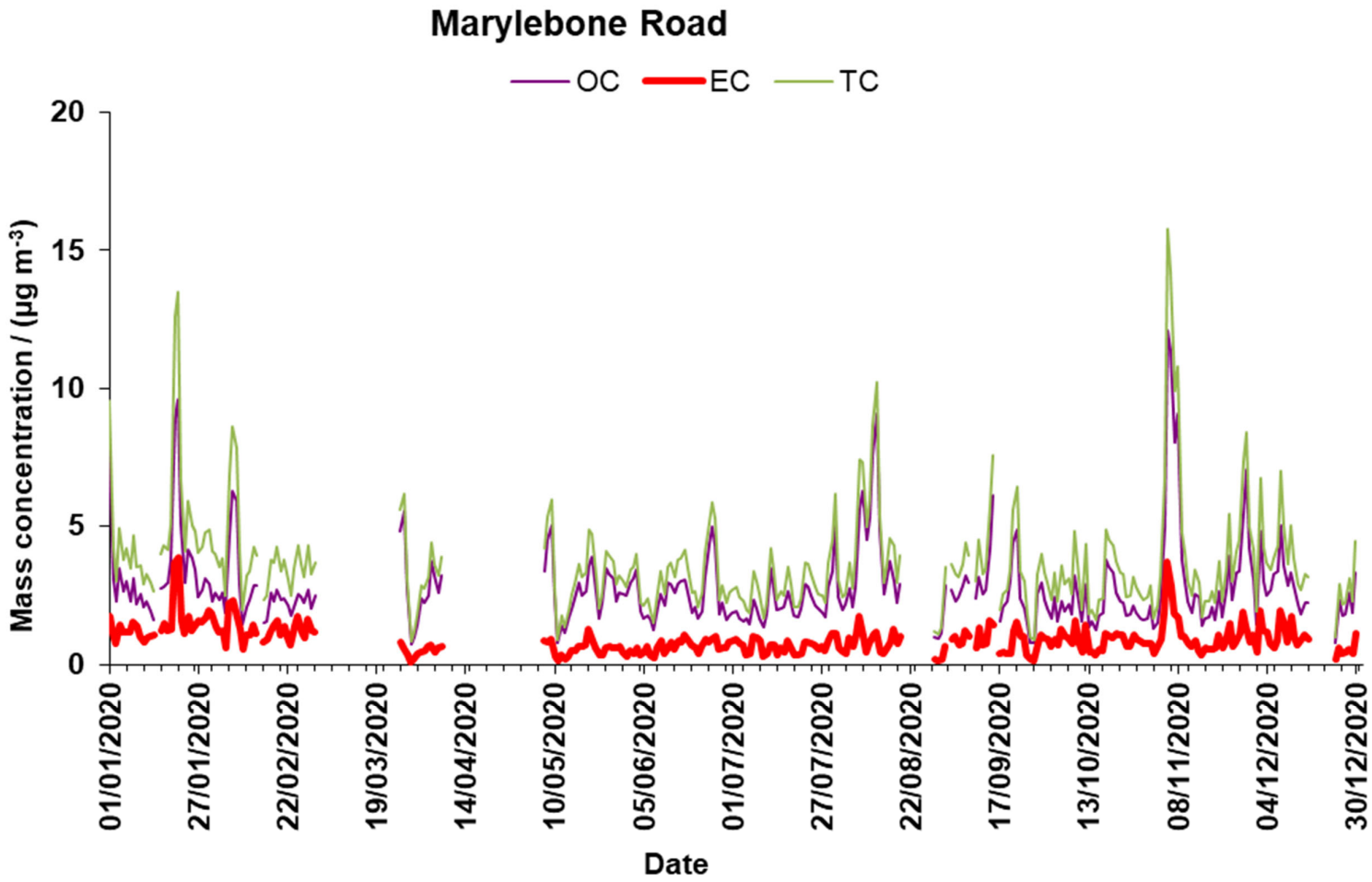


Figure 36 - $PM_{2.5}$ OC, EC, and TC Mass concentrations (µg m^{-3}) at London Marylebone Road during 2020

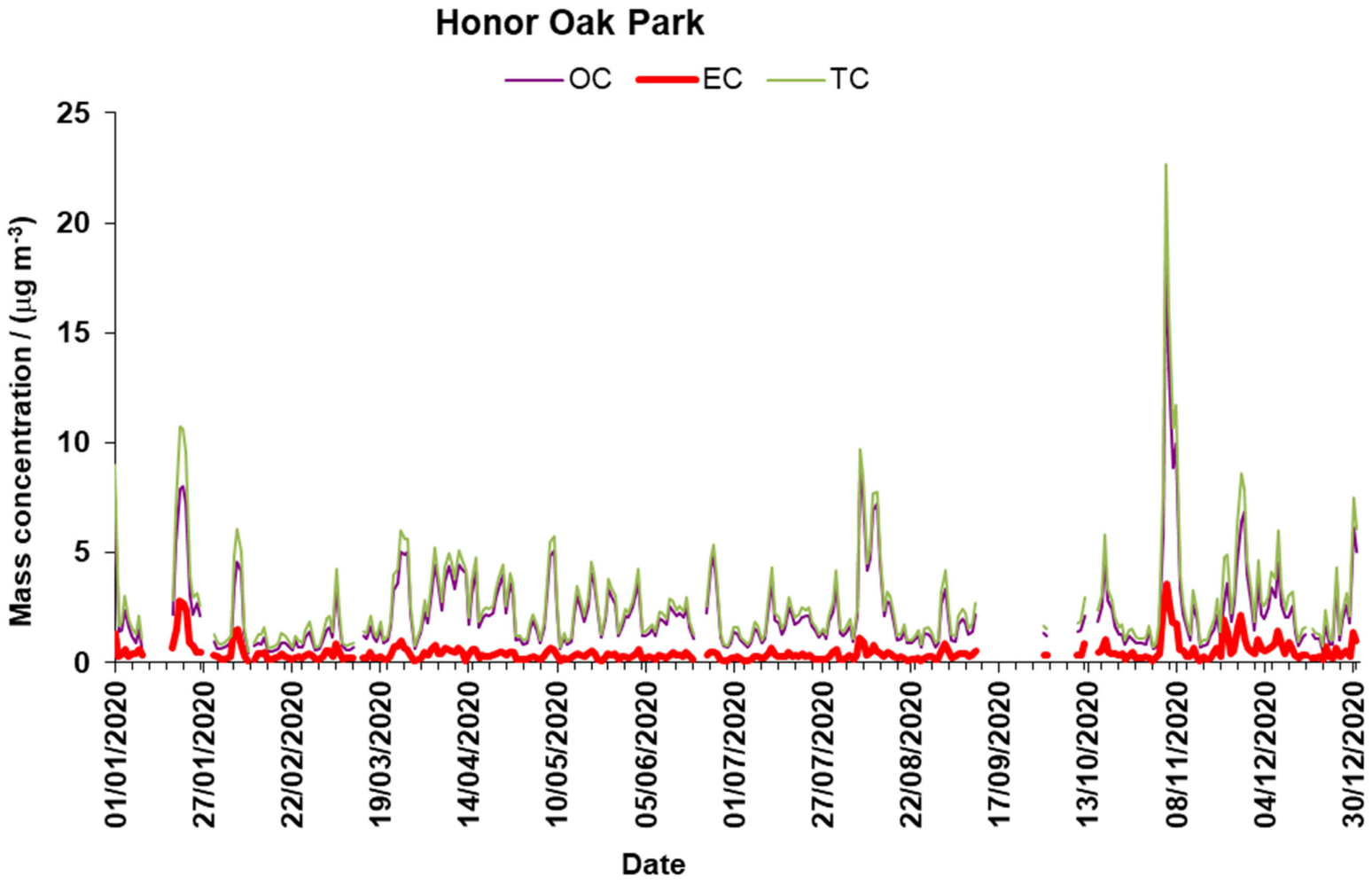


Figure 37- $PM_{2.5}$ OC, EC, and TC Mass concentrations (µg m^{-3}) at London Honor Oak Park during 2020

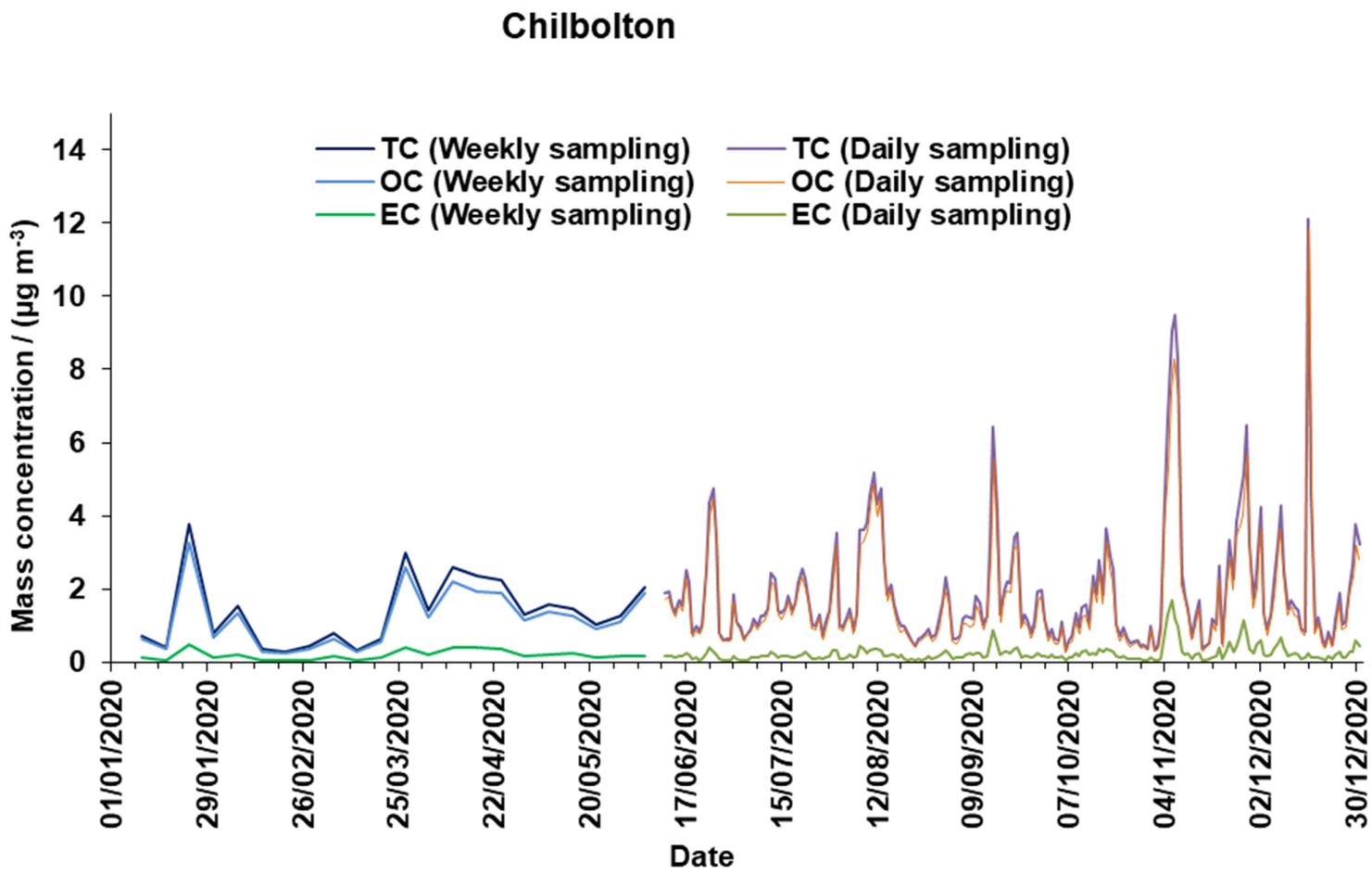


Figure 38 - $PM_{2.5}$ OC, EC, and TC Mass concentrations (µg m^{-3}) at Chilbolton during 2020
(sampling changed from weekly to daily in June 2020; the weekly data points are plotted as the week-ending of the sampling week)

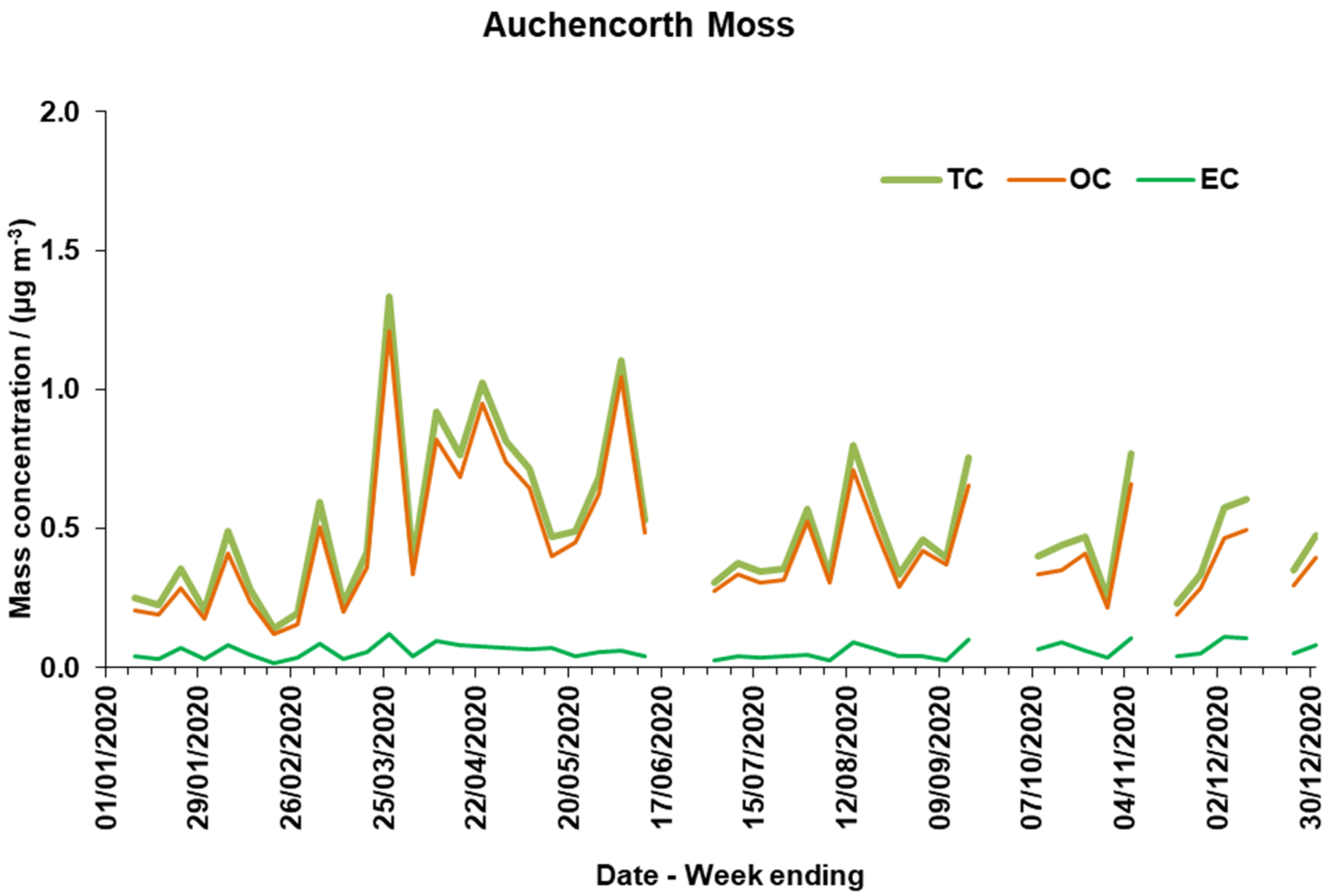


Figure 39 - $PM_{2.5}$ OC, EC, and TC Mass concentrations (µg m^{-3}) at Auchencorth Moss during 2020

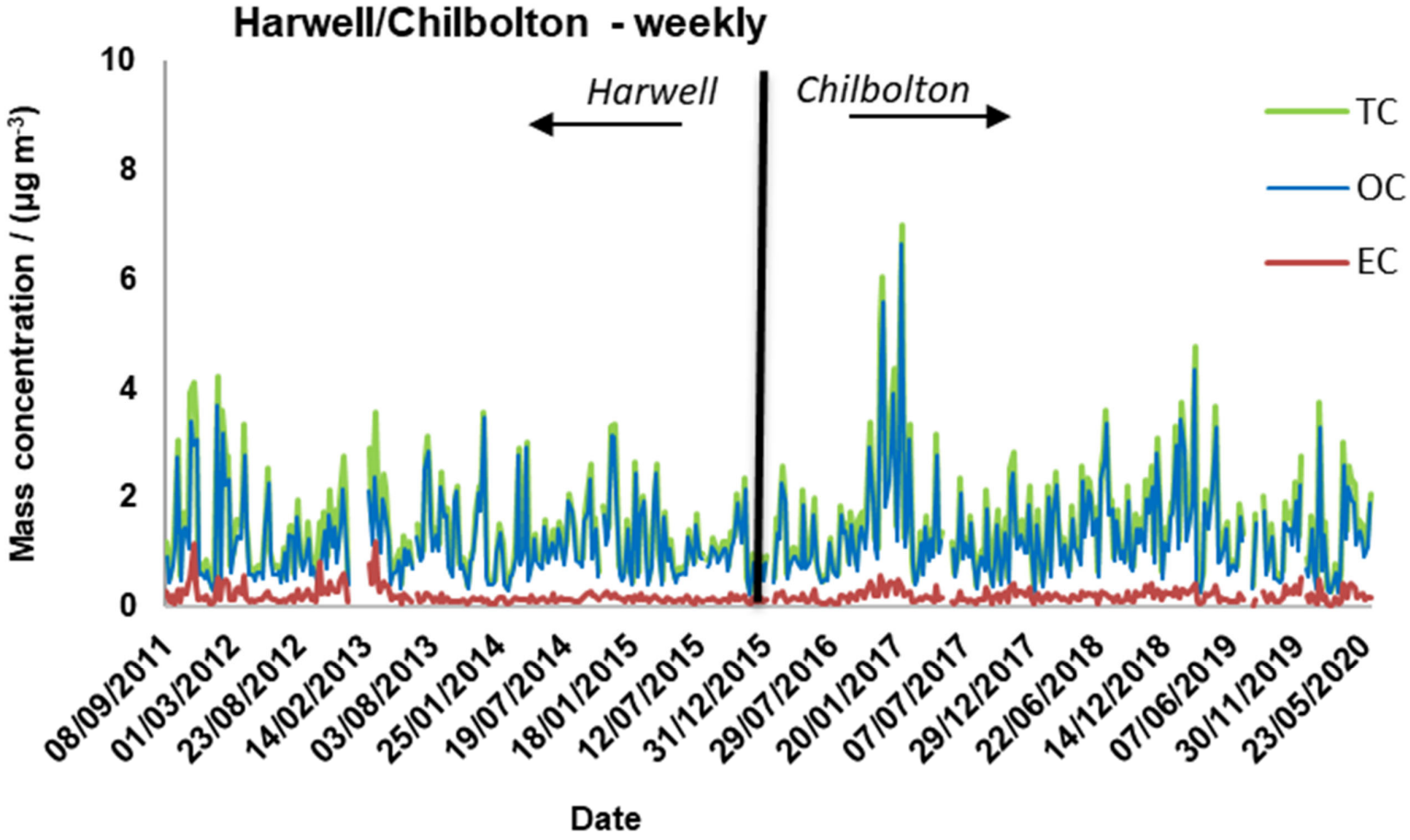


Figure 40 - Time series of the weekly OC, EC, and TC Mass concentrations in the $PM_{2.5}$ fraction at Harwell/Chilbolton Observatory since the installation of the sampler up to June 2020, (µg m^{-3}). The sampler moved from Harwell to Chilbolton in February 2016.

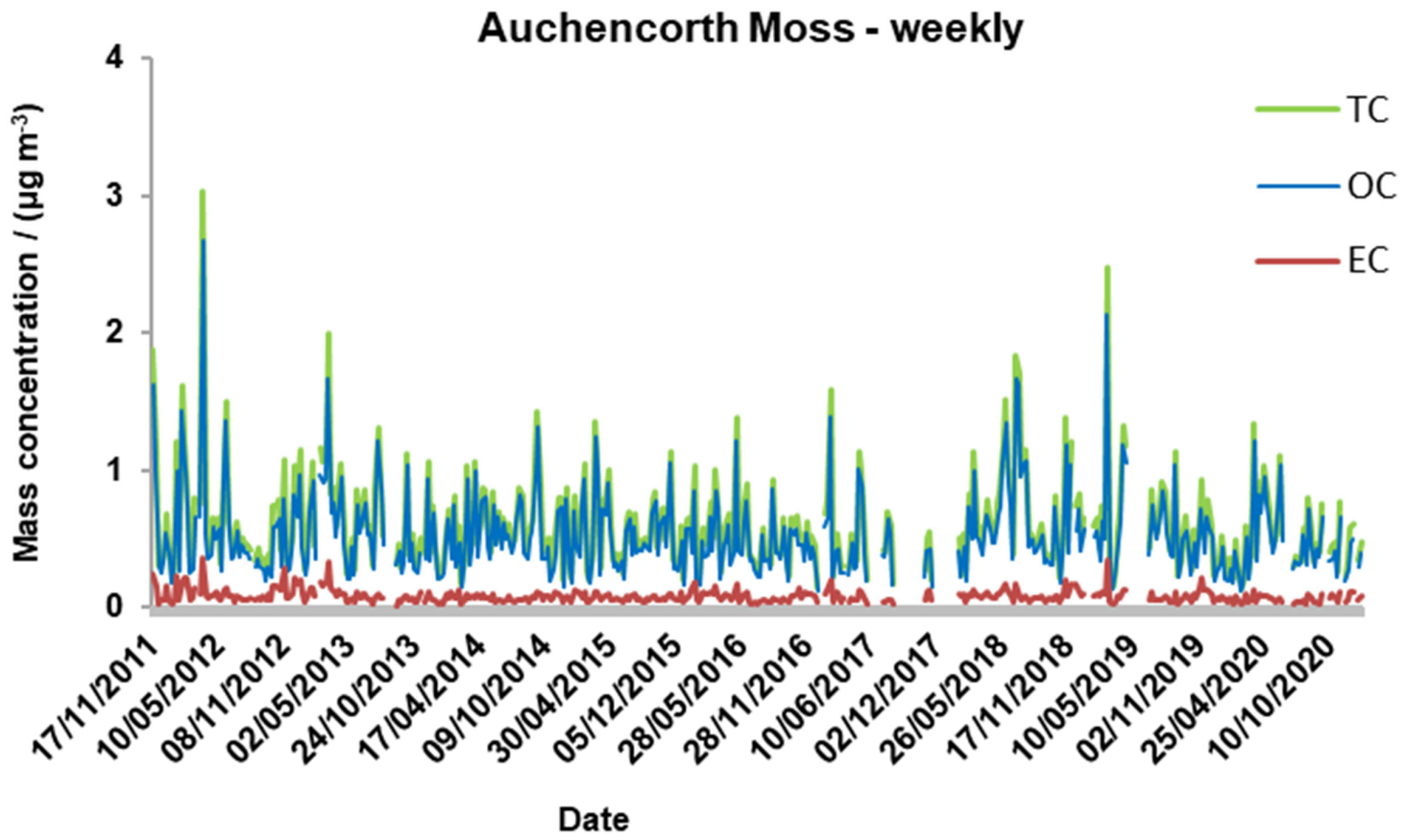


Figure 41 - Time series of OC, EC, and TC in the $PM_{2.5}$ fraction at Auchencorth Moss since the installation of the sampler up to the end of 2020, weekly samples (µg m^{-3})

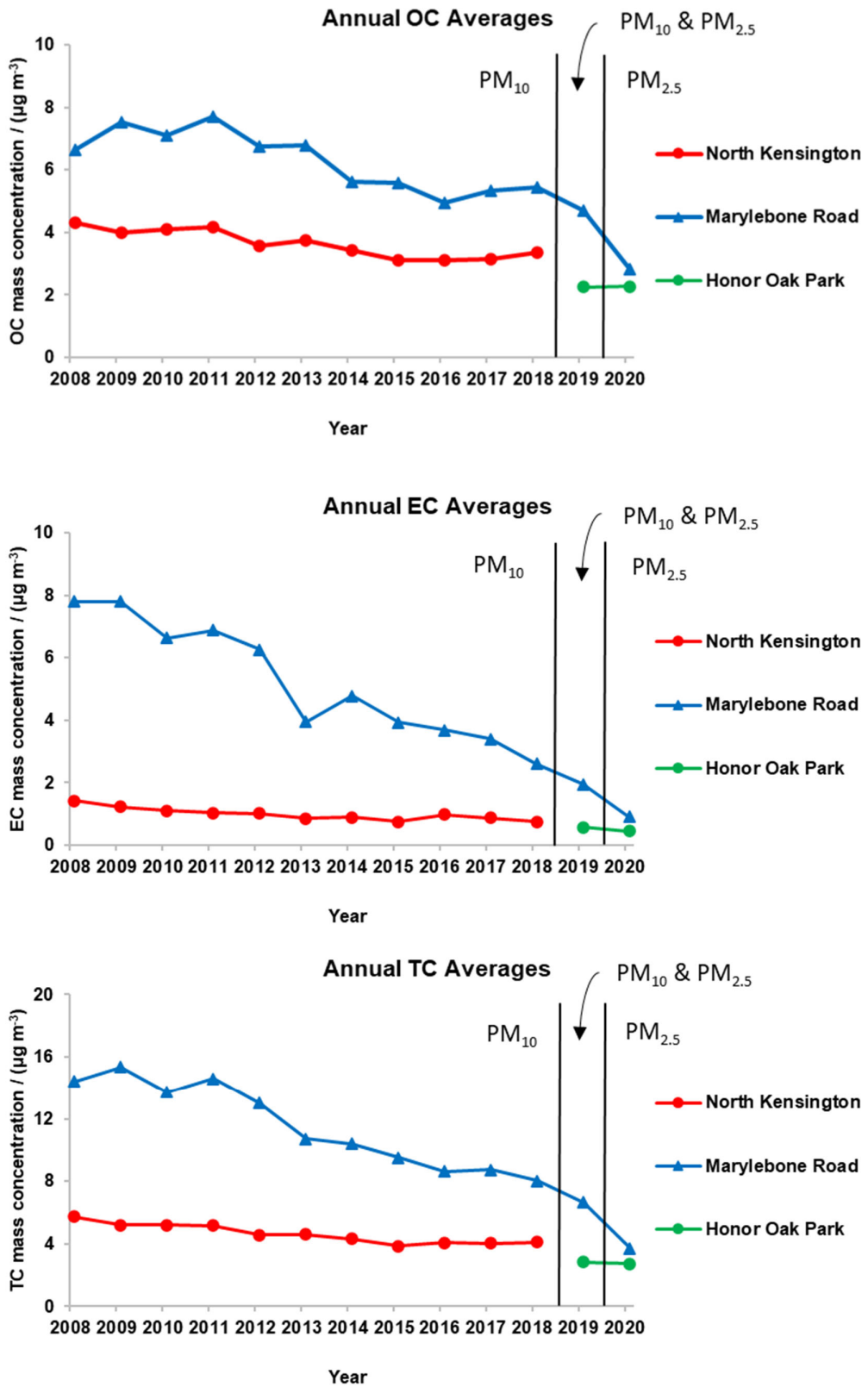


Figure 42 - Annual trends for OC, EC, and TC measurements. PM_{10} sampling heads were changed to $PM_{2.5}$ at London Honor Oak Park and London Marylebone Road in February 2019 and October 2019, respectively).

4.6 BLACK CARBON AND UV-ABSORBING PARTICULATE MATTER

4.6.1 Introduction

Black Carbon (BC) is a measure of the mass concentration of airborne soot-like carbon based on the optical absorption of specific wavelengths by particulates collected on a filter. Ideally it is a similar metric to Elemental Carbon (EC), a measure of soot-like carbon determined by thermo-optical (chemical) techniques, though in practice the EC fraction of total carbon depends strongly on the method chosen. The term “Equivalent Black Carbon” is formally recommended for data which simply converts an aerosol absorption coefficient to a mass concentration as described in section 2.4.6. The Aethalometer AE33 model calculates mass concentration at seven wavelengths: 950 nm, 880 nm, 660 nm, 590 nm, 520 nm, 470 nm, and 370 nm. In this report, the BC term refers to mass concentration of particulate matter measured at 880 nm. Data from the remaining channels, together with annual mean are shown in Table 9. These Aethalometer measurements can be used in source apportionment studies and to determine the particle absorption wavelength dependence.

Table 9 - Annual mean of particulate matter concentrations measured at specific wavelength (indicated in nm in brackets) by the AE33 Aethalometer in 2020. UVPM is calculated by subtracting the BC mass concentration from the UV mass concentration

	PM mass concentration (µg m^{-3})							
Site	**UV** (370)	**Blue** (470)	**Green** (520)	**Yellow** (590)	**Red** (660)	**BC** (880)	**IR-2** (950)	**UVPM**
Auchencorth Moss	0.16	0.16	0.15	0.14	0.13	0.13	0.13	0.03
Ballymena Ballykeel	1.11	0.98	0.90	0.86	0.82	0.77	0.77	0.34
Belfast Centre	1.13	1.09	1.02	1.00	0.95	0.91	0.85	0.22
Birmingham A4540 Roadside	2.13	2.16	2.05	2.01	1.93	1.90	1.70	0.23
Birmingham Ladywood	0.95	0.92	0.87	0.84	0.80	0.77	0.80	0.17
Cardiff Centre	0.93	0.88	0.82	0.79	0.75	0.72	0.74	0.21
Chilbolton Observatory	0.56	0.49	0.45	0.42	0.40	0.37	0.41	0.18
Detling	0.67	0.62	0.57	0.56	0.53	0.51	0.55	0.16
Glasgow High Street	0.98	1.00	0.95	0.94	0.90	0.90	0.87	0.08
Glasgow Townhead	0.70	0.70	0.66	0.65	0.63	0.61	0.62	0.08
Kilmakee Leisure Centre (Dunmurry)	1.05	0.92	0.84	0.81	0.76	0.72	0.75	0.33
London Marylebone Road	1.68	1.67	1.58	1.55	1.47	1.43	1.44	0.25
London N. Kensington	1.01	0.94	0.87	0.84	0.80	0.77	0.77	0.23
Strabane 2	2.61	2.17	1.94	1.83	1.70	1.57	1.45	1.03
Average	**1.12**	**1.05**	**0.98**	**0.95**	**0.90**	**0.86**	**0.85**	**0.25**

BC and UVPM concentration data for 2020 are presented and discussed in the following sections as time series graphs, summary graphs and tables. It should be noted that the aethalometers at all sites were upgraded in November 2019 from model AE22 to model AE33. Since then, both Aethalometers (model AE22 and AE33) have been sampling air in parallel from the same inlet at traffic and urban background sites in London. Preliminary results from this comparison campaign, however, suggest that concentrations measured by the AE33 model are approximately 30 % higher than from the AE22 model. Thus, all results provided in this report should be treated with caution especially when comparing 2020 with previous years when the AE22 model was used. The aim of this campaign is to show continuity of data and quantify any differences in measurements. Results from this comparison are currently being prepared for publication.

4.6.2 2020 time series – Black Carbon

Figure 43 to Figure 47 show the black carbon concentrations measured in 2020. The time resolution of the measurements is hourly. Data has been split into regions of the UK for presentation purposes. The maximum y-axis on these charts has generally been set to 20 $\mu g\ m^{-3}$ to enable easy comparison between charts. Figure 43 and Figure 45 (40 $\mu g\ m^{-3}$) are exceptions to this.

As seen in previous years, Northern Ireland sites generally measured increased concentrations during the colder months of October to March indicating the contribution from domestic heating.

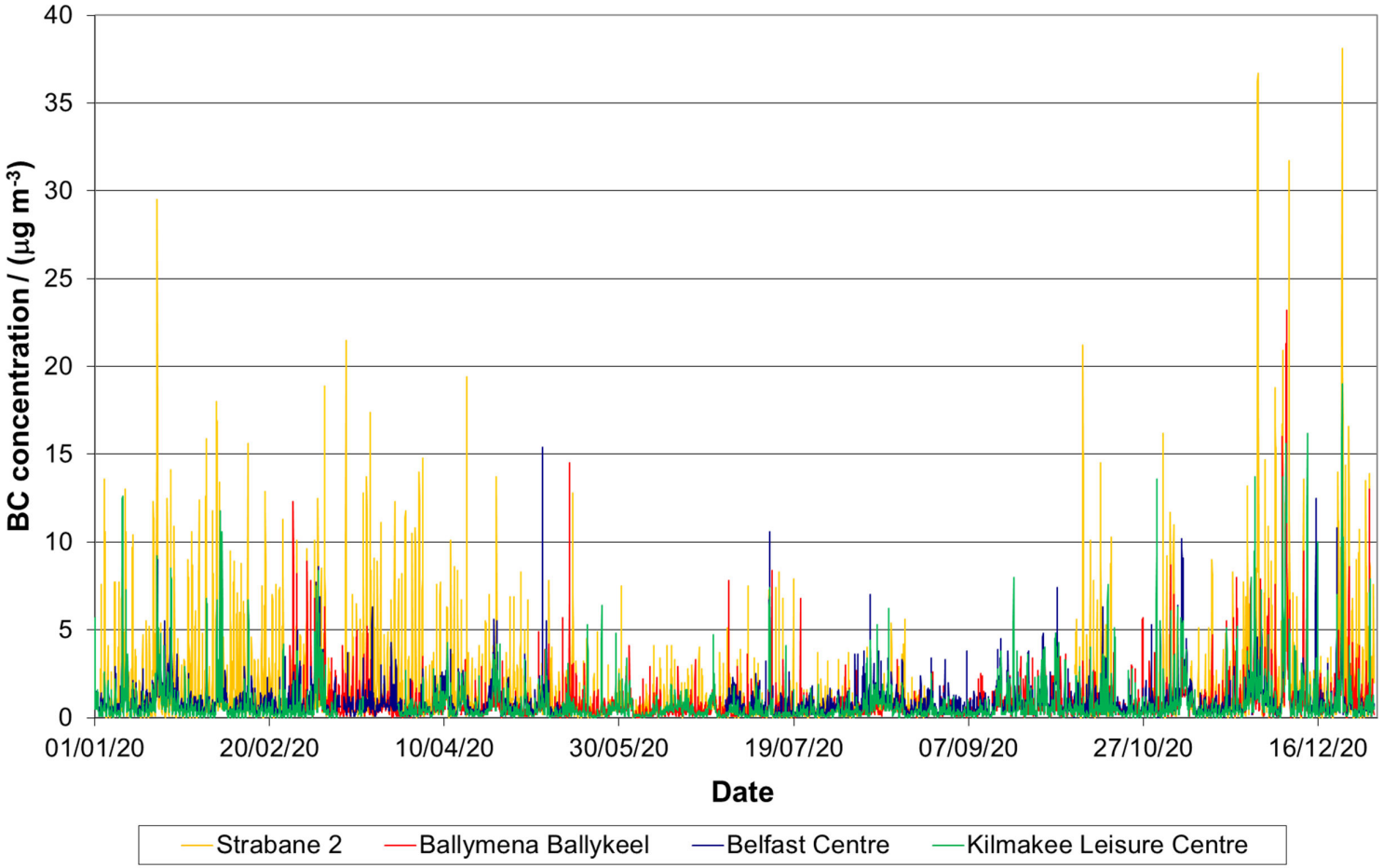


Figure 43 - Black Carbon concentrations during 2020 in Northern Ireland

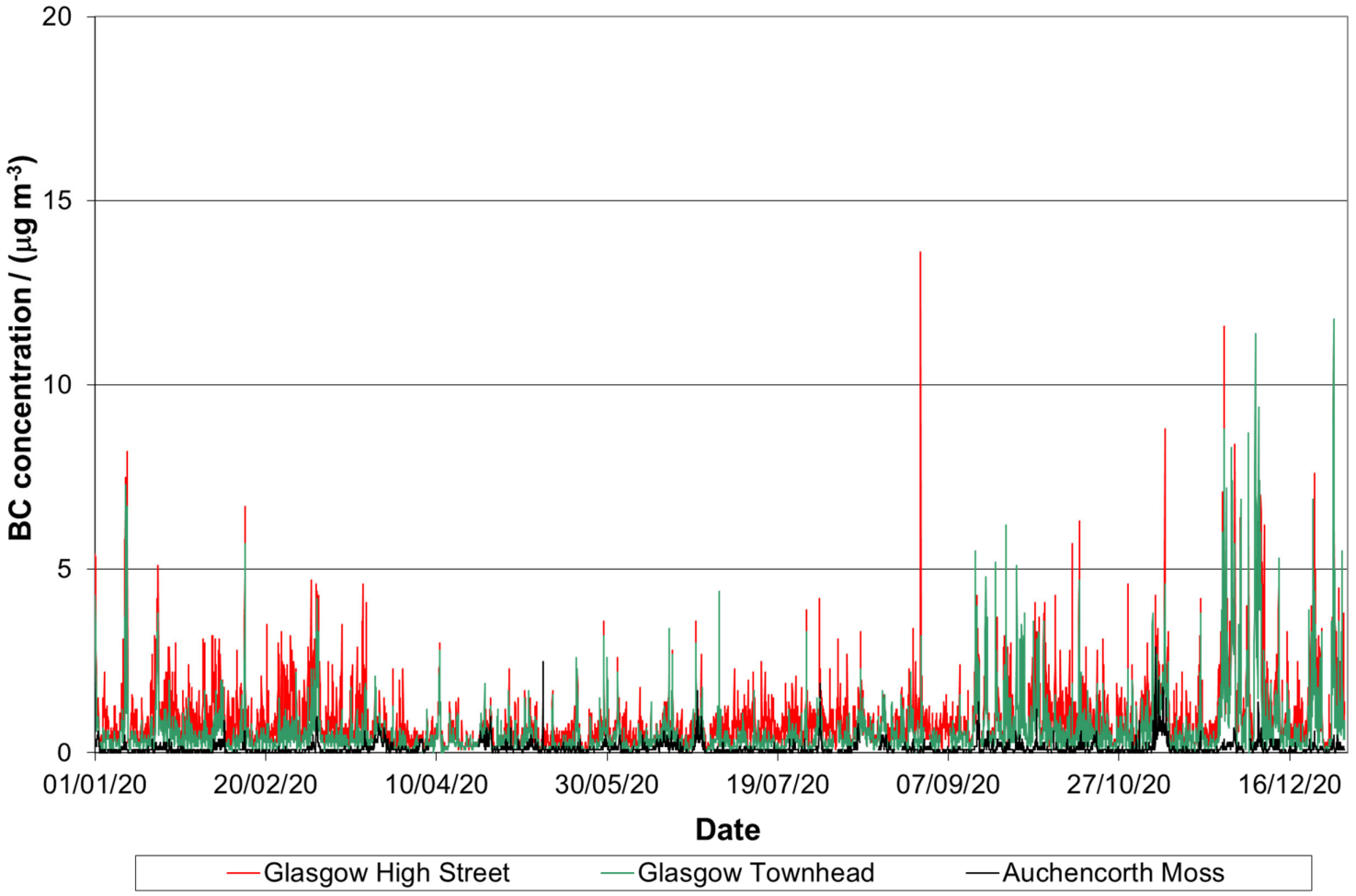


Figure 44 - Black Carbon concentrations during 2020 in Scotland

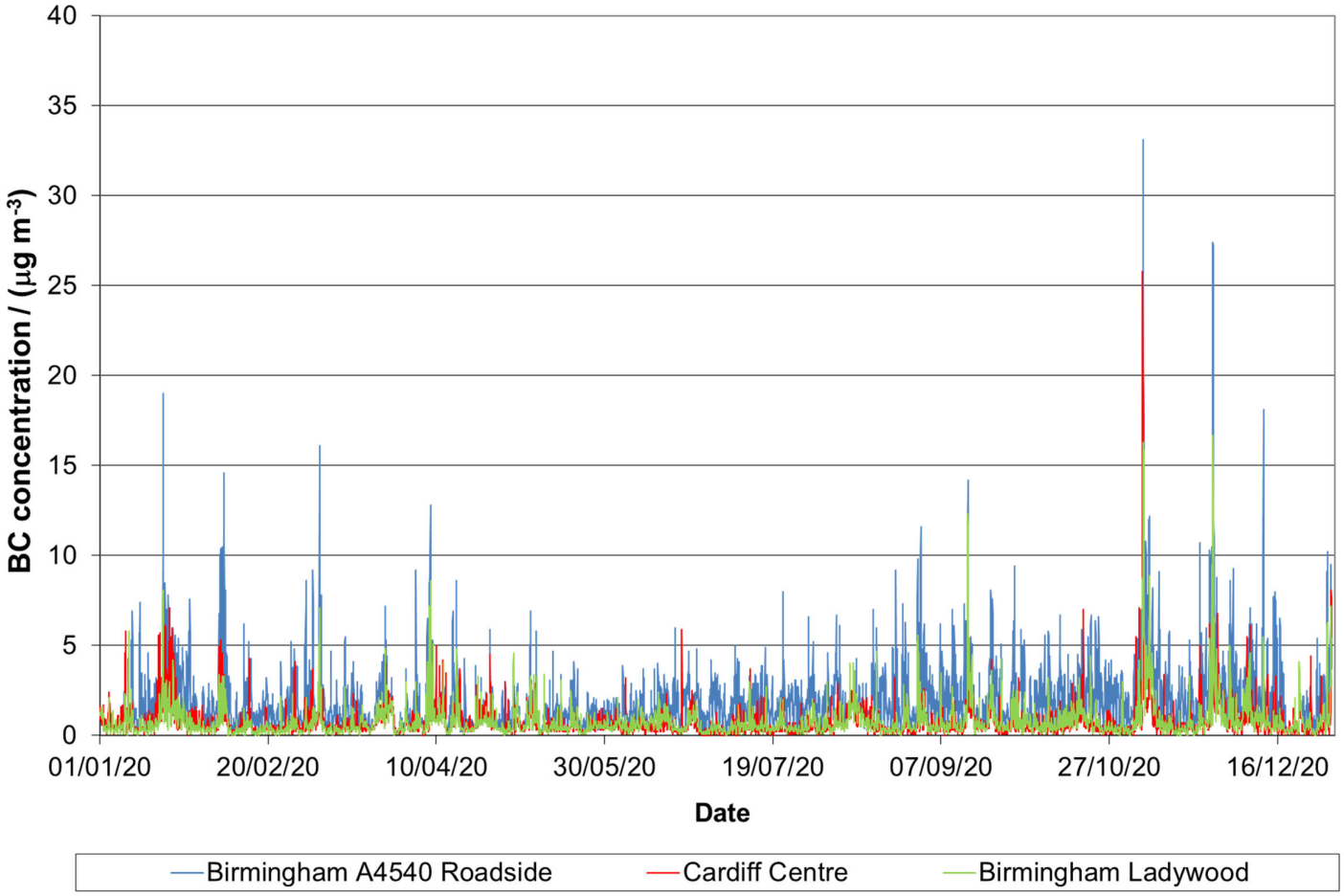


Figure 45 - Black Carbon concentrations during 2020 in Wales and the Midlands

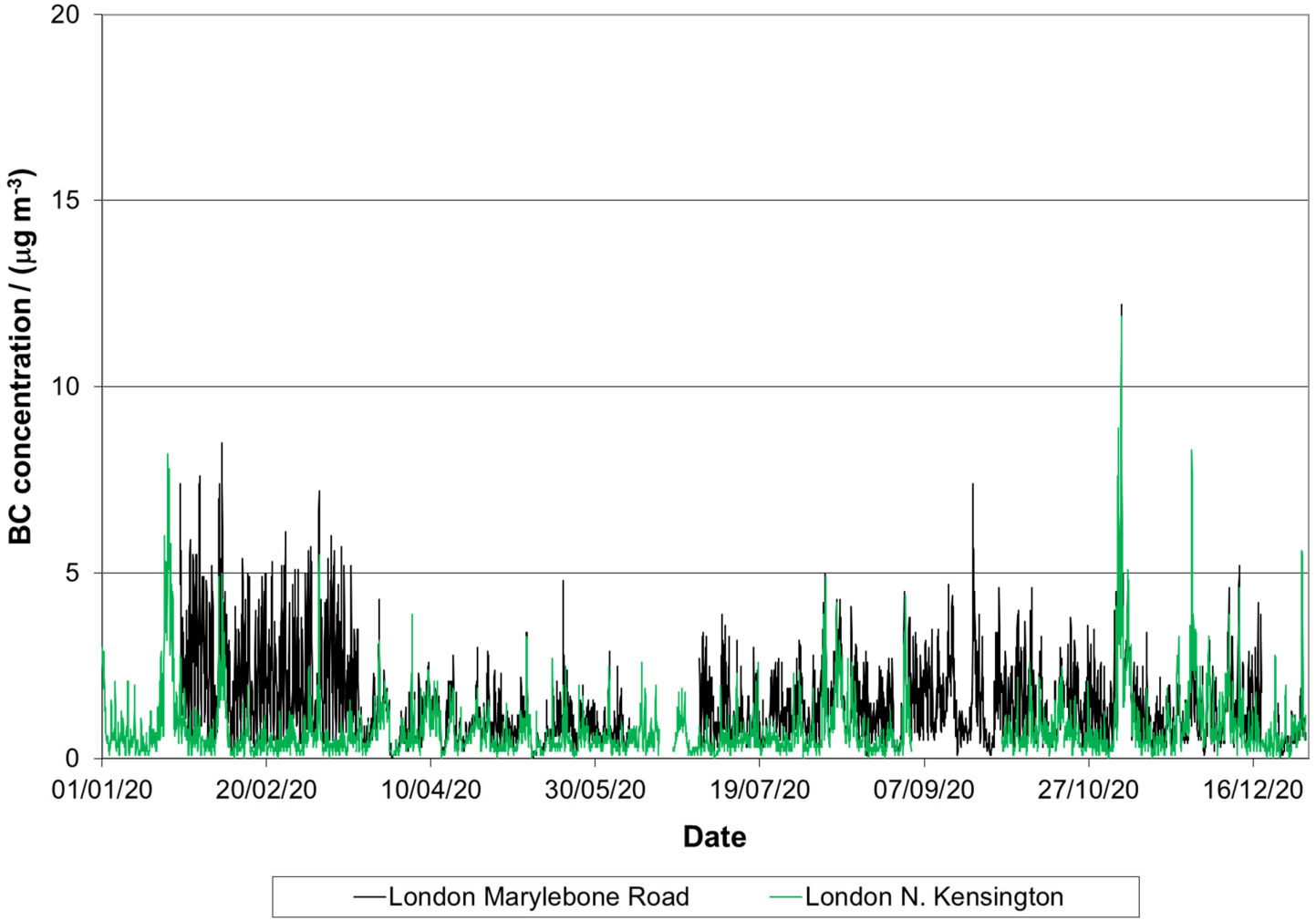


Figure 46 - Black Carbon concentrations during 2020 in London

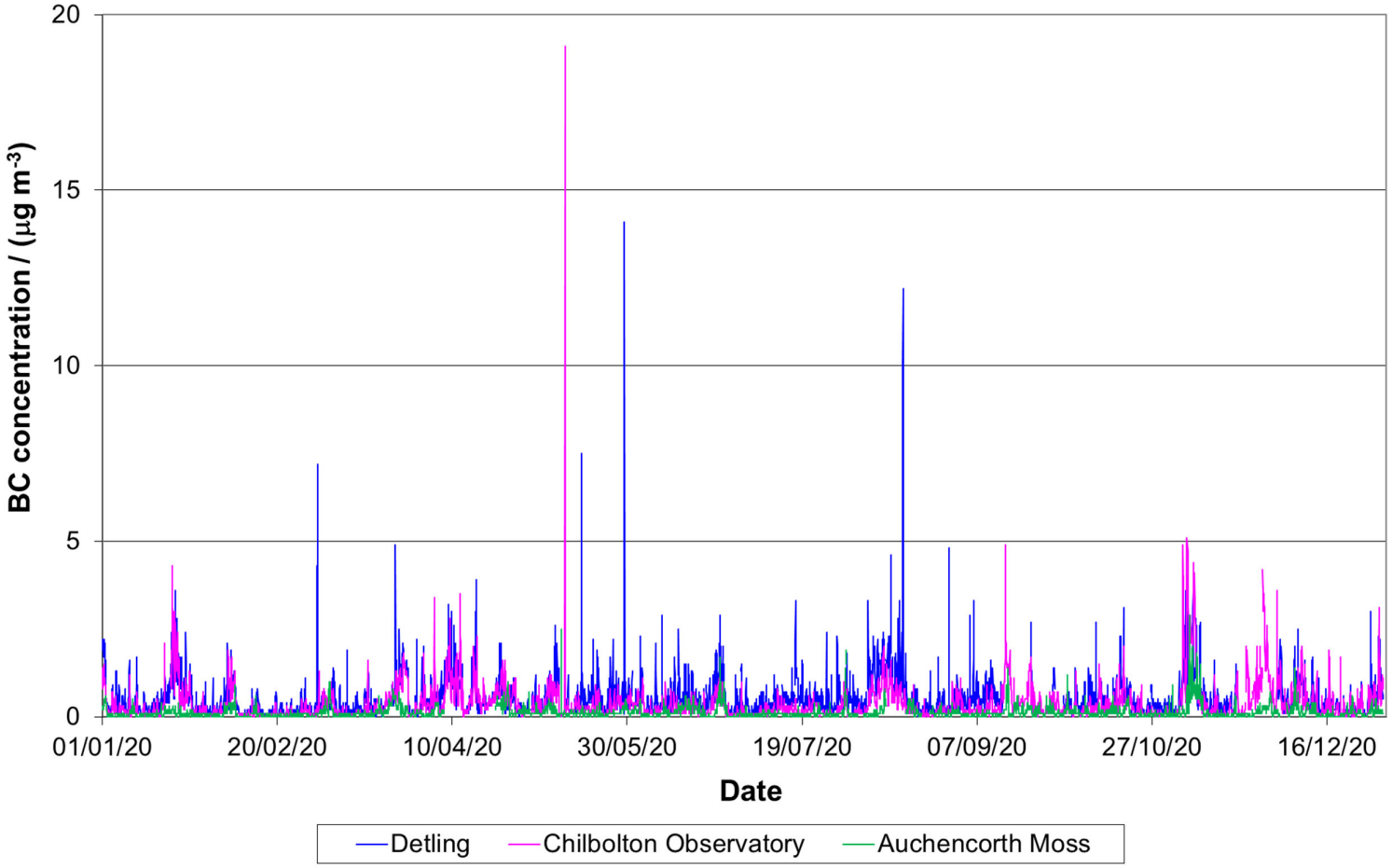


Figure 47 - Black Carbon concentrations during 2020 at Rural Locations

4.6.3 2020 times series – UVPM

Figure 48 to Figure 52 show the UVPM concentrations measured in 2020. The time resolution of the measurements is hourly. Data has been split into regions of the UK for presentation purposes. The y-axis on the UVPM time series graphs have not been fixed to the same value for every chart, because the UVPM is much more dependent on local site-specific conditions. The cause of the very short-term negative concentration spikes in the UVPM concentrations is, however, not clear. It may be due to the semi-volatile nature of the aromatic organic species that adsorb at the 370 nm wavelength. Combustion exhaust streams may contain filterable particles at high concentrations together with semi-volatile UV-active material that will be temporarily retained on the filter tape leading to a distinct increase in UV absorption. Over time these organic species evaporate from the tape and reduce the enhanced UV adsorption. If the effect of evaporation is greater than that of newly deposited material, negative UV component concentrations would be seen.

Another possible reason for positive and negative spikes in roadside data is the internal timing of the measurement process within the Aethalometer AE33. If concentrations are changing rapidly, the subtraction of the Black Carbon concentration from the ‘UV’ concentration could give misleading results.

The Northern Ireland sites measured increased UVPM concentrations during the cold periods in October to March (Figure 48).

Monthly averages for 2019 and 2020 at these sites are shown in Figure 53. In general, data for both sites follow the same pattern (U-shape) with the lowest level of UVPM concentrations in summer months.

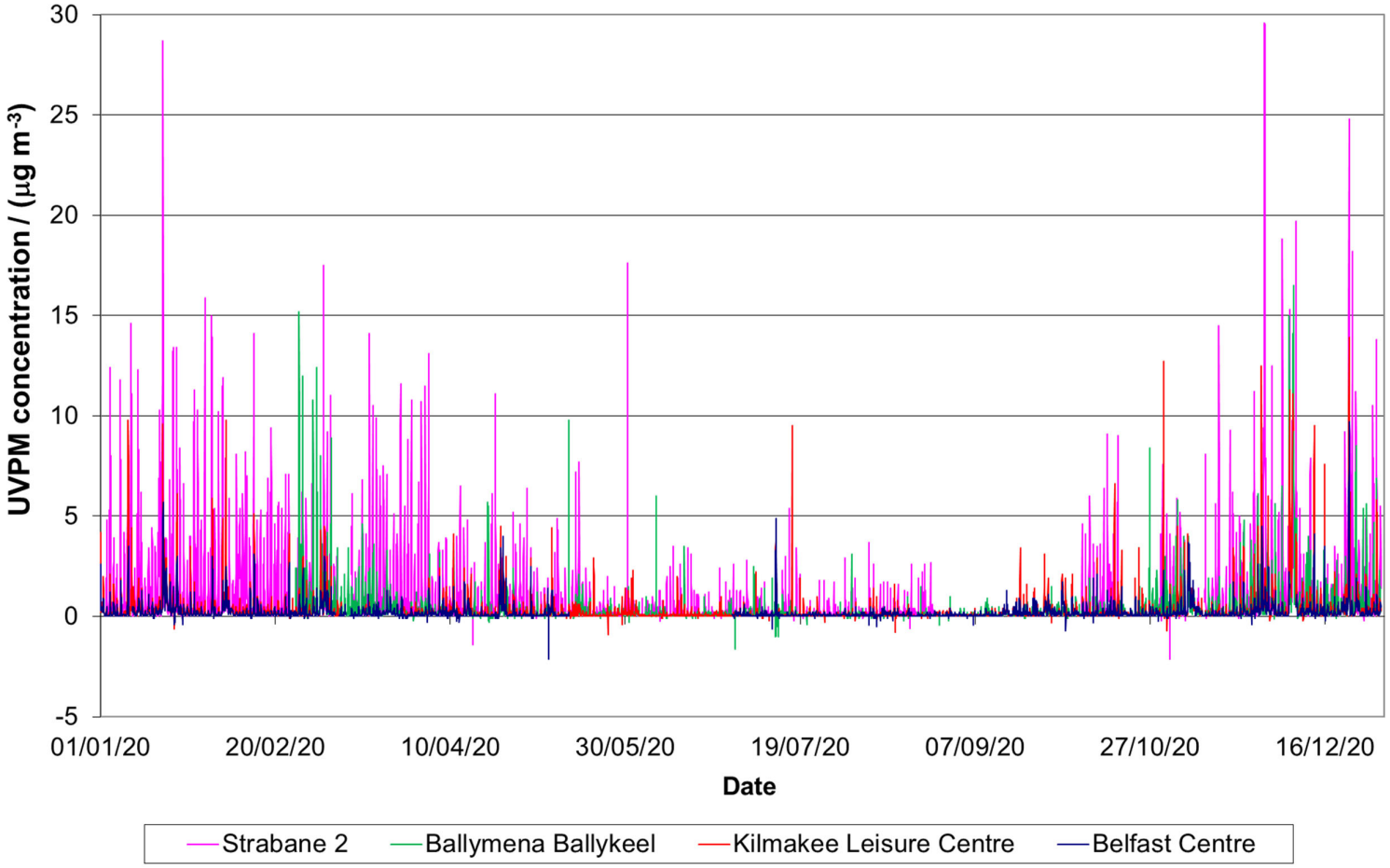


Figure 48 - UVPM concentrations during 2020 in Northern Ireland

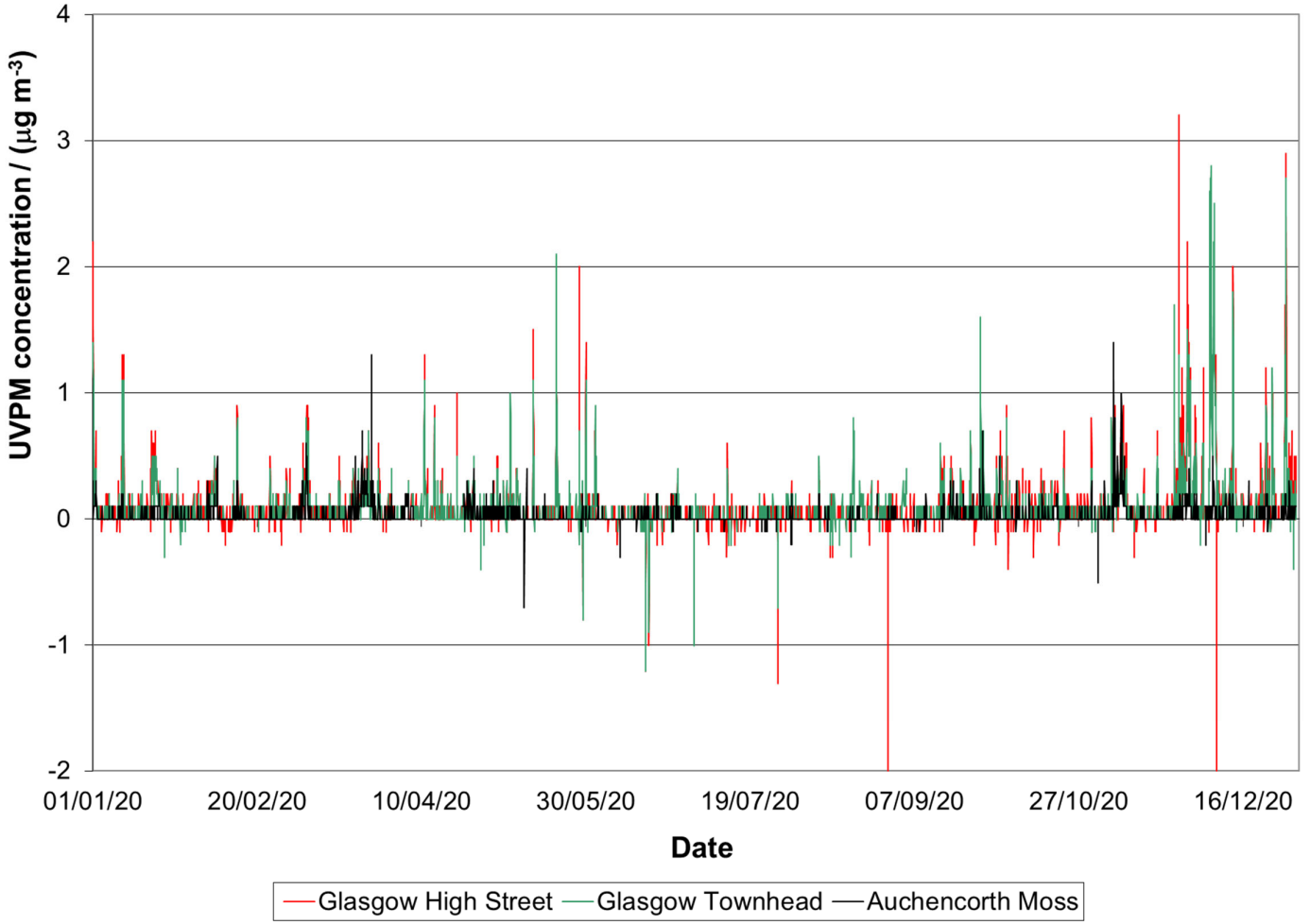


Figure 49 - UVPM concentrations during 2020 in Scotland

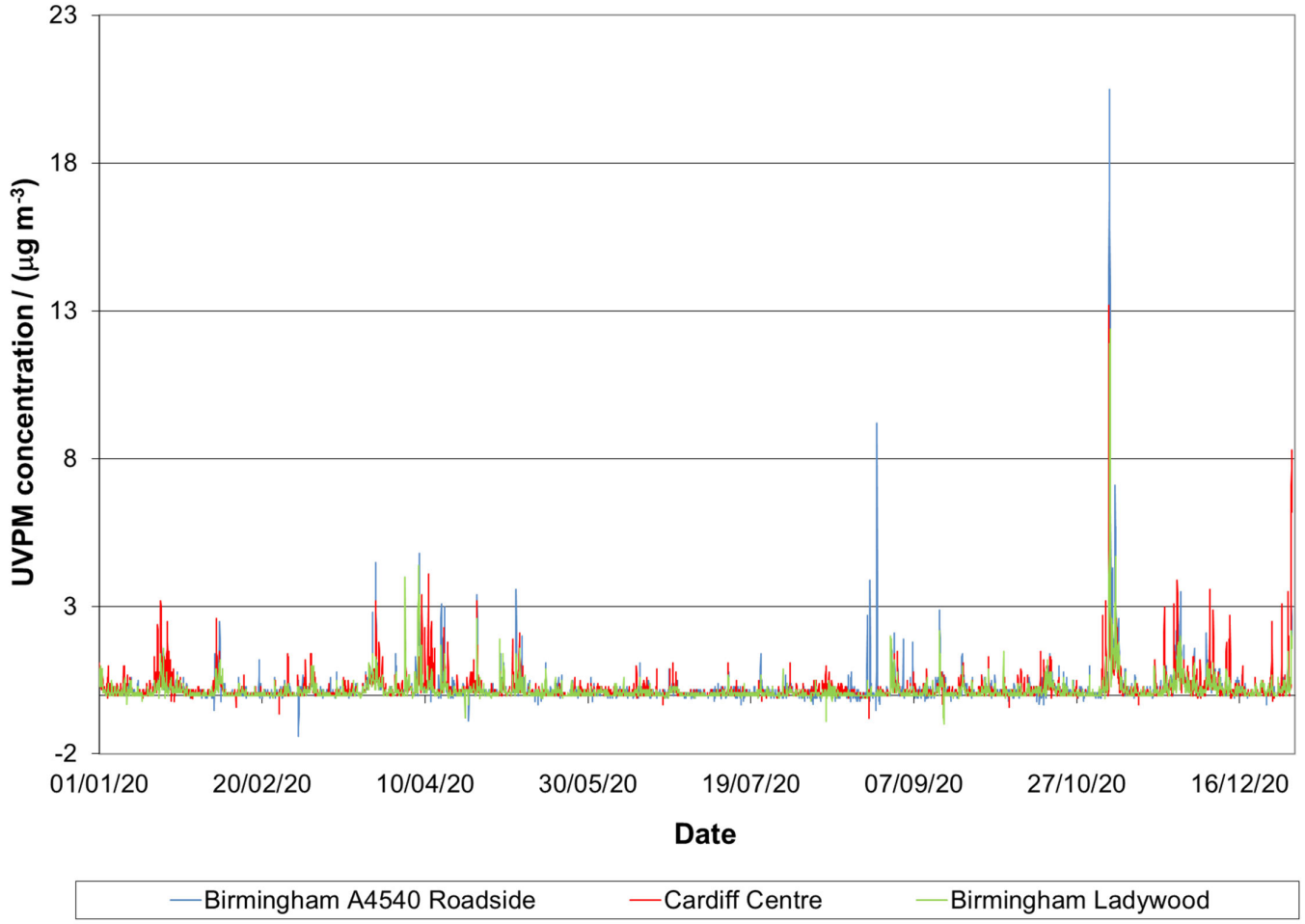


Figure 50 - UVPM concentrations during 2020 in Wales and the Midlands

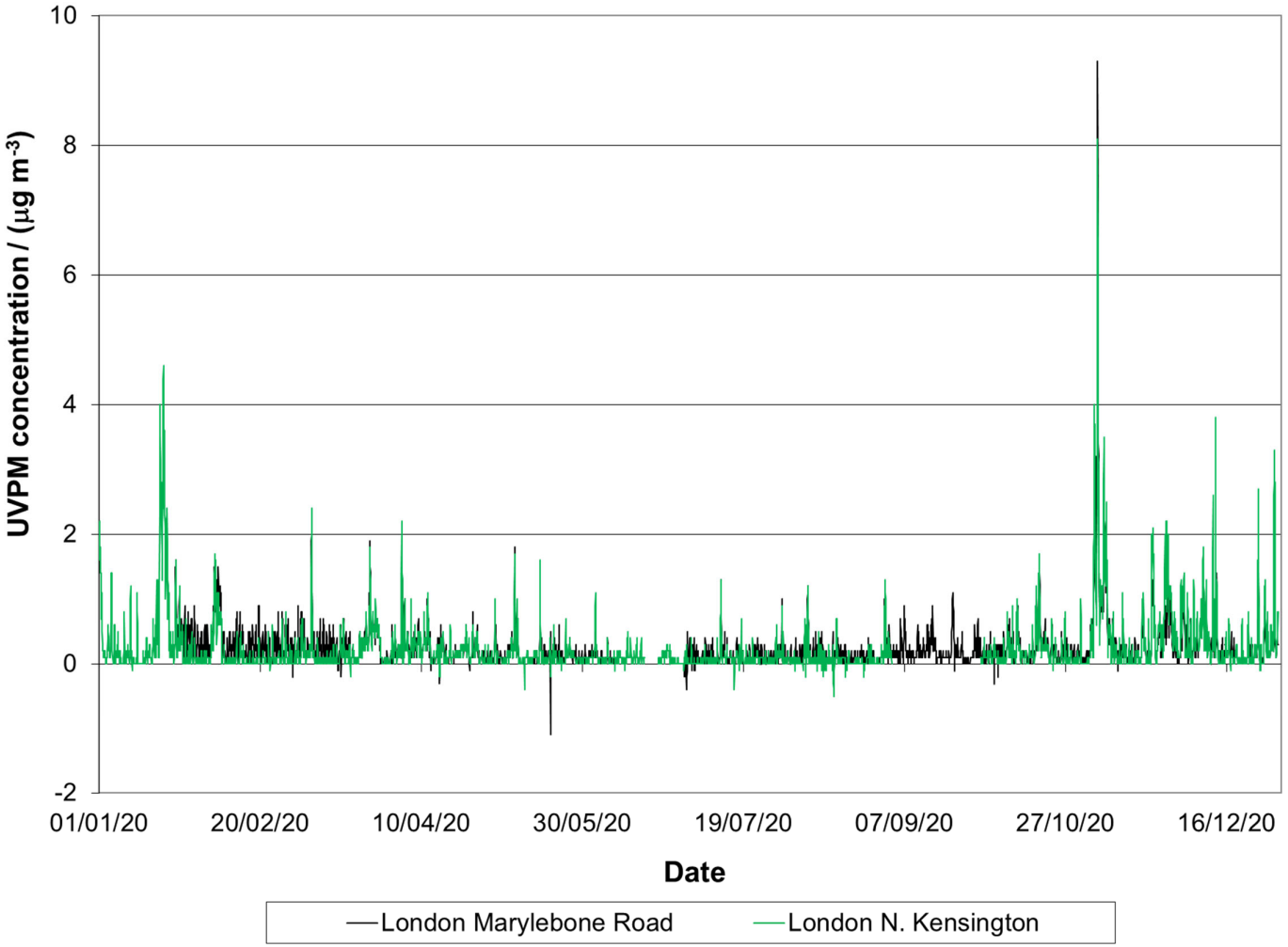


Figure 51 - UVPM concentrations during 2020 in London

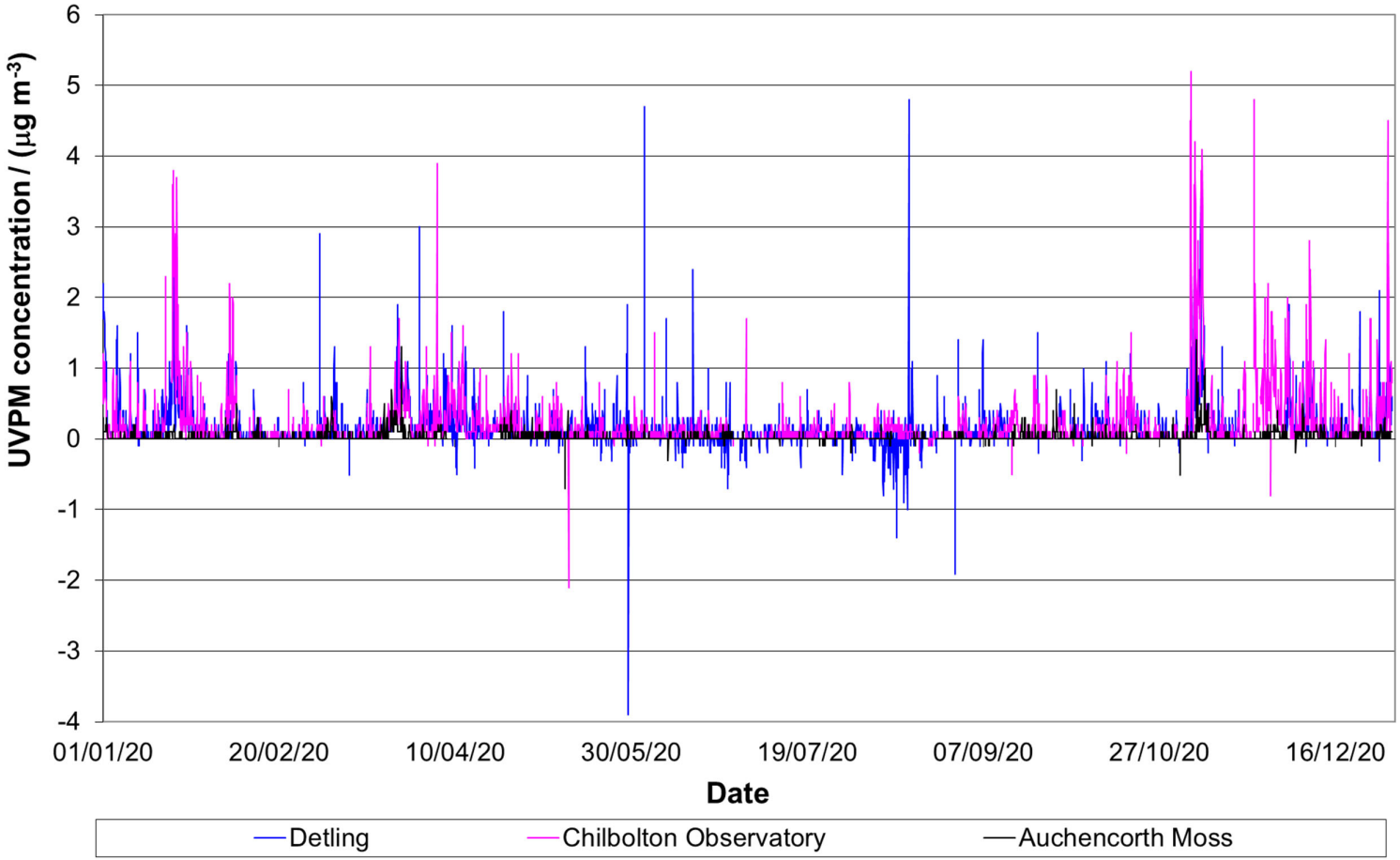


Figure 52 - UVPM concentrations during 2020 at Rural Locations

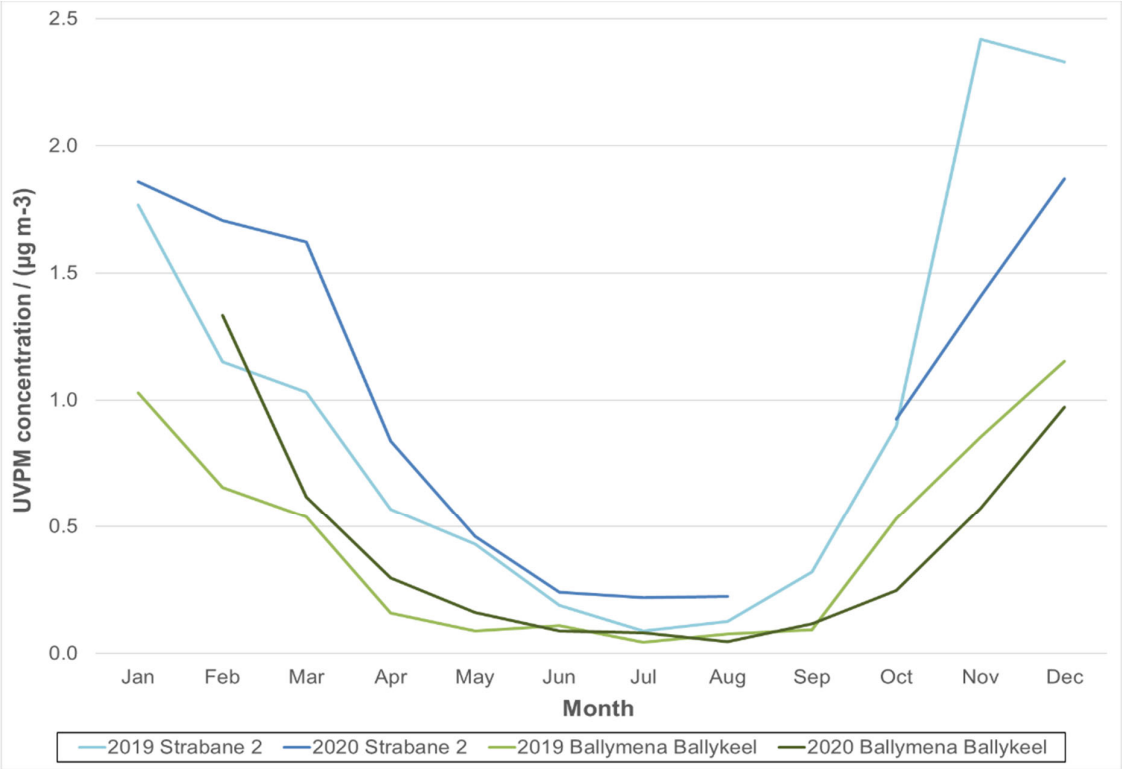


Figure 53 - UVPM concentrations at Strabane 2 and Ballymena Ballykeel sites, shown as monthly averages for 2019 and 2020

4.6.4 2020 annual averages – Black carbon

The annual mean concentrations are presented as a bar graph (Figure 54) to aid the comparison of sites:

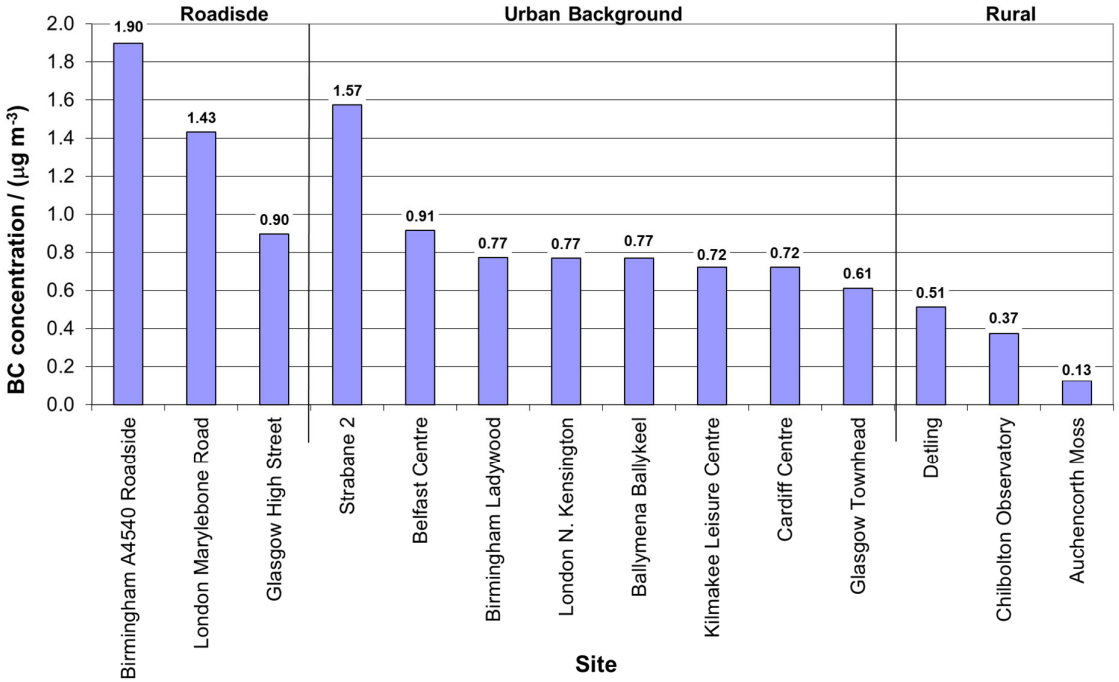


Figure 54 - Annual Mean Black Carbon Concentrations for 2020

Black Carbon urban and roadside increments for London, Birmingham and Glasgow have been calculated by subtracting rural background measurements. Table 10 shows these calculated urban and roadside increment results for London, Birmingham, and Glasgow conurbations.

Table 10 - Urban and Roadside increments in Black Carbon concentrations in 2020

	BC increment (µg m^{-3})	
Conurbation	**Urban**	**Roadside**
London	0.29	0.71
Birmingham	0.39	1.12
Glasgow	0.46	0.33

The urban increments for London, Birmingham and Glasgow were all similar in 2020. The roadside increment for Birmingham was larger than that for London, where it has dropped from 1.0 µg m^{-3} in 2019. Department for Transport (DfT) traffic count data for 2020 are given for all three roads passing the monitoring sites as a comparison (Table 11)[18].

Table 11 - 2020 Average daily traffic count data for Marylebone Road (London), A4540 (Birmingham) and Glasgow High Street Roadside sites

Road (Count Point ID)	Motorcycles	Cars & Taxis	Buses & Coaches	All HGVs	All Motor Vehicles
London Marylebone Road (27236)	2570	38004	2218	2165	54552
Birmingham A4540 (27736)	136	31140	59	2724	39951
Glasgow High Street (10821)	29	9574	106	354	12292
Ratio London to Birmingham	*18.9*	*1.2*	*37.6*	*0.8*	*1.4*
Ratio London to Glasgow	*88.6*	*4.0*	*20.9*	*6.1*	*4.4*
Ratio Birmingham to Glasgow	*4.7*	*3.3*	*0.6*	*7.7*	*3.3*

The London Marylebone Road roadside BC increment in 2020 was a factor of 2.3 higher than the Glasgow High Street roadside increment. This is somewhat lower than the ratio of all types of motor vehicles between the sites, especially in number of buses, a factor of ~21. This factor is even higher when compared to Birmingham A4540 site, which could reflect the cleaner fleet in London. Changes in emissions from London buses and taxis are discussed further in section 4.6.8. The London Marylebone Road BC roadside increment, however, was lower by a factor of 0.6 than the Birmingham A4540 BC roadside increment, however, the Glasgow High Street BC roadside increment was 3.7 times higher that of Birmingham A4540. This might suggest that HGVs are a predominant source of BC at Birmingham A45040.

Figure 55 shows how the urban and roadside increments in London have changed over the period 2012 to 2020. The average urban increment is roughly stable, with increases during the cold periods indicating the contribution from domestic heating. The roadside increment for London has clearly dropped steadily over the period. It should be noted that increment calculations are only possible for periods where parallel measurements are gathered from all London sites including two rural sites: Chilbolton Observatory and Detling. Both sites had issues with leaks in 2017 and 2018 which caused the gaps in Figure 55.

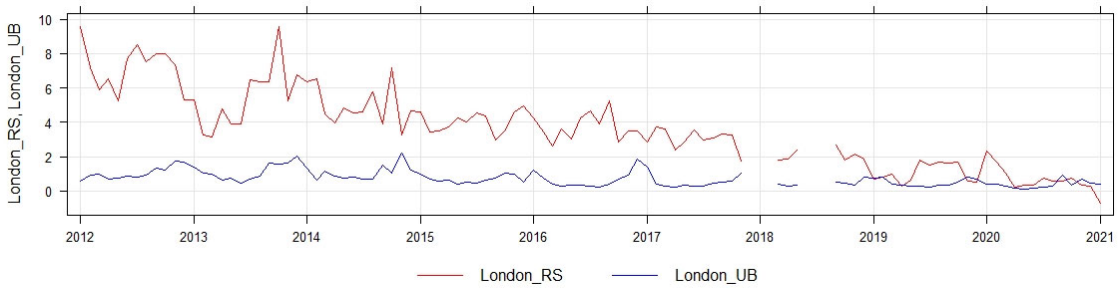


Figure 55 - Urban (UB) and roadside (RS) increments in London for the period 2012 to 2020

4.6.5 2020 annual averages – UVPM

The annual mean concentrations are presented as a bar graph (Figure 56) to aid the comparison of sites:

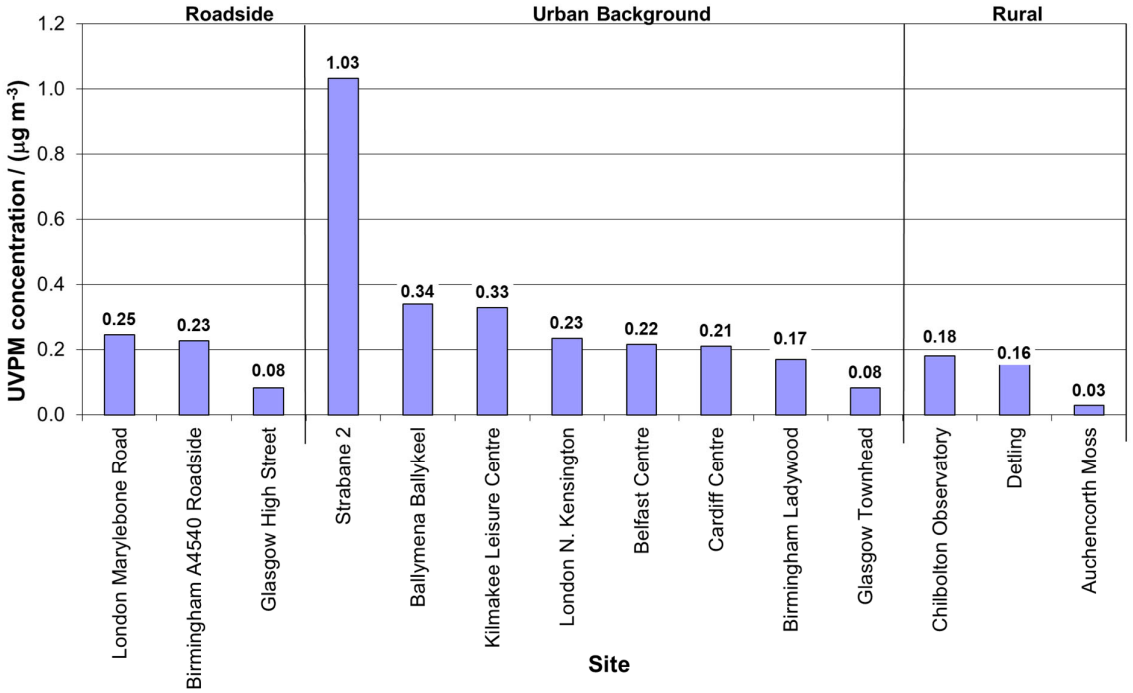


Figure 56 - Annual Mean UVPM concentrations for 2020

UVPM urban and roadside increments for London, Birmingham and Glasgow have been calculated by subtracting rural background measurements. Table 12 shows increment results for London, Birmingham, and Glasgow conurbations.

Table 12 - Urban and Roadside increments in UVPM concentrations in 2020

	UVPM increment (µg m^{-3})	
Conurbation	**Urban**	**Roadside**
London	0.05	0.04
Birmingham	-0.01	0.05
Glasgow	0.05	0.01

The urban and roadside increments at all sites were small, indicating that domestic emissions in the three conurbations were small, and that road traffic was not a significant source for the UVPM. There was no significant difference in increments between 2019 and 2020.

Using the same method, the urban increment in UVPM concentration in Northern Ireland has been calculated relative to Belfast where gas heating has largely displaced oil and coal since 2000. The results are shown in Table 13.

Table 13 - Increment in UVPM concentration in Northern Ireland

	Increment compared to Belfast (µg m^{-3})	Increment compared to Belfast (%)
Dunmurry	0.11	52
Ballymena	0.14	64
Strabane	0.93	430

The increments at Dunmurry (Kilmakee Leisure Centre), Ballymena and Strabane are in line with a history of solid fuel usage for secondary heating in Dunmurry, and a significant usage of non-smokeless fuel in Strabane. Changes in the UVPM increment in Northern Ireland over the last nine years are summarised in Figure 57.

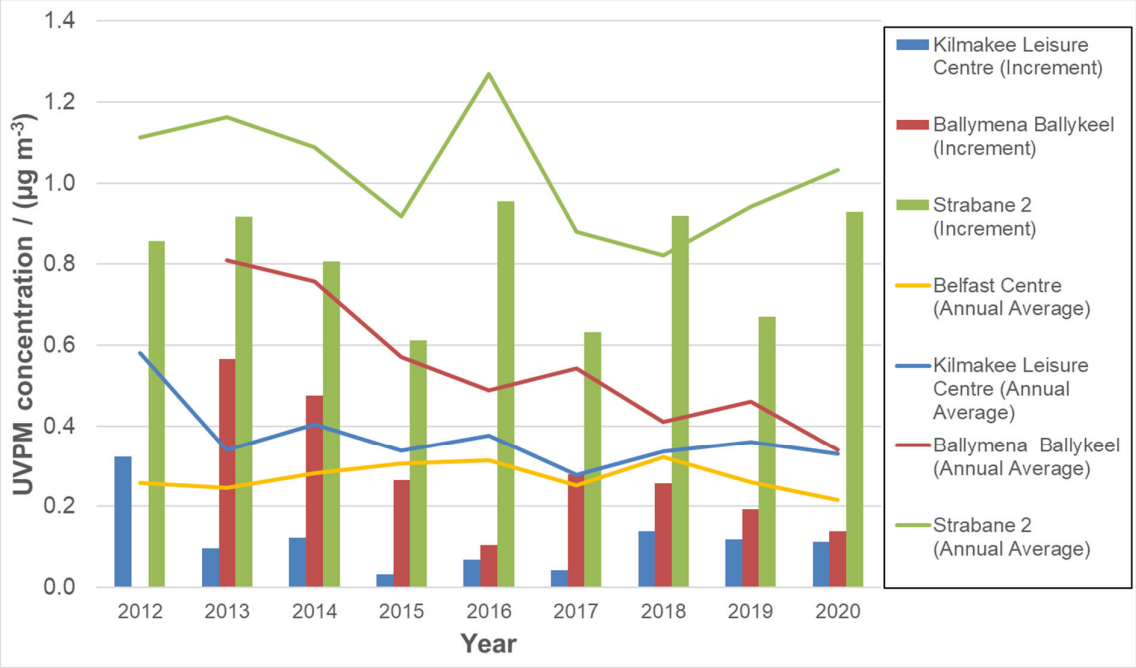


Figure 57 - Annual Mean UVPM concentrations and increments compared to Belfast for 2012-2020

4.6.6 Diurnal, weekly, and monthly profiles – BC and UVPM

This section presents analysis of the BC and UVPM concentrations with respect to temporal variations. All results have been grouped by site classification: Roadside, Urban Background and Rural Background. The units on the y-axes are mass concentration in $\mu g\ m^{-3}$ for BC and UVPM; the scales vary by site. The 2020 data are presented in Figure 58 to Figure 70.

Data from 2009-2020 are presented in Figure 71 to Figure 75. These 12-year average plots only include those sites which have been operating for the whole of this period. The Chilbolton Observatory site was seen to show significantly different concentrations from that at Harwell, so the latter site has been removed from the long-term time series plots. Charts of variations over the day of the week and the month using the data from 2009 – 2020, are considered to be less biased when compared to the single year (2020) measurements presented in Figure 58 to Figure 70.

For all of the charts, the continuous central line is the mean value and the shaded area about this line represents the uncertainty in the mean y-value due to the spread of the results over that averaging period, expressed with a level of confidence of 95%. It is not the overall measurement uncertainty. The shaded area on the x-axis in Figure 58 to Figure 70 is for display purposes only, to allow the uncertainty in the mean value to be seen more clearly. Figure 58 to Figure 75 are generated using the Open-Air Tools run on the R software platform[15,16].

BC and UVPM data at Roadside sites for 2020

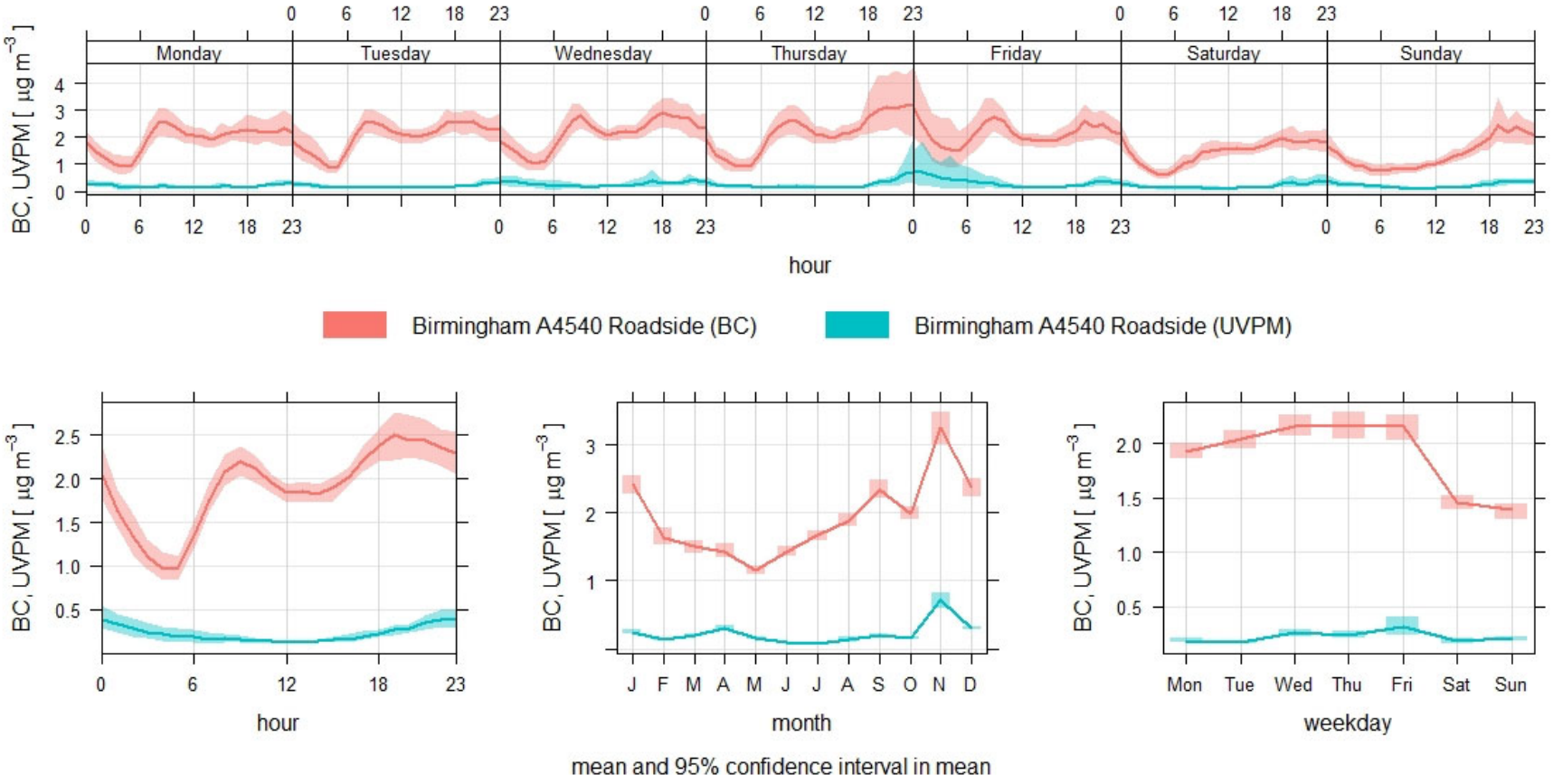


Figure 58 - Temporal variations of BC and UVPM concentrations at Birmingham A4540 Roadside for 2020

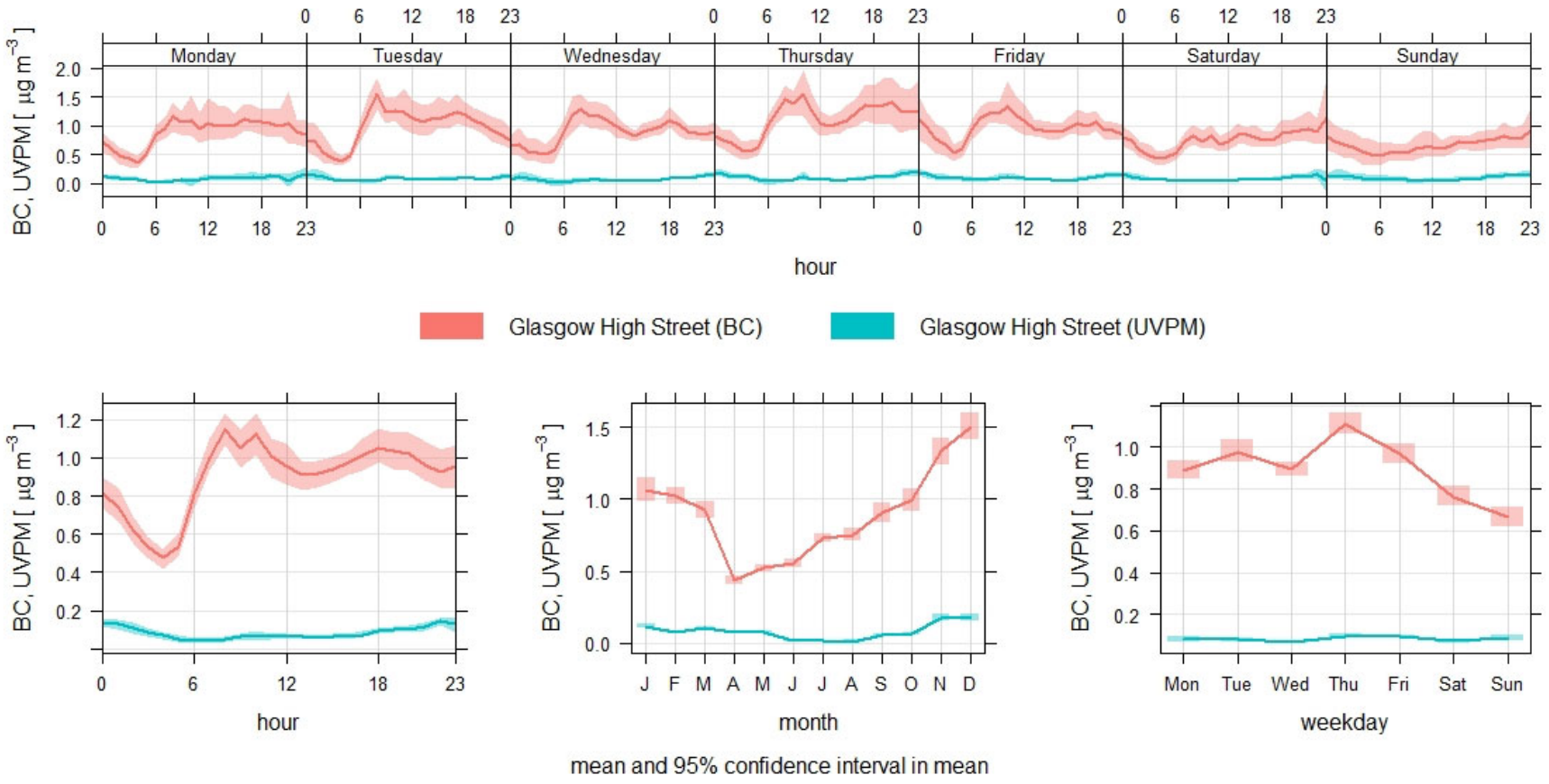


Figure 59 - Temporal variations of BC and UVPM concentrations at Glasgow High Street for 2020

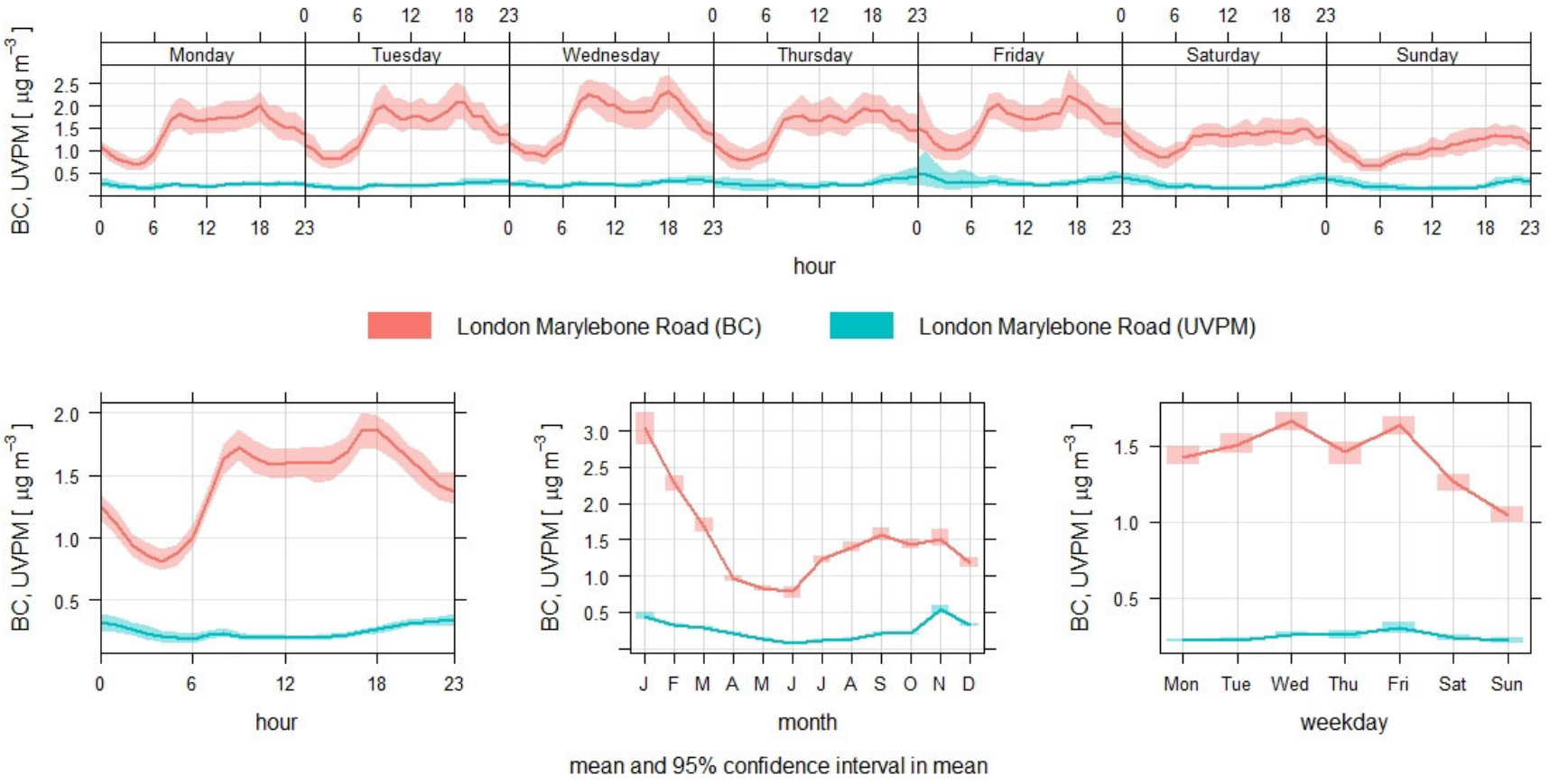


Figure 60 - Temporal variations of BC and UVPM concentrations at London Marylebone Road for 2020

BC and UVPM data at Urban Background sites for 2020

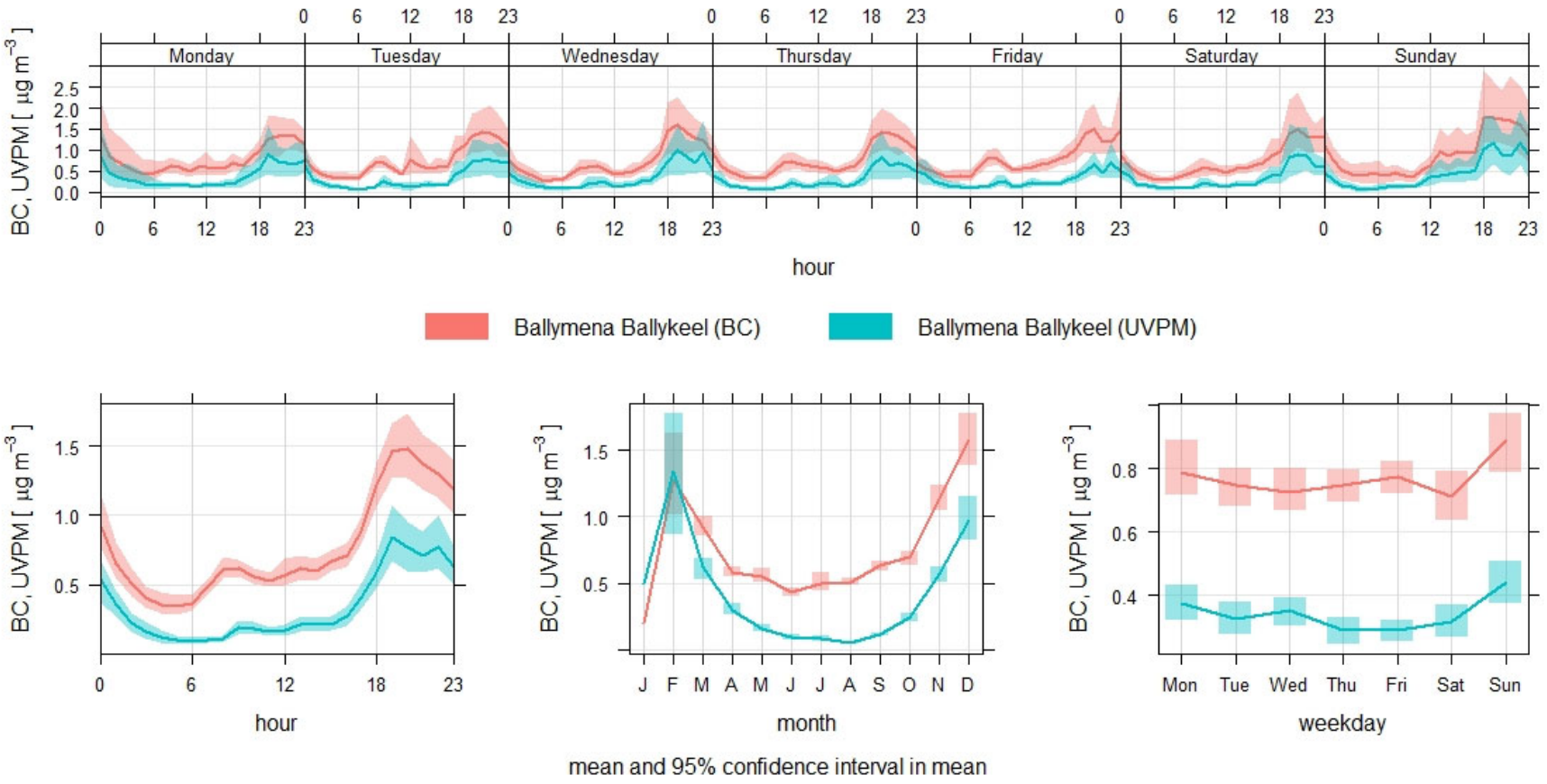


Figure 61 - Temporal variations of BC and UVPM concentrations at Ballymena Ballykeel for 2020

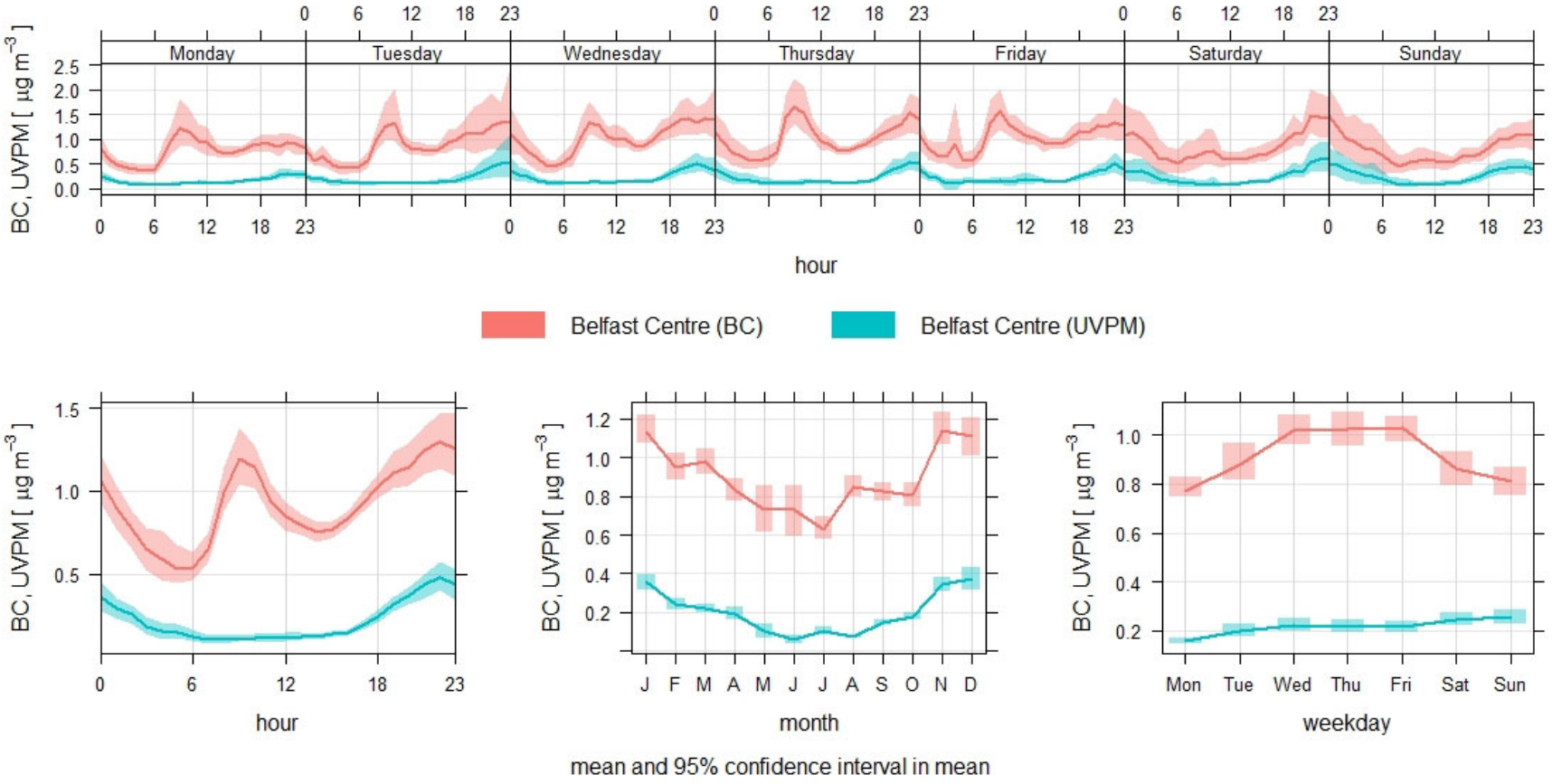


Figure 62 - Temporal variations of BC and UVPM concentrations at Belfast Centre for 2020

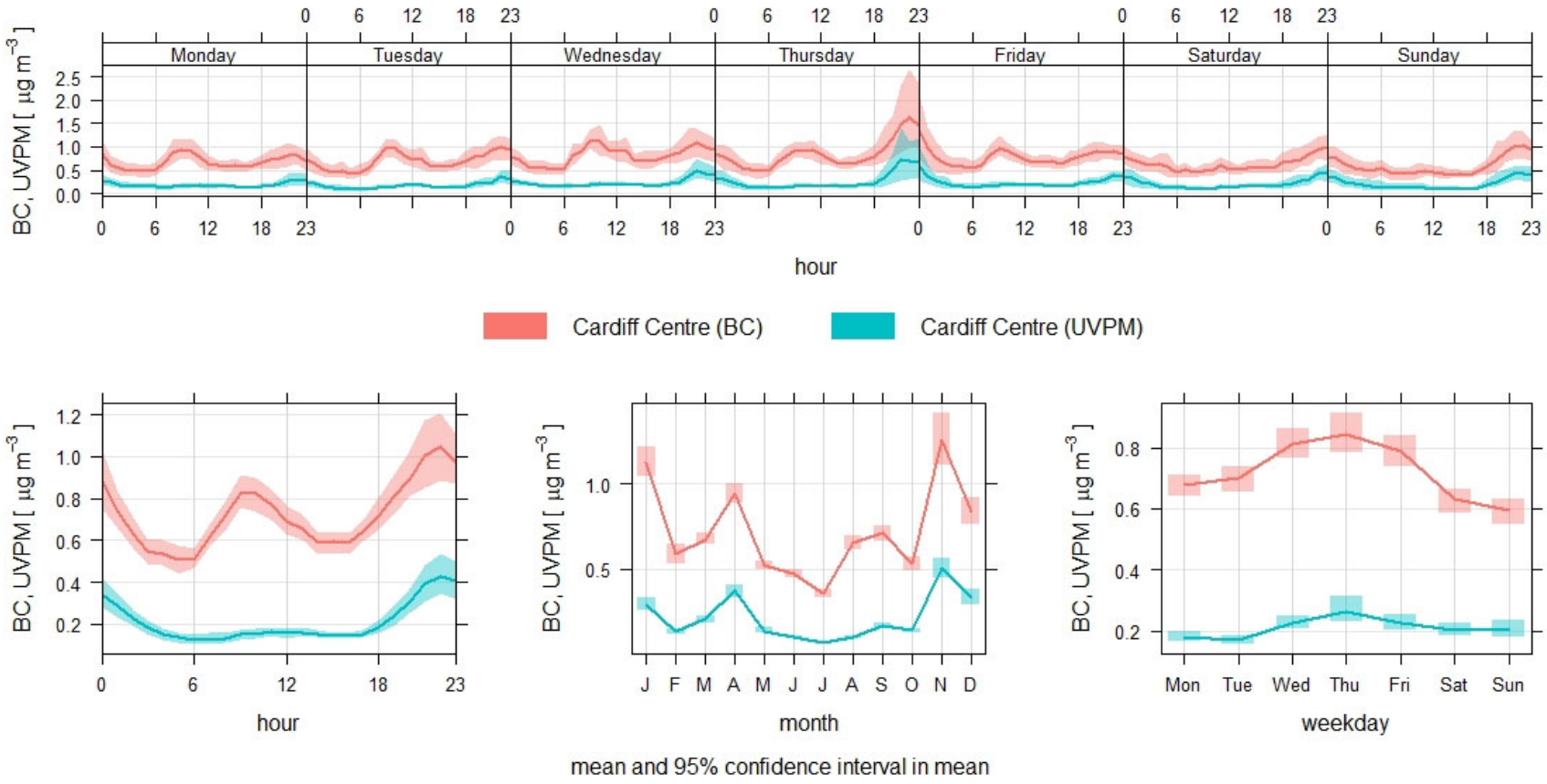


Figure 63 - Temporal variations of BC and UVPM concentrations at Cardiff Centre for 2020

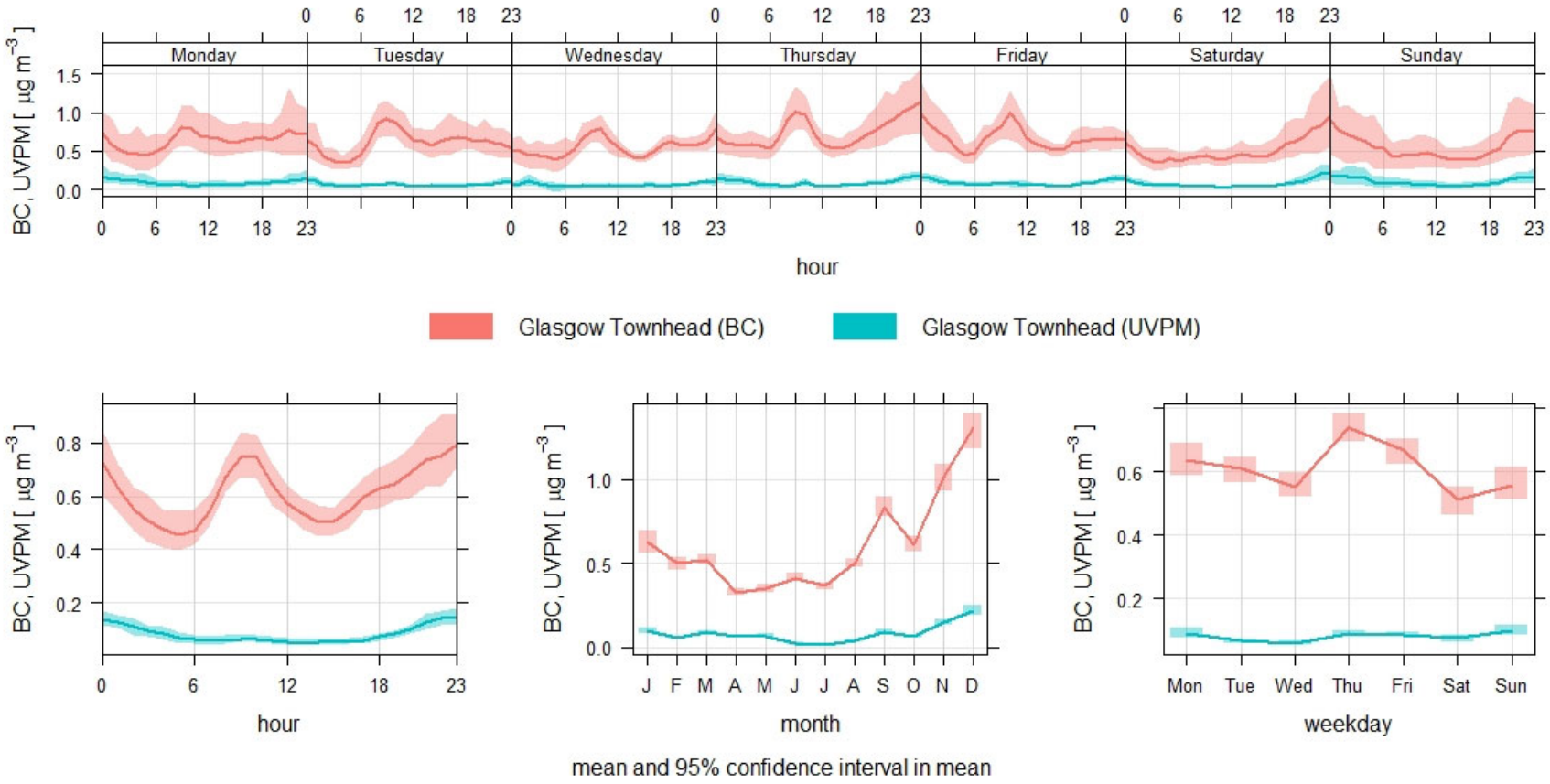


Figure 64 - Temporal variations of BC and UVPM concentrations at Glasgow Townhead for 2020

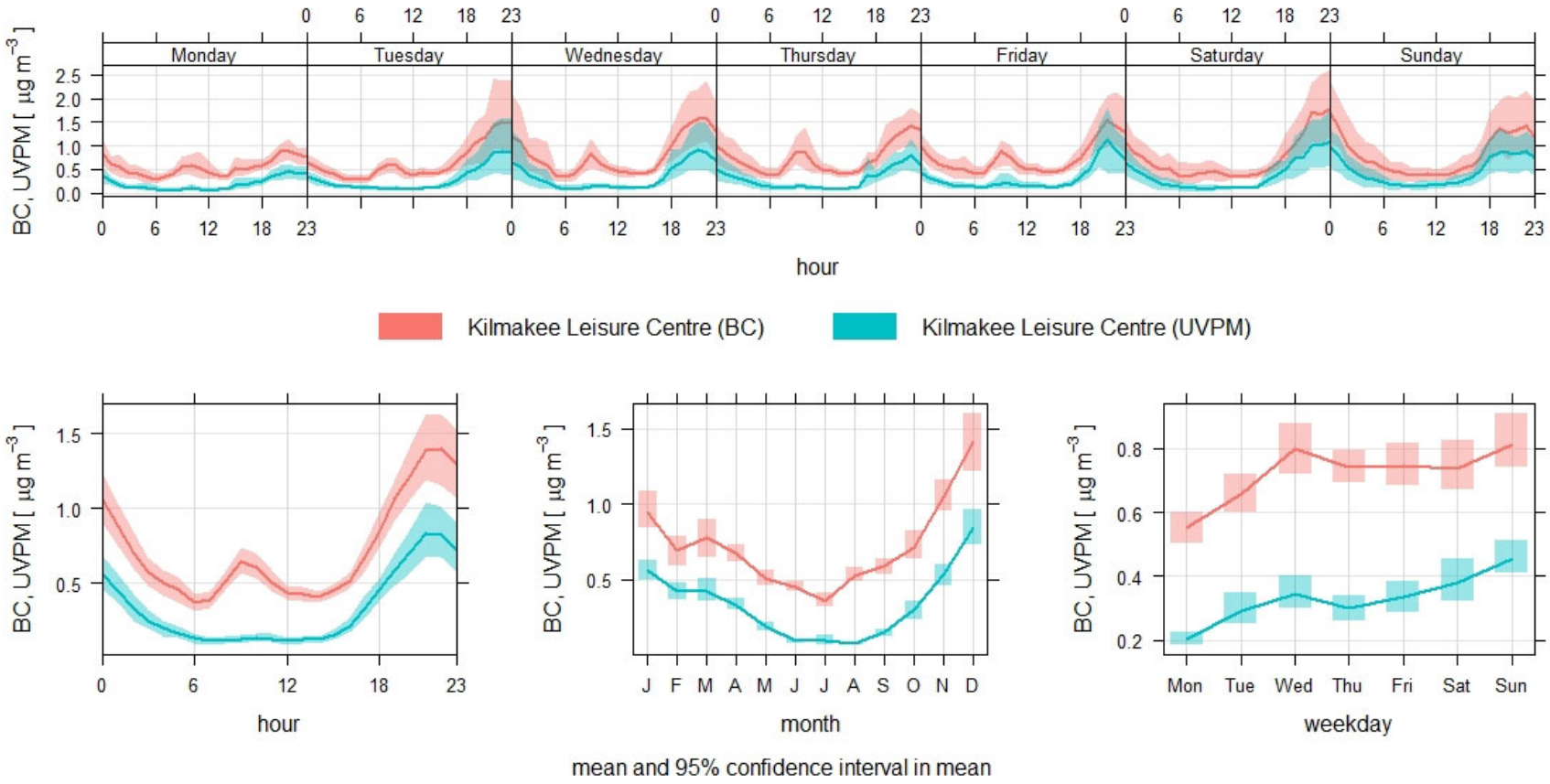


Figure 65 - Temporal variations of BC and UVPM concentrations at Kilmakee Leisure Centre for 2020

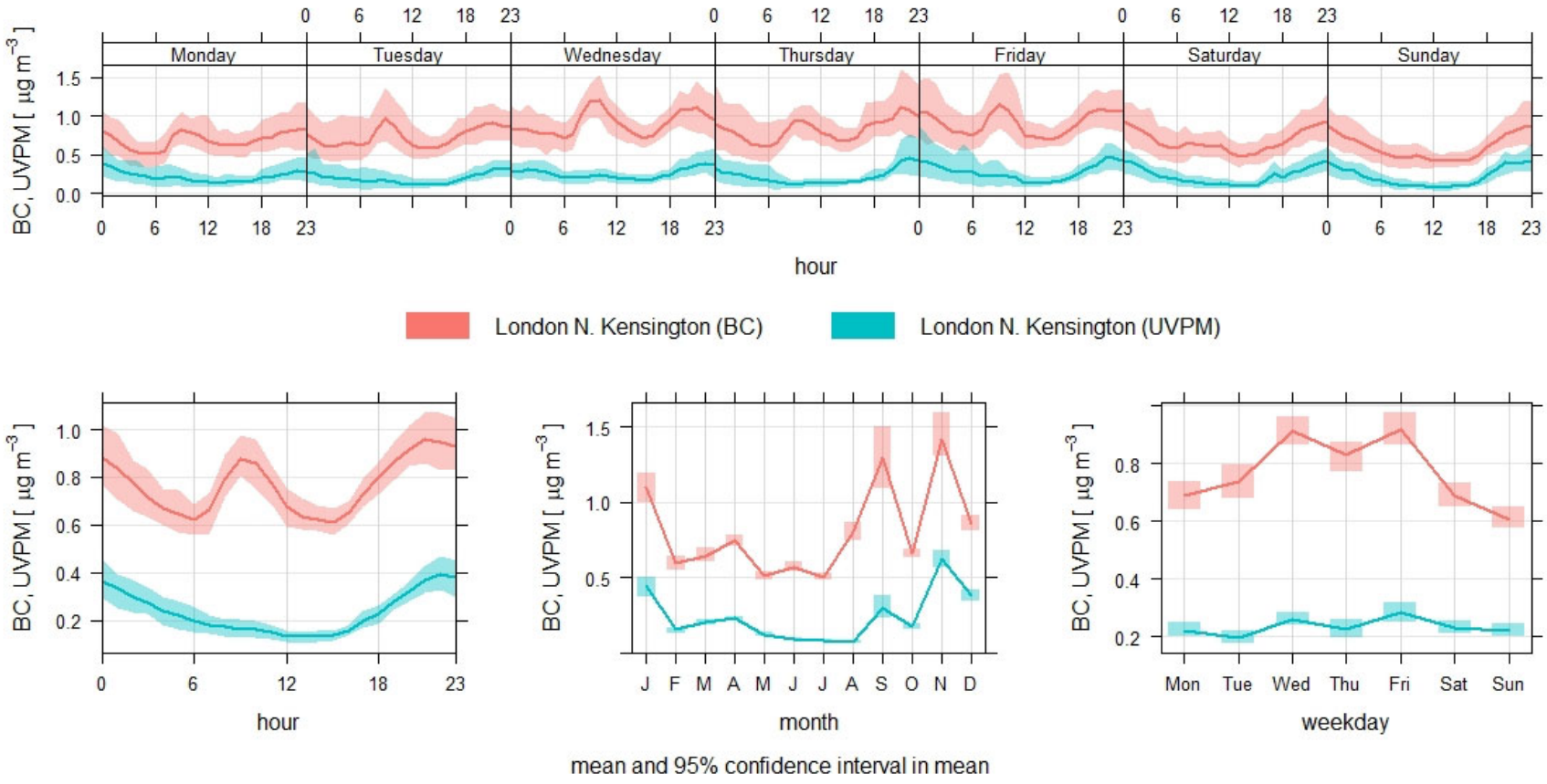


Figure 66 - Temporal variations of BC and UVPM concentrations at London N. Kensington for 2020

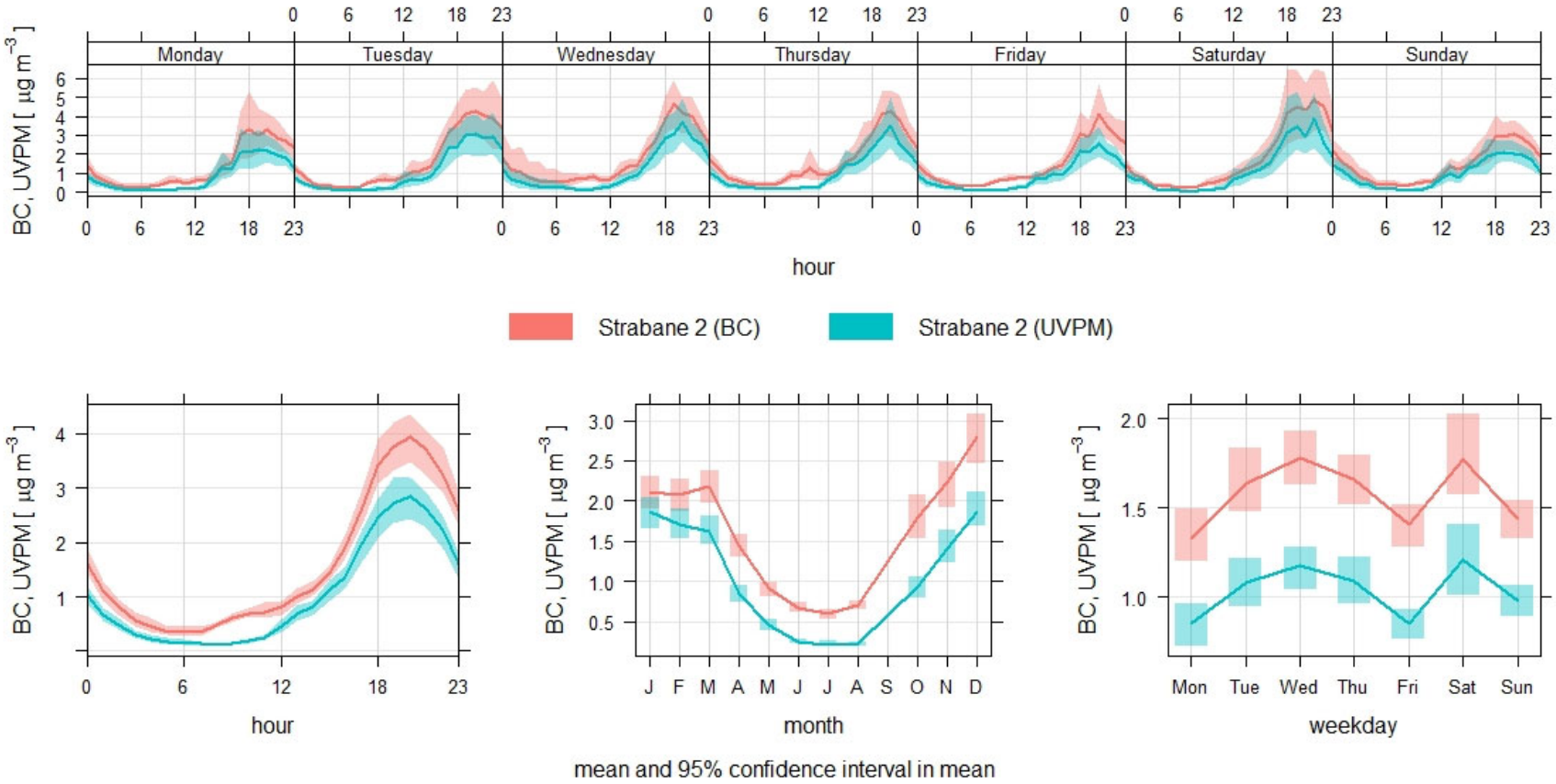


Figure 67 - Temporal variations of BC and UVPM concentrations at Strabane 2 for 2020

BC and UVPM data at Rural Background sites for 2020

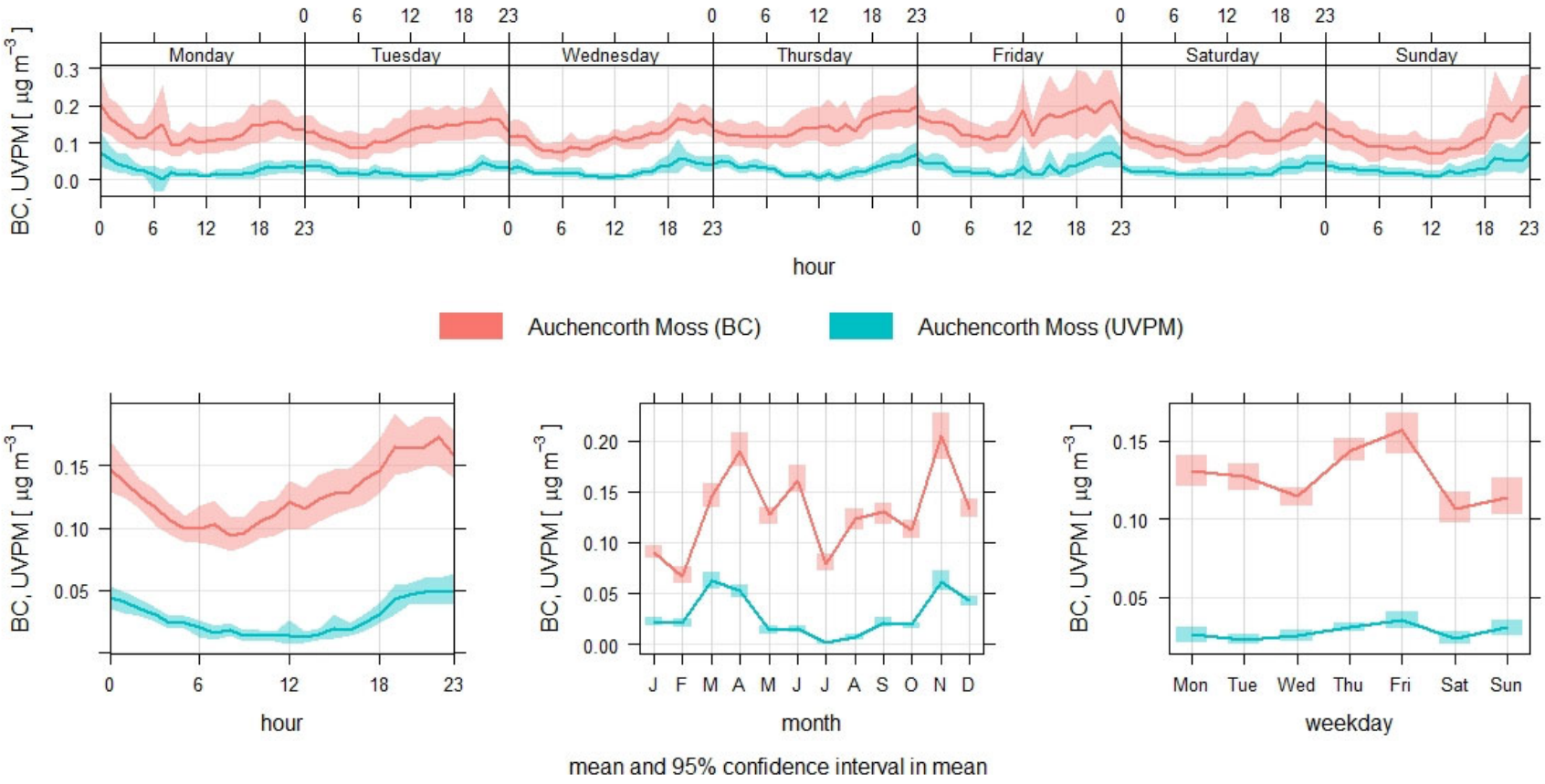


Figure 68 - Temporal variations of BC and UVPM concentrations at Auchencorth Moss for 2020

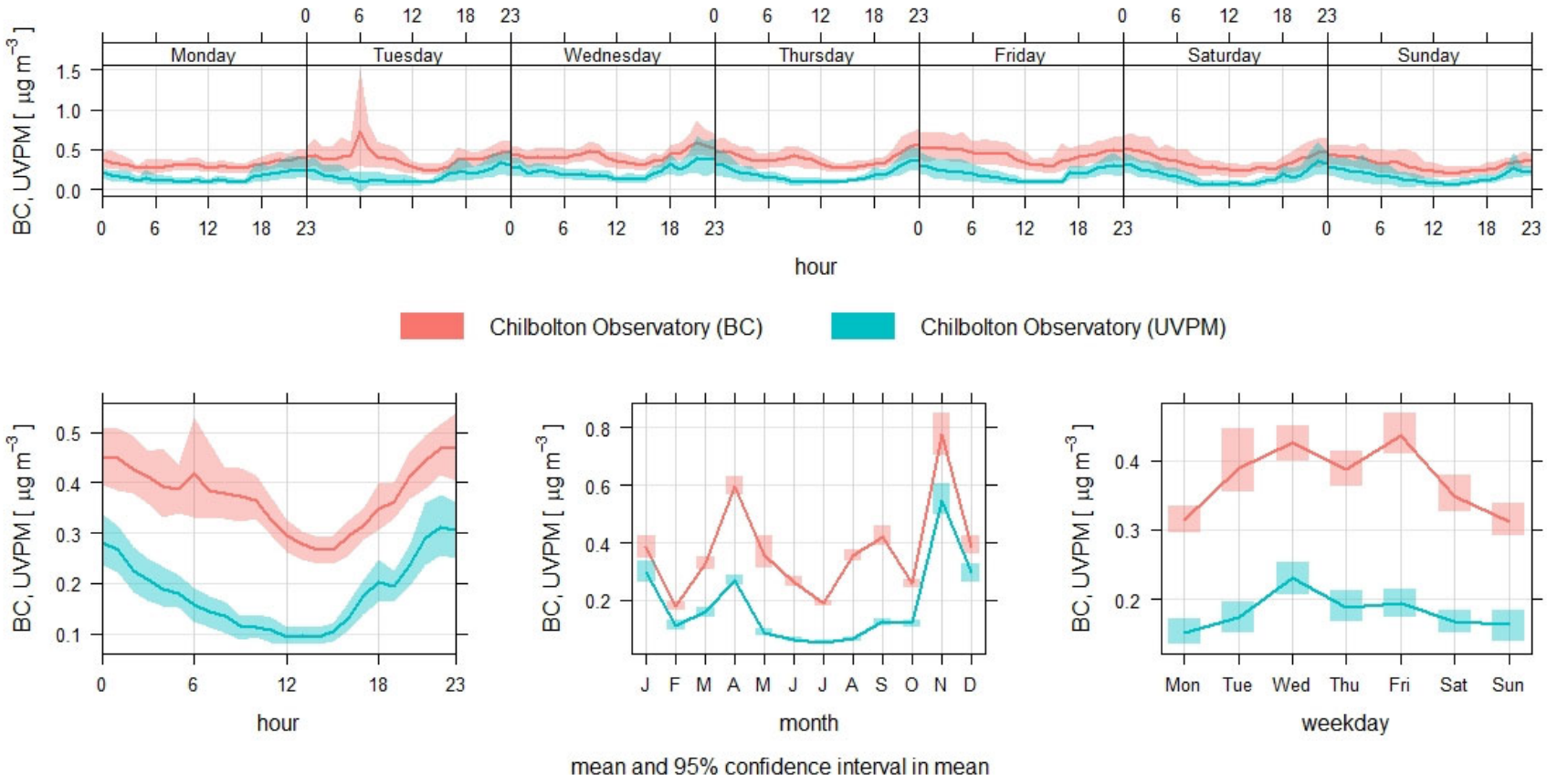


Figure 69 - Temporal variations of BC and UVPM concentrations at Chilbolton Observatory for 2020

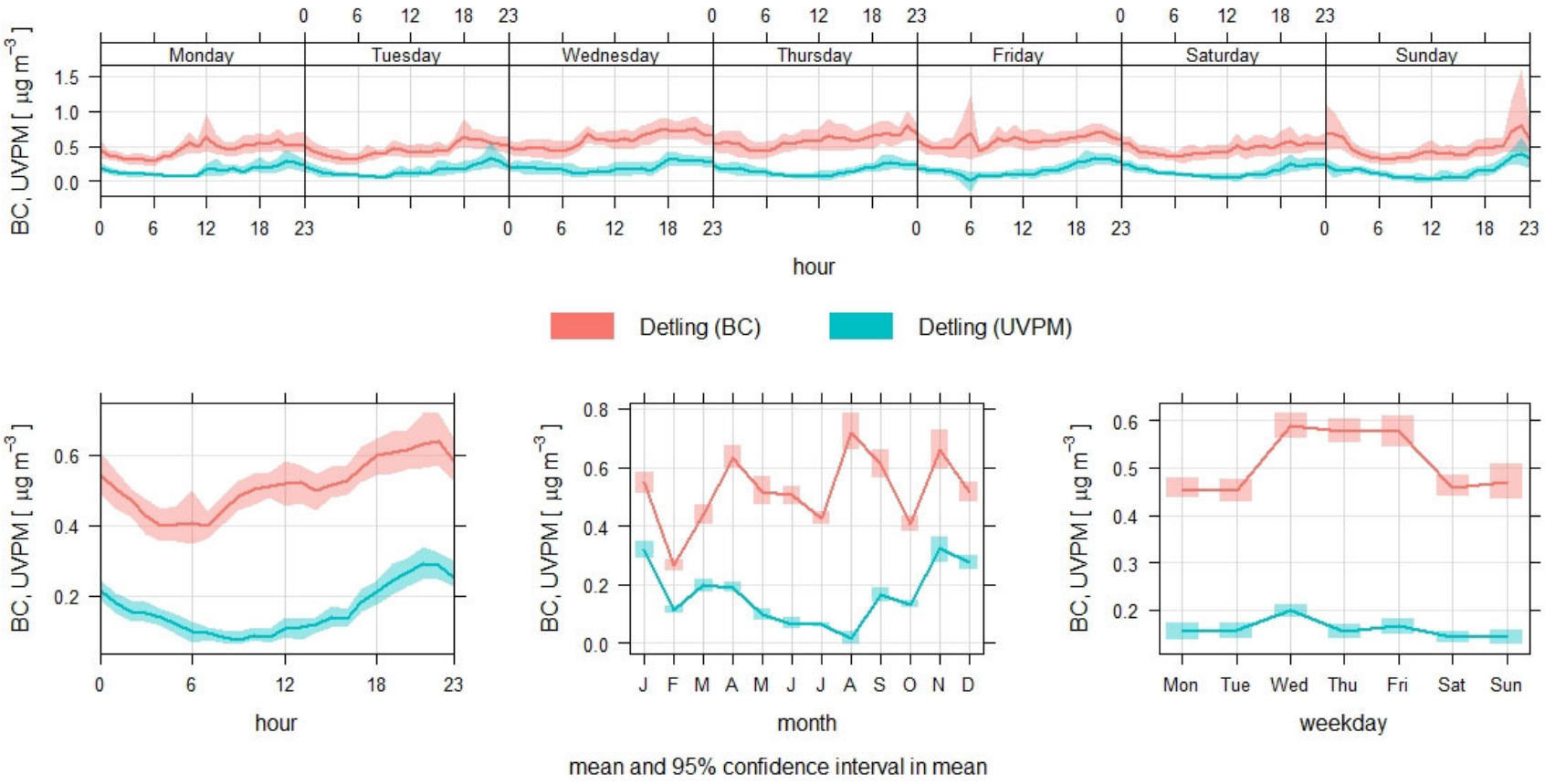


Figure 70 - Temporal variations of BC and UVPM concentrations at Detling for 2020

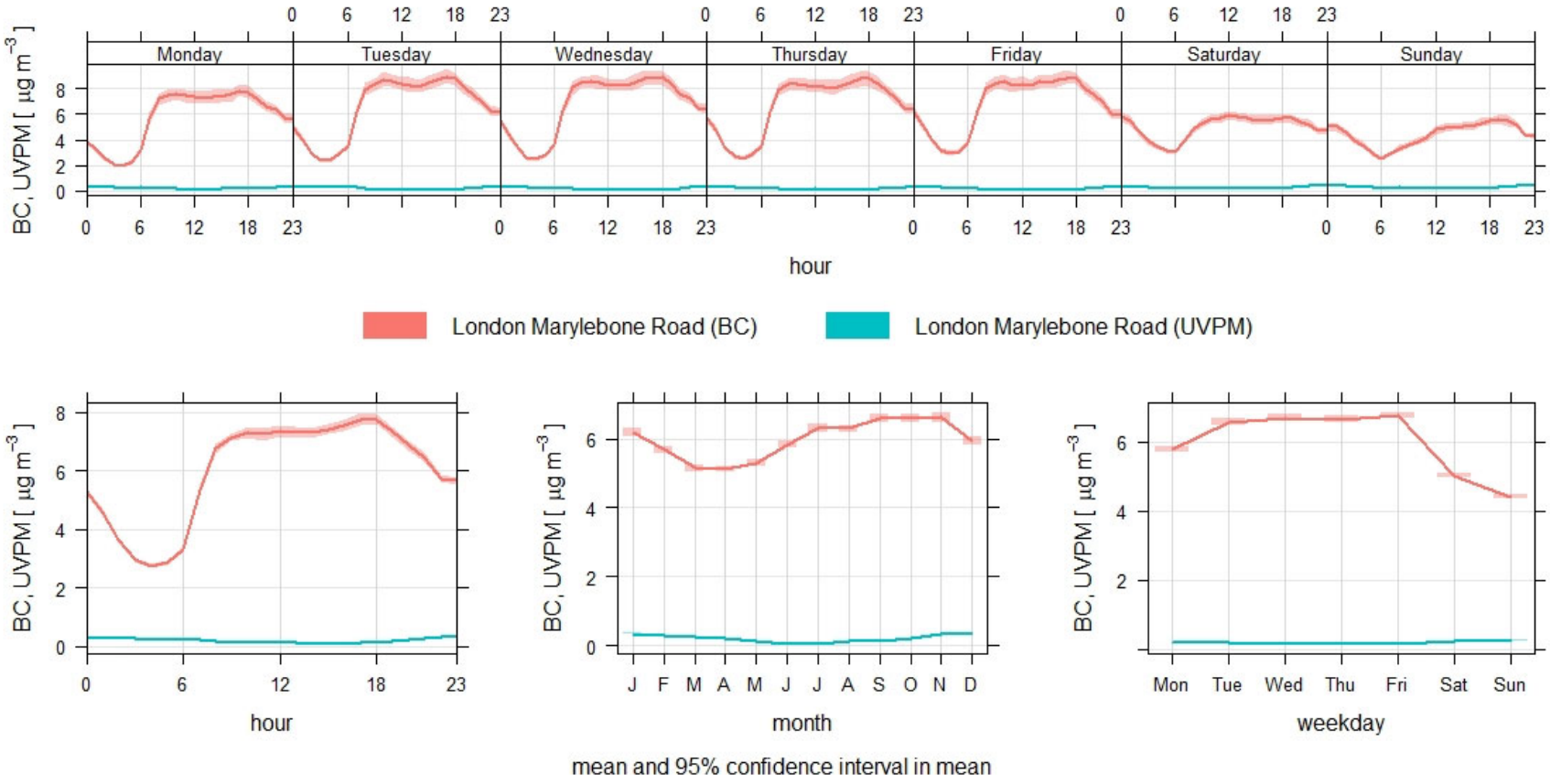


Figure 71 - Temporal variations of BC and UVPM concentrations at London Marylebone Road for 2009-2020

BC and UVPM data at Urban Background Sites for 2009 – 2020

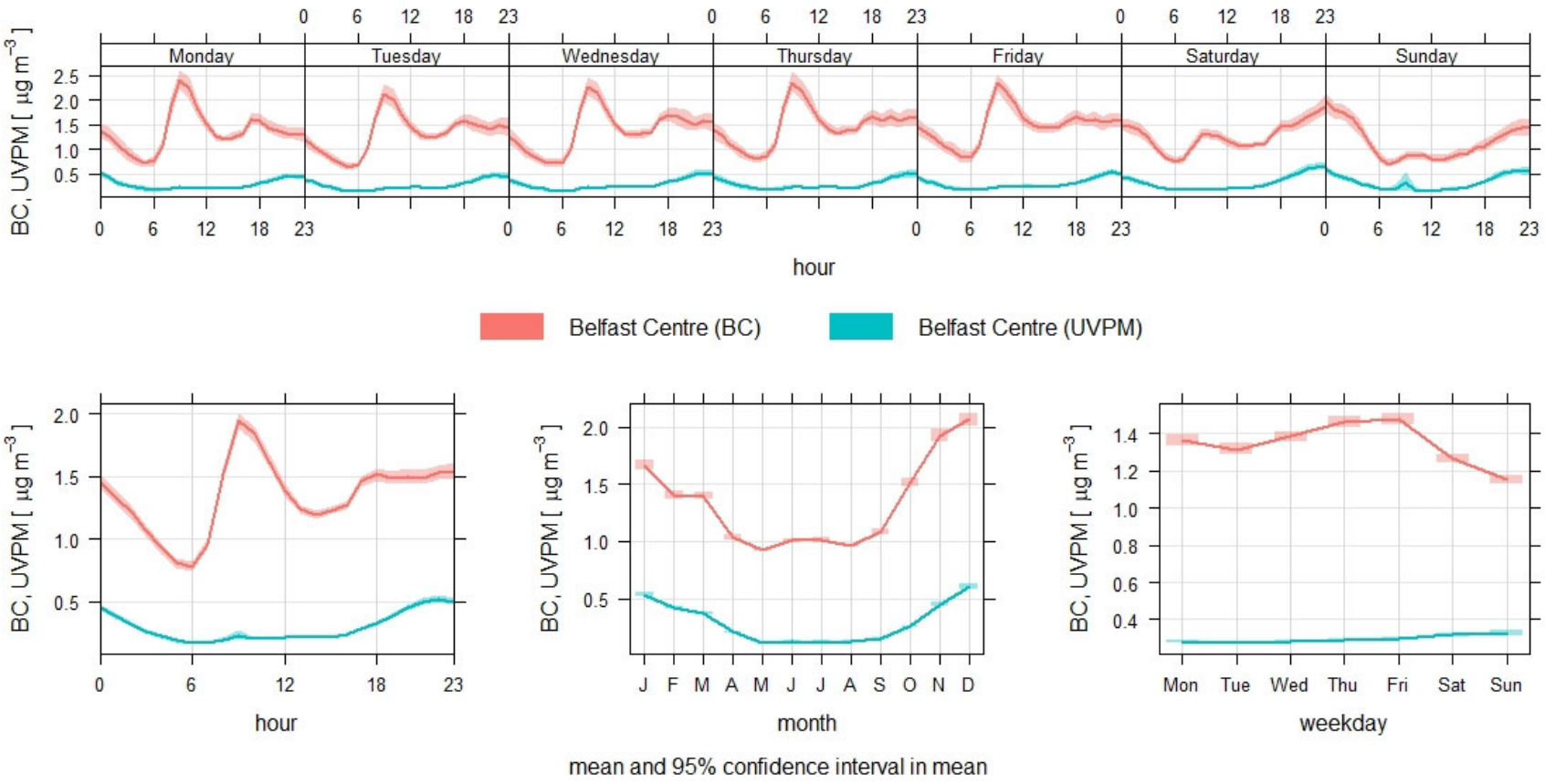


Figure 72 - Temporal variations of BC and UVPM concentrations at Belfast Centre for 2009-2020

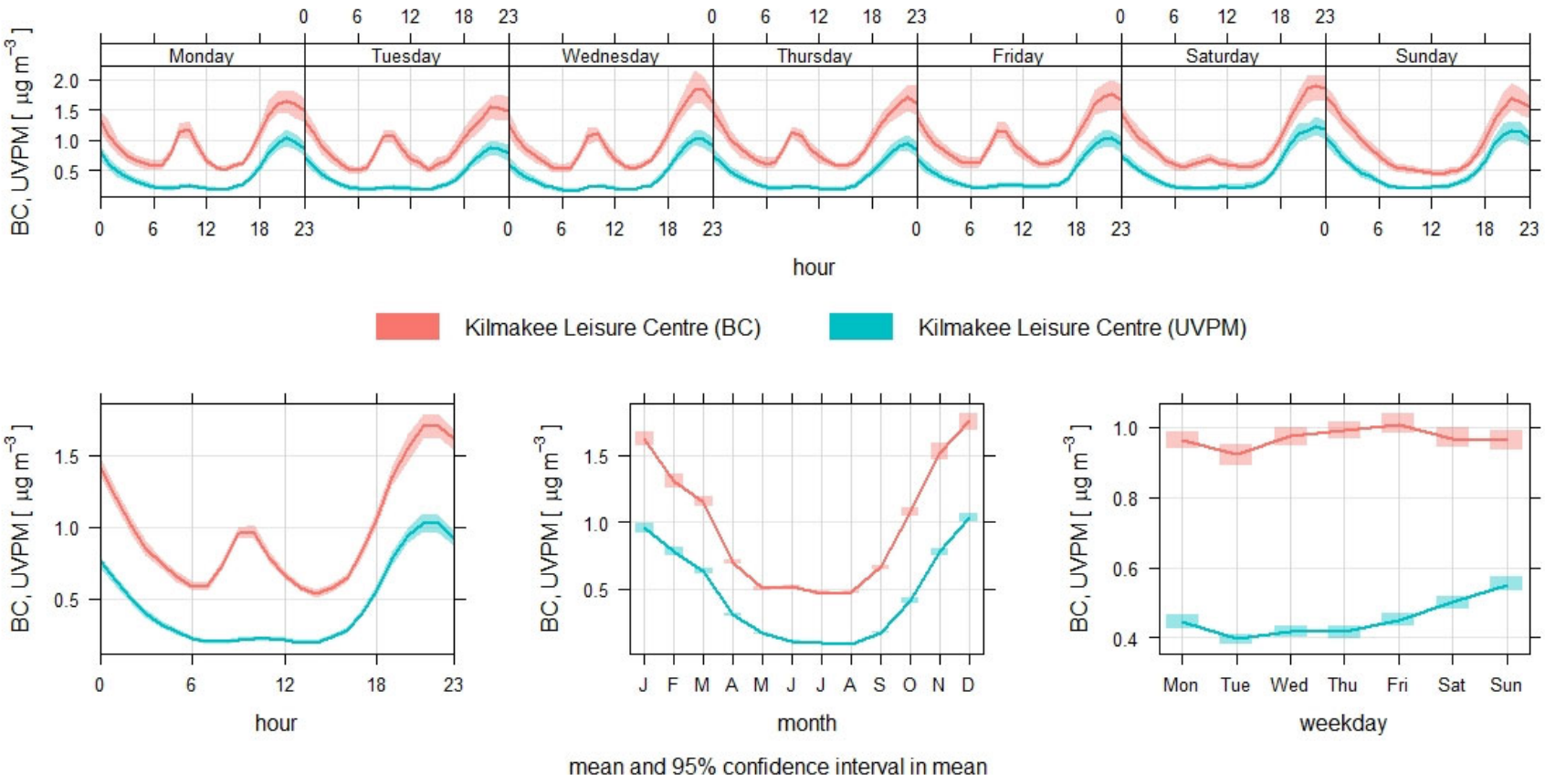


Figure 73 - Temporal variations of BC and UVPM concentrations at Kilmakee Leisure Centre for 2009-2020

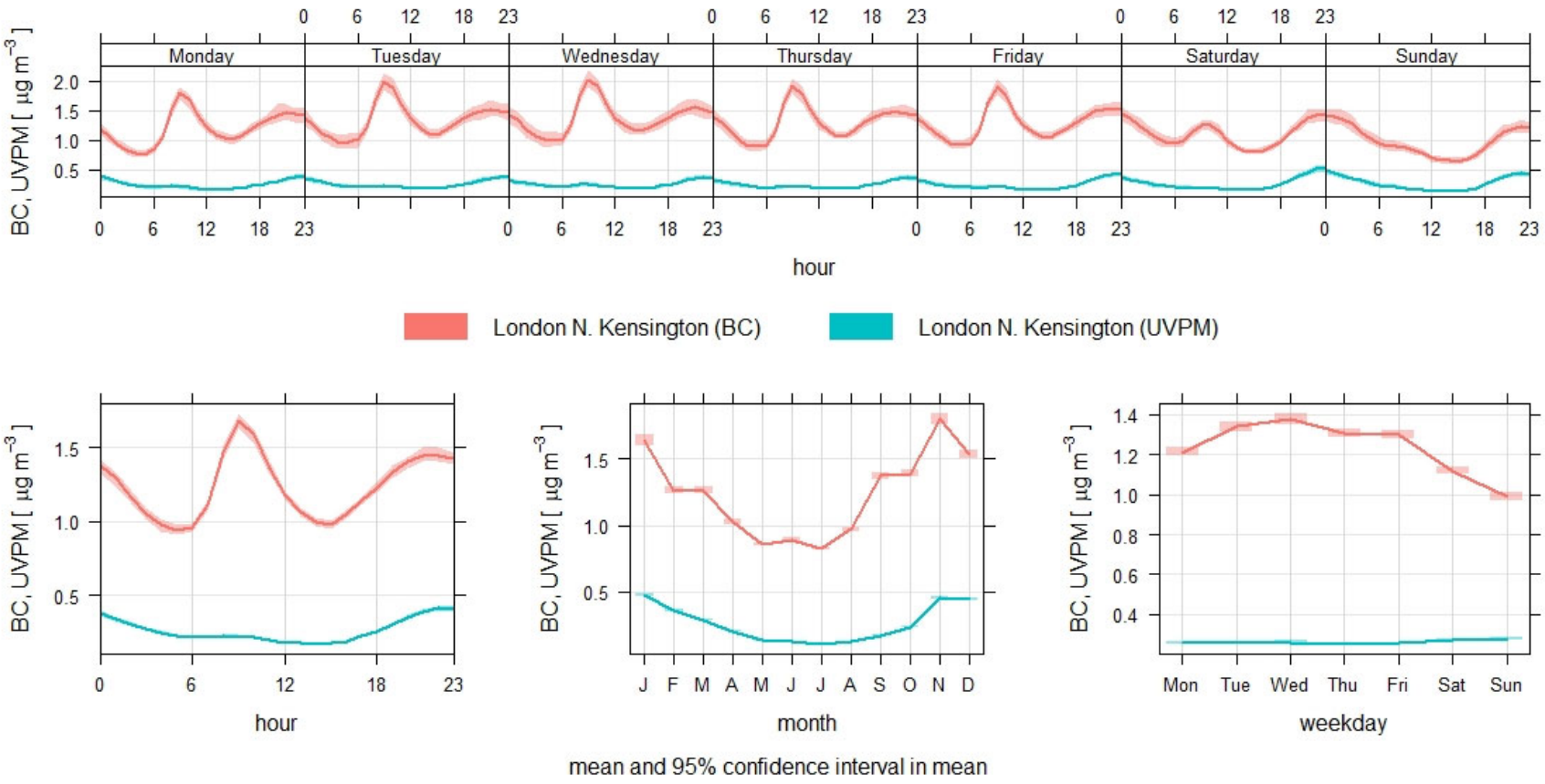


Figure 74 - Temporal variations of BC and UVPM concentrations at London N. Kensington for 2009-2020

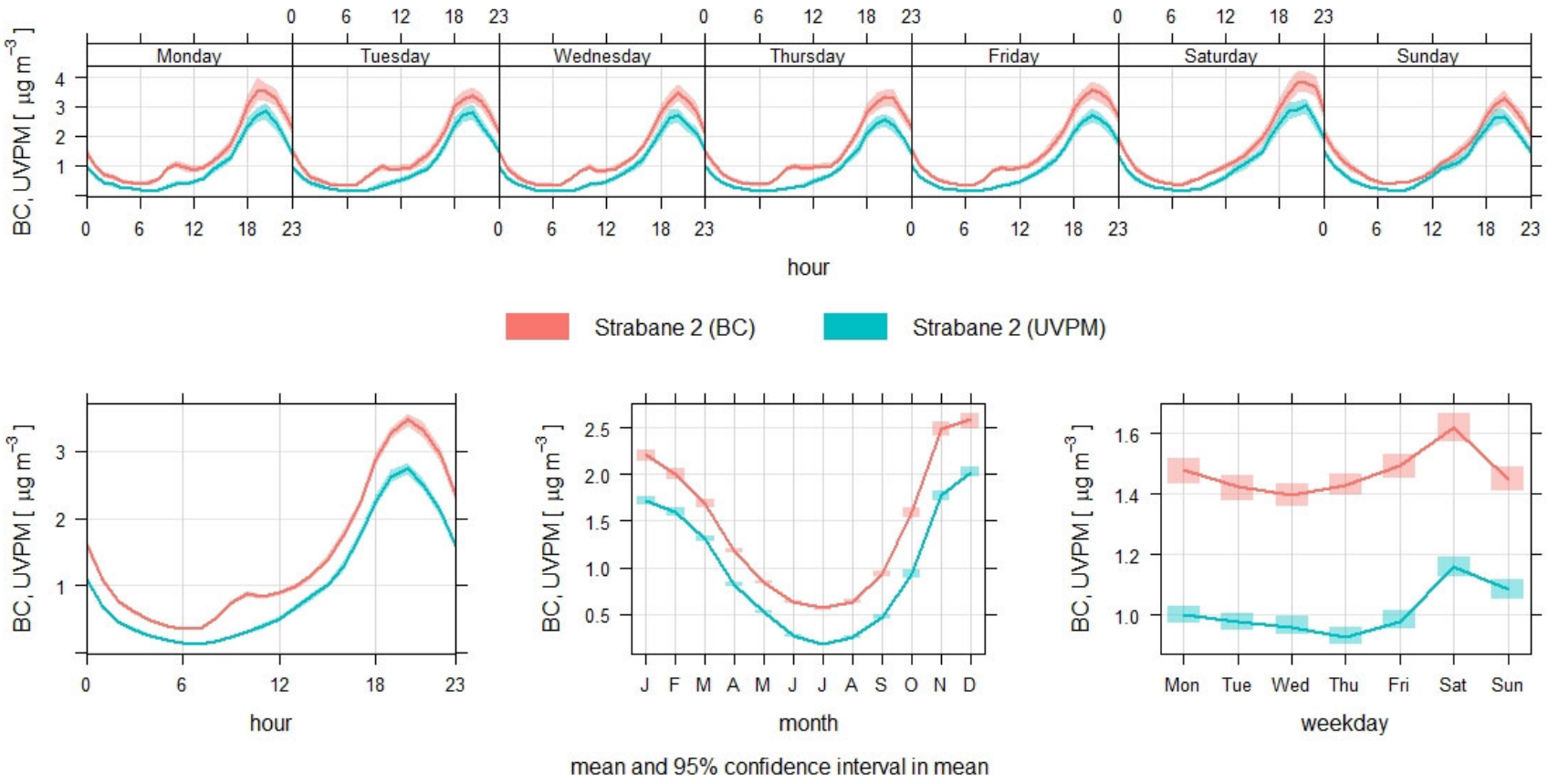


Figure 75 - Temporal variations of BC and UVPM concentrations at Strabane 2 for 2009-2020

Roadside sites

On weekdays the Black Carbon concentrations at the roadside sites followed the expected profile for traffic movements through the day, with raised concentrations in the morning and evening rush hours. This double peak can be seen at all the roadside sites. The weekend days showed slightly lower and more constant Black Carbon concentrations, particularly at London Marylebone Road.

In general, seasonal variations are not expected when traffic is the dominant source. However, due to lockdown restrictions and reduced traffic significantly lower BC concentrations were measured at all three roadside sites in spring and summer months. Much higher concentrations were measured at Birmingham A4540 and Glasgow High Street in winter months, whereas at London Marylebone Road site concentrations were lower and stable in the second half of 2020. There was little UVPM signature in any of the roadside sites.

Urban Background sites

Concentrations measured at Belfast Centre, Cardiff Centre, Glasgow Townhead, Kilmakee Leisure Centre, and London North Kensington showed a signature from traffic, seen as a peak in the morning rush hour with little corresponding increase in UVPM concentrations. Peaks related to the evening rush hour were also seen, but these often also showed an increase in UVPM concentrations. This indicates a domestic emission source which is likely from secondary heating. Strabane 2 site is predominantly influenced by emissions from domestic heating, which can be seen during weekdays and weekends.

The long-term Black Carbon and UVPM concentrations for the period 2009-2020 showed some seasonal dependence, with a decrease in concentration over the summer months and an increase in concentration in the winter months. These results are consistent with previously reported seasonal dependences (2009-2019) indicating that the lockdown restrictions in 2020 have not been a dominant factor on the long-term averages. Thus, to reveal any monthly variability in either BC or UVPM emissions each concentration can be normalised (divided by the annual mean of that component) allowing patterns to be compared even when results are on very different scales. This can be seen in Figure 76, using Belfast Centre as an example.

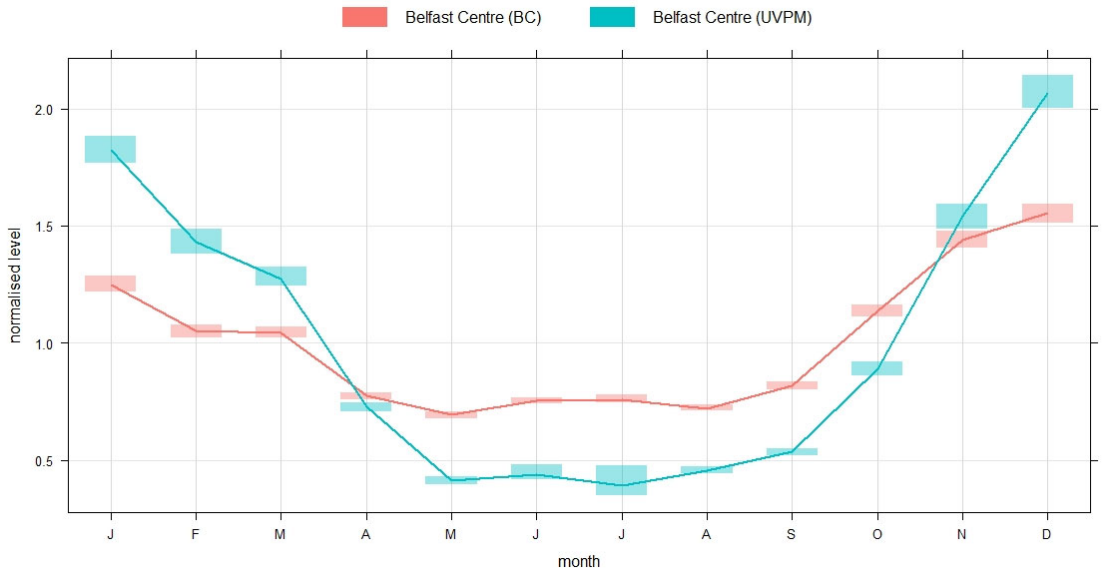


Figure 76 - Normalised monthly variability at Belfast Centre site for the period 2009 - 2020

BC and UVPM concentrations at the Northern Irish sites of Strabane, Ballymena and Dunmurry Kilmakee followed similar hourly, daily and seasonal trends. Concentrations at these sites were dominated by emissions from domestic heating. The highest levels were seen at Strabane, which is not on the natural gas network and where domestic heating mainly comes from oil. Strabane is in a smokeless zone; however, it appears that solid fuel burning may be occurring in residential areas. Due to the large emission factors of PAHs from smoky coal[19] compared to oil and gas, it does not take many buildings burning this coal to have a big influence on ambient concentrations. There is little evidence of traffic emissions during the rush hour periods.

Ballymena and Dunmurry Kilmakee are on the natural gas network, and this is the predominant source of domestic heating, however coal is often used as secondary heating in the evenings. Due to the difference in emission factor discussed above this can have a significant effect on ambient concentrations. Figure 77 gives the normalised monthly variability and Figure 78 gives the hourly variability.

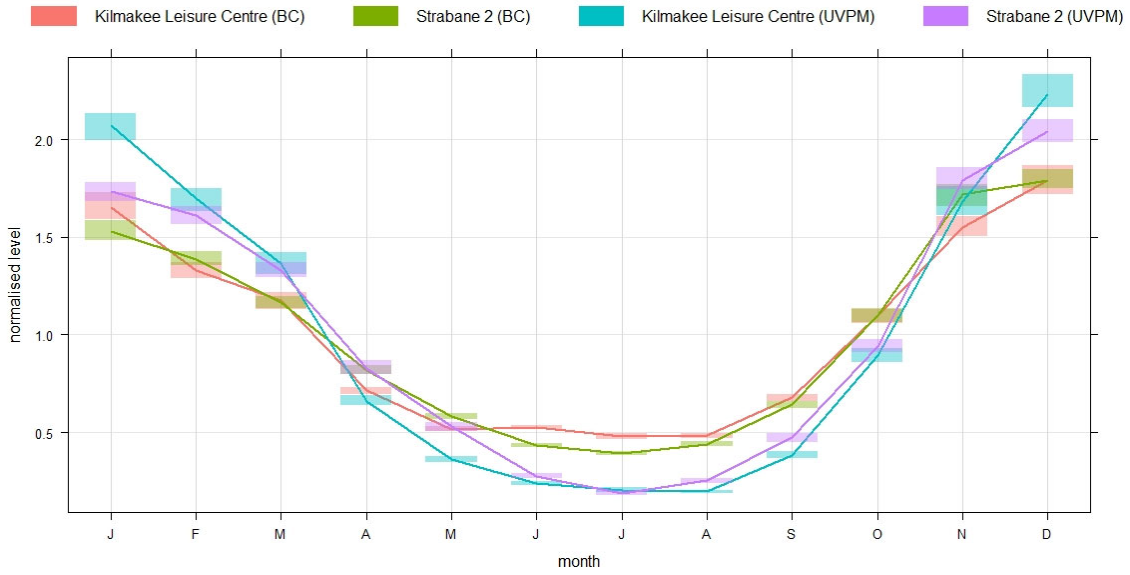
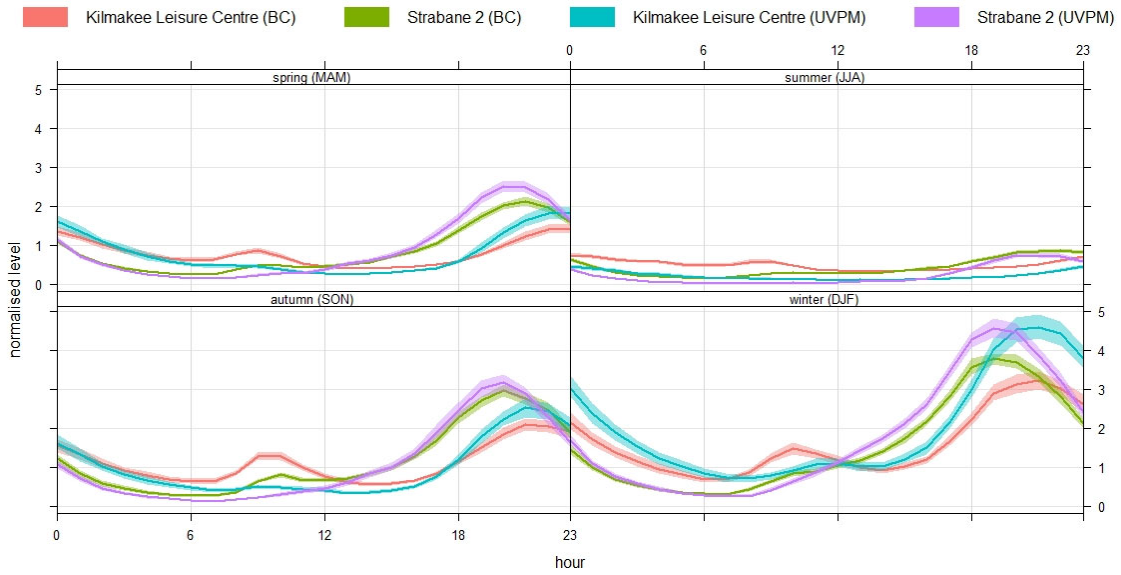


Figure 77 - Normalised monthly variability at Strabane and Dunmurry Kilmakee for the period 2009 – 2020



Note: In the above charts the shaded area on the y-axis represents the uncertainty in the mean y-value due to the spread of results, expressed with a level of confidence of 95%.

Figure 78 - Seasonal diurnal BC and UVPM concentrations measured at Strabane and Dunmurry Kilmakee for the period 2009 – 2020

The evening concentrations of both BC and UVPM peaked an hour earlier in Strabane than they did in Dunmurry Kilmakee. Also, there was still a signature of domestic emission during summer in Strabane that was not present at Dunmurry Kilmakee.

Rural sites

The rural background site concentrations were lower than the other site classifications and without visible morning and evening rush hour peaks. The rise in concentrations in the evening were later than would be expected for a traffic signal and were also seen in the UVPM suggesting a domestic heating source.

4.6.7 Long-term trends

Figure 79 and Figure 80 show the trend in Black Carbon concentrations from the long-running sites in the Network, as monthly averages over the full calendar years 2009 to 2020. The Theil-Sen method in OpenAir[15,16] was used to calculate the regression parameters including slope and uncertainty in the slope.

The Theil-Sen method chooses the median slope among all lines through pairs of two-dimensional sample points. The Theil-Sen estimator tends to yield accurate confidence intervals even with non-normal data and heteroscedasticity (non-constant error variance). It is also resistant to outliers.

Bootstrap resampling provides the confidence interval for the regression slope. For these analyses the 2.5^{th} and 97.5^{th} percentile slopes are taken from all possible slopes.

Over the period 2009 to 2020 all the long-running sites in the network apart from Strabane have shown a significant downward trend in Black Carbon concentrations. The decrease at London Marylebone Road is much larger than the other sites and Black Carbon concentrations have been falling consistently since 2011.

Figure 81 and Figure 82 show the long-term trends in UVPM concentration.

The London Marylebone Road UVPM concentration showed a significant upward trend over the period 2009 to 2020, this was probably due to the reduced Black Carbon concentrations over the latter years. As the Aethalometer measures the UVPM by the difference between the BC and UV channel. However, trend for Marylebone Road and Kilmakee Leisure Centre sites should be treated with caution due to the low concentrations involved.

To show how pollutant concentrations can depend strongly on the weather, the 2009-2020 UVPM concentrations at Strabane, which were strongly affected by domestic solid fuel use, are plotted in Figure 83, along with average temperature for same period. Temperature measurements from Armagh have been used as this is the nearest Met Office site with a long time series.

The UVPM concentration was inversely related to the average ambient temperature. This is a good indication that the main source of UVPM emissions is local domestic heating in Strabane. This was evident in both the winter and the summer indicating that there were still solid fuel emissions in the summertime. The relationship is shown in Figure 84 as a scatter plot.

There was a clear linear relationship between increased UVPM concentrations with a drop in ambient temperature, due to the increase in fuel usage in cold weather periods. There is an indication that the UVPM source became significant when average temperatures were below $15^{o}C$, linking the UVPM to fuels used for domestic heating systems.

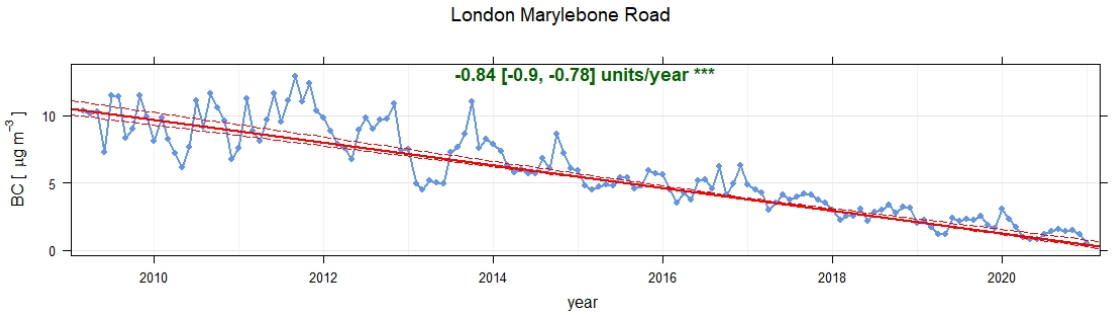


Figure 79 - BC trends measured at the roadside site, 2009 – 2020

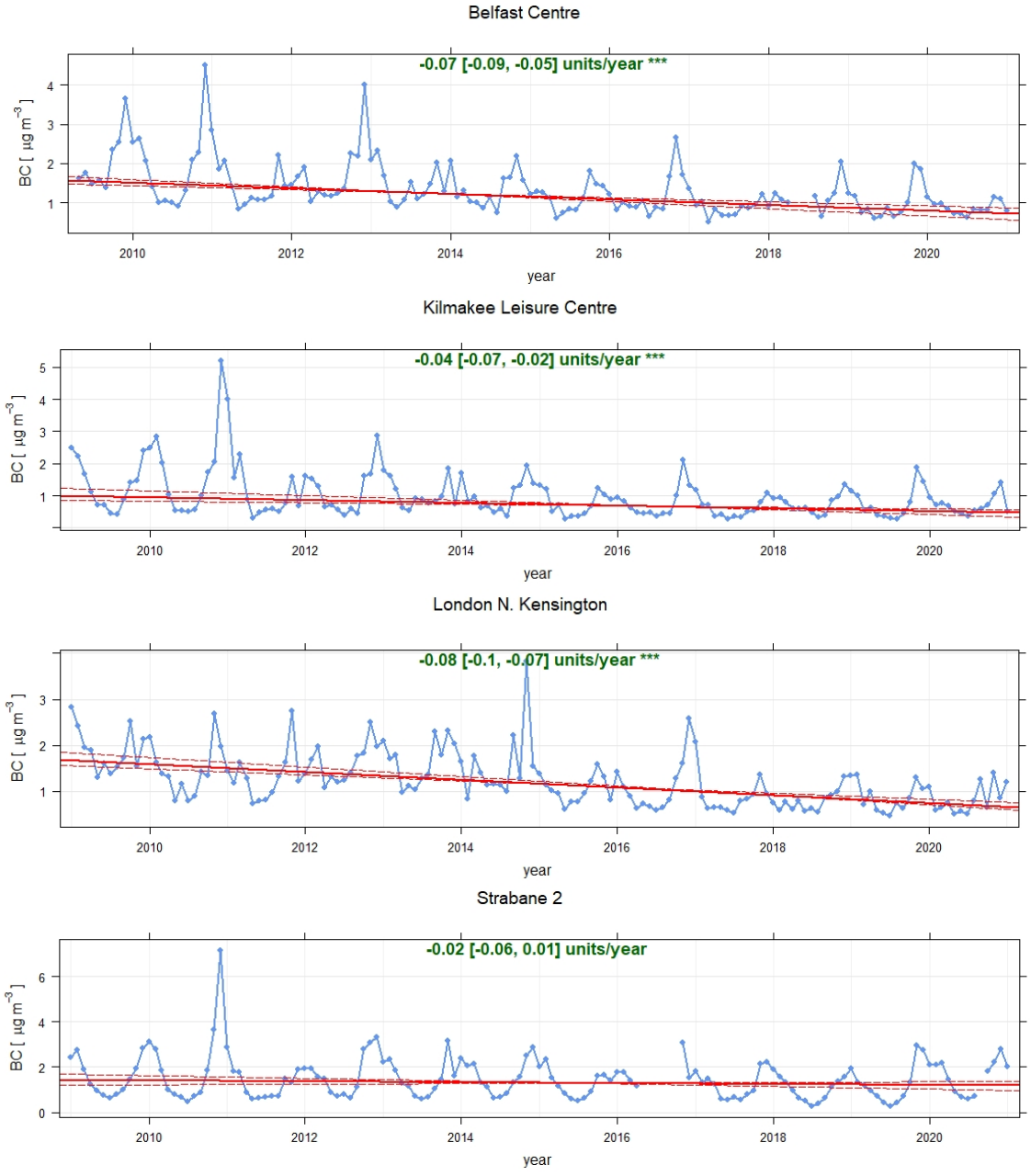


Figure 80 - BC trends measured at urban background sites, 2009 – 2020

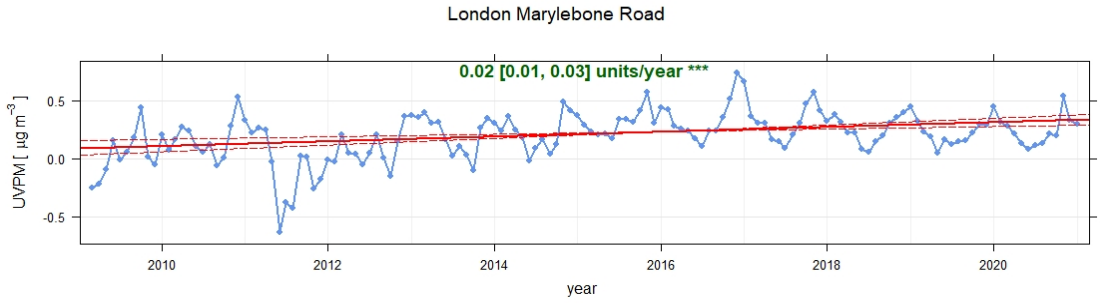


Figure 81 - UVPM concentrations measured at roadside sites, 2009 – 2020

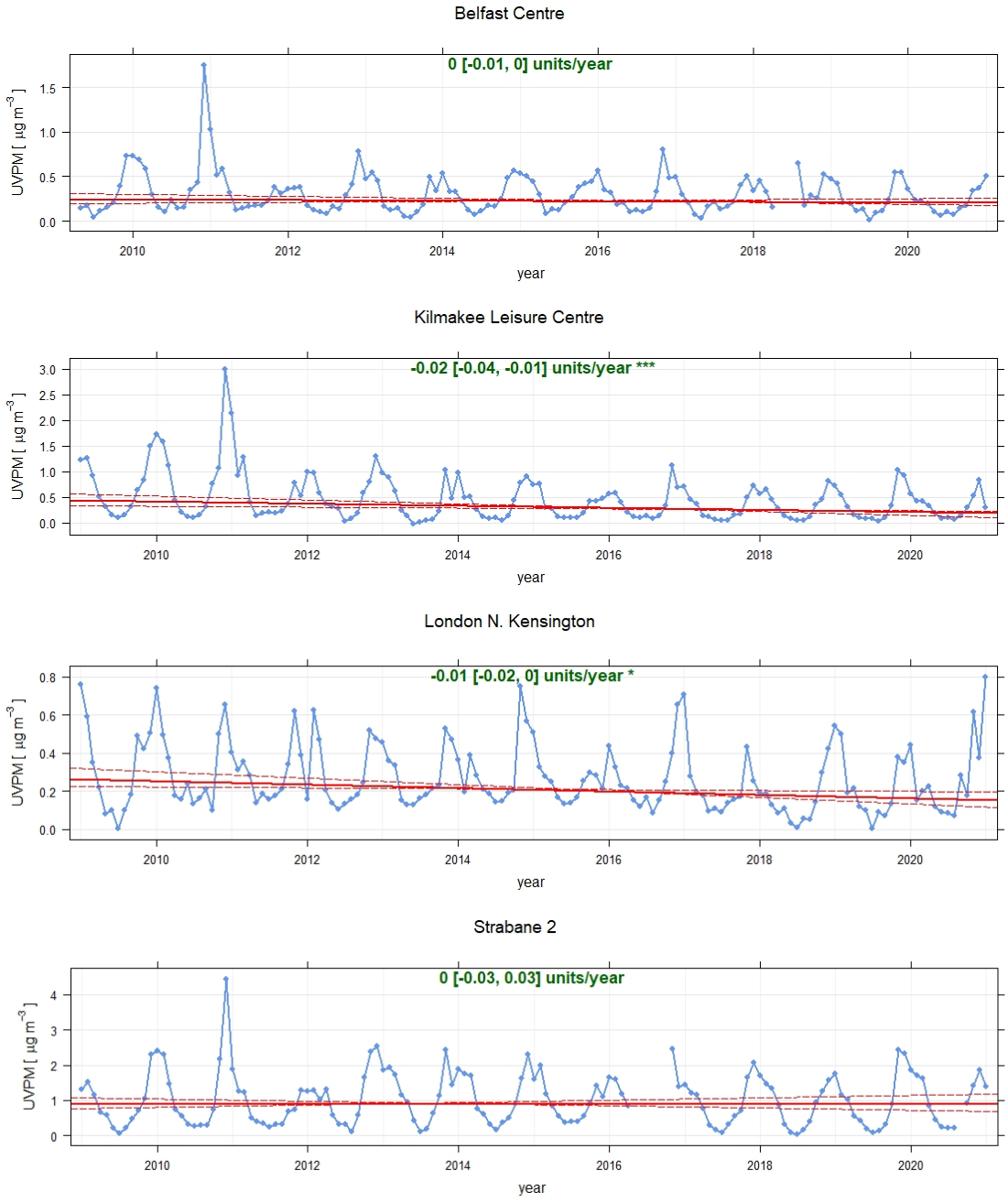


Figure 82 - UVPM concentrations measured at urban background sites, 2009 – 2020

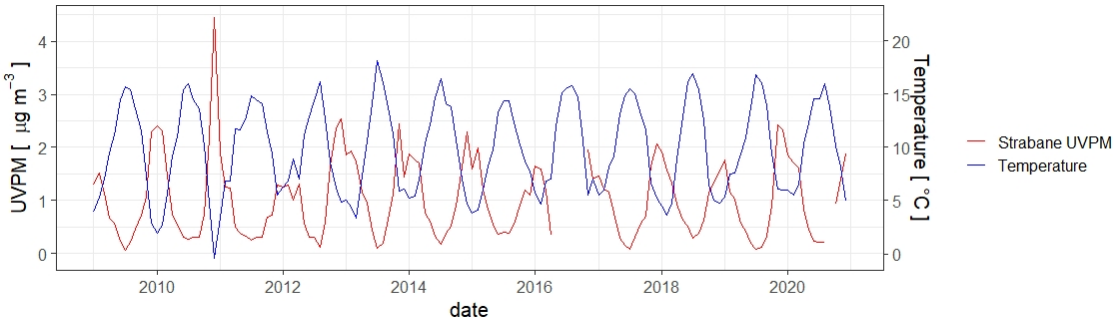


Figure 83 - Strabane monthly UVPM concentration and average ambient temperature for 2009-2020

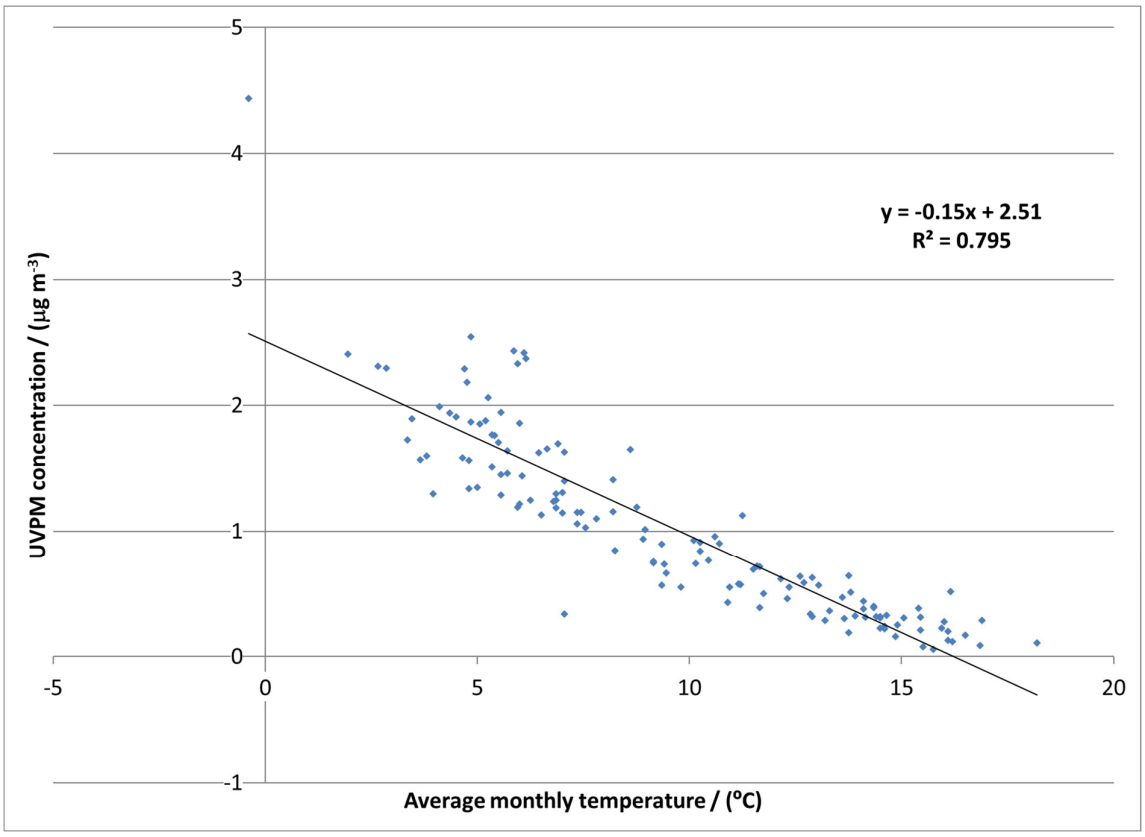


Figure 84 - Scatter plot of monthly UVPM concentration versus ambient temperature at Strabane 2 site over the period 2009 -2020

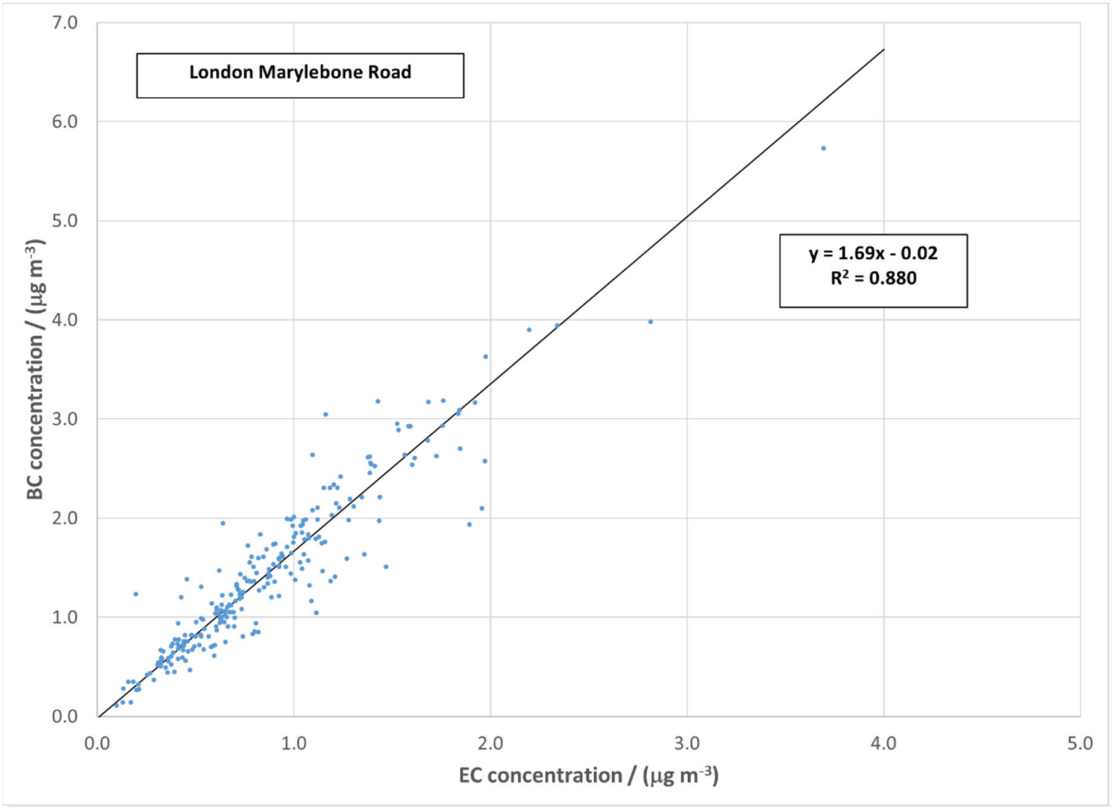
4.6.8 Comparisons with other pollutants

Comparisons are possible between Elemental Carbon and Black Carbon concentrations at two sites, and between Polycyclic Aromatic Hydrocarbon (PAH) and UVPM concentrations at seven sites. Comparisons were also made with particle mass concentration measurements where these instruments were collocated with the Aethalometer.

4.6.8.1 Elemental Carbon

Daily Elemental Carbon (EC) measurements were made at London Marylebone Road, Chilbolton Observatory, and until 2018, at London North Kensington, at which point those measurements moved to the London Honor Oak Park site. Co-located measurements of Black Carbon ($PM_{2.5}$) have been averaged into daily measurements and plotted as scatter plots against the EC concentrations in Figure 85. The regression is calculated according to the Reduced Major Axis (RMA) method[20], which is based on minimising the product of the *x* and *y* deviations between the data values and "fitted values" instead of the least squares method, which minimises the sum of the squared deviations between the dependent variable (y) and the "fitted values". RMA is better suited to air quality measurements as pollutant concentrations are often related to each other, so there is no real separation into dependent and independent variables.

In principle, the chemically based Elemental Carbon metric and the optically based Black Carbon metric both quantify the "soot" component of airborne particles. 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.



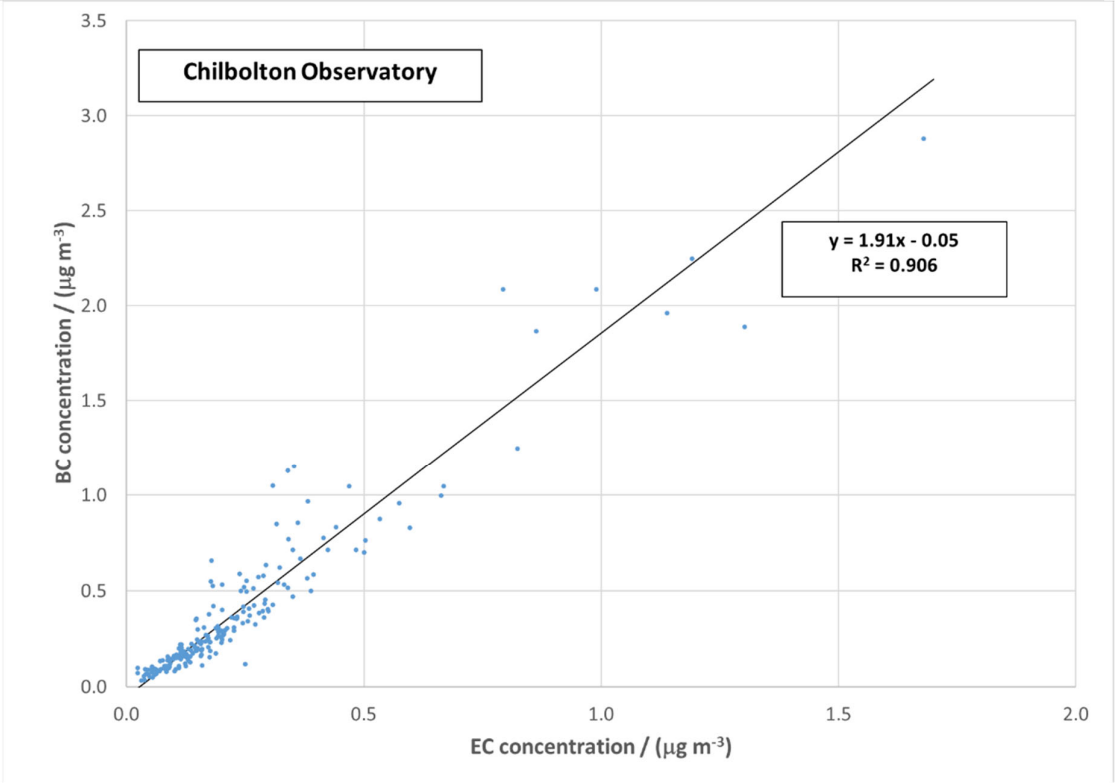


Figure 85 - Comparison between BC and EC at the London Marylebone Road and Chilbolton Observatory sites in 2020

There was a good linear relationship (R^2 > 0.87) between the EC and BC concentrations at the Chilbolton Observatory and London Marylebone Road sites in 2020 (see Table 14).

Table 14 - Relationship between Black Carbon ($PM_{2.5}$) and Elemental Carbon (PM_{10} & $PM_{2.5}$) 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
2020	1.91 x - 0.05	0.906	-	-	1.69 x - 0.02	0.880

Notes
*There was insufficient BC data collected at Harwell in 2009 to form a reliable relationship as the Aethalometer was only installed in November 2009. The January 2016 to October 2019 EC data are from Chilbolton Observatory (using a PM_{10} Partisol sampler) and so may not be directly comparable to the Harwell data from previous years. The Chilbolton 2020 data used in this comparison are from using the $PM_{2.5}$ Leckel sampler which began daily measurements from June 2020.
**The EC instrument was moved to London Honor Oak Park at the end of 2018.

The regression parameters between Black Carbon and Elemental Carbon in 2020 were somewhat different between sites, and on a year-to-year basis. 2020 results may not be directly comparable to the period from 2009 to 2019 due to upgrade of the Aethalometer model (November 2019) and limited EC data at the Chilbolton Observatory site (EC instrument was installed in June 2020). In all cases, however, the intercept value was relatively small which indicates that there was no significant zero offset between the two methods.

The concentrations of Elemental Carbon at London Marylebone Road have followed a similar trend. Figure 86 shows the annual Black Carbon and Elemental Carbon concentrations along with the average daily traffic flow past the site, from the DfT traffic count webpage[18].

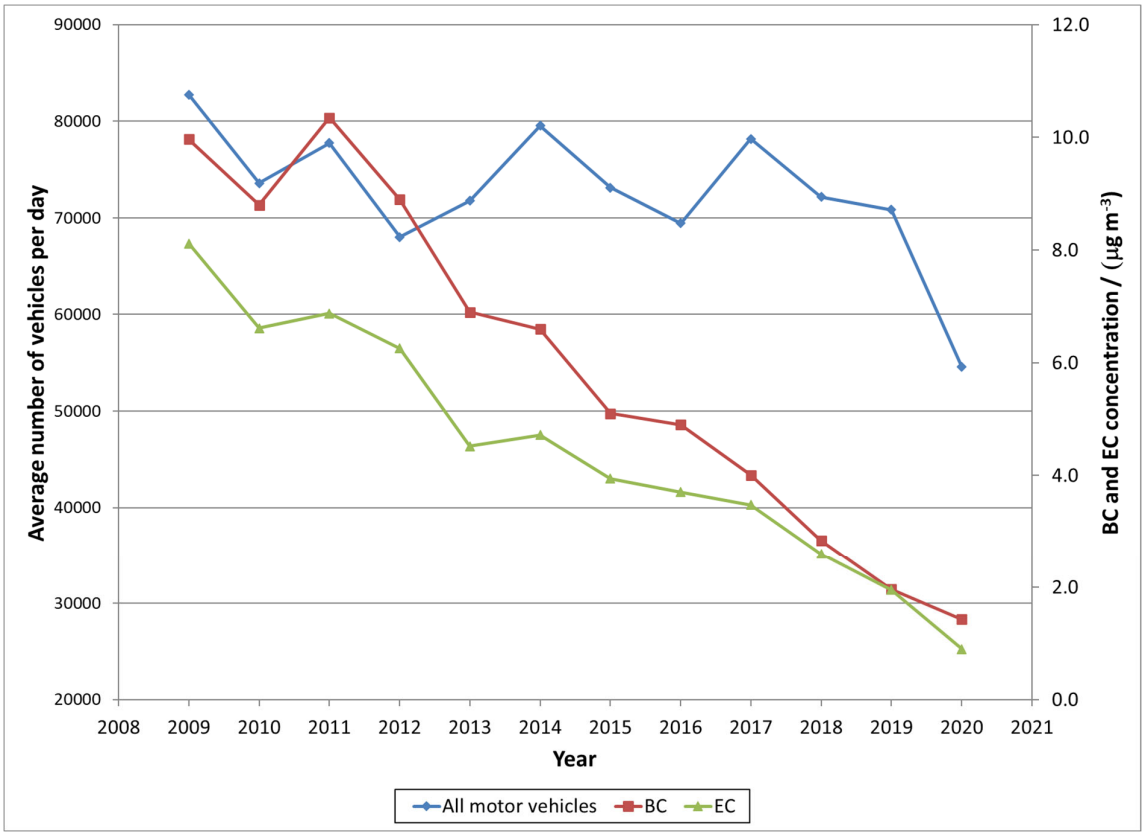


Figure 86 - Annual Average Black Carbon, Elemental Carbon and Motor Vehicles per day at London Marylebone Road for the period 2009 – 2020

The changes in Black Carbon and Elemental Carbon concentrations followed changes in the total traffic flow for the years 2009 to 2012 but since 2013 to 2019 they have decreased while traffic flows have been effectively constant. This would indicate that Black Carbon emissions per vehicle have decreased over the last years. The drop in emissions per vehicle type may be linked to the increased proportion of low emission buses (hybrid, electric and fuel cell / hybrid) in the London bus fleet[21]. Also, 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 emissions from road transport. On 8th April 2019 the Ultra-Low Emission Zone (ULEZ) replaced the T-Charge in central London. The emission standards are: Euro IV for petrol cars and vans and Euro VI for diesel cars, vans, lorries, coaches, and buses. Although London Marylebone Road itself is not included in the ULEZ, further decrease in number of buses and coaches (-2.3 %) as well as HGVs (-3.3 %) was observed in 2019.

In 2020, due to Covid-19 lockdown restrictions, vehicle numbers decreased significantly when compared to the previous year by a factor of 1.3. Although BC and EC followed the same trend, the decrease in concentrations were by factors of 1.4 and 2.2, respectively.

Table 15 shows the composition of the London bus fleet over the period 2010 to 2020. 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.

Table 15 - Composition of London bus fleet, 2010 to 2020 (as of 31 March)

		Number of buses										
Bus Type	**Drive train type**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**	**2019**	**2020**
New Routemaster	Hybrid	0	0	5	8	168	432	736	953	1,000	1,000	1,000
Routemaster	Diesel	18	18	19	20	19	19	10	10	10	10	7
Artic	Diesel	320	260	0	0	0	0	0	0	0	0	0
Single deck	Diesel	2,676	2,930	2,661	2,608	2,606	2,662	2,617	2,612	2,587	2,435	2406
	Fuel Cell/Hybrid	0	5	5	5	8	8	8	8	10	10	2
	Hybrid	27	27	33	28	23	23	18	18	13	0	0
	Electric	0	0	0	0	2	8	17	66	91	150	201
Double deck	Diesel	5,554	5,505	5,806	5,716	5,315	5,045	4,804	4,390	3,463	2,873	2,605
	Hybrid	29	79	233	352	643	799	981	1,564	2,227	2,669	2773
	Electric	0	0	0	0	0	0	5	5	5	5	115
TOTAL		8,624	8,824	8,762	8,737	8,784	8,996	9,196	9,626	9,406	9,152	9,109
% low emission		0.6	1.3	3.1	4.5	9.6	14.1	19.2	27.2	35.6	41.9	44.9

4.6.8.2 Polycyclic aromatic hydrocarbons (PAH)

Monthly concentrations of benzo[a]pyrene (Bap) are measured at Auchencorth Moss, Ballymena Ballykeel, Kilmakee Leisure Centre, Glasgow Townhead, Chilbolton Observatory, and London Marylebone Road under the UK PAH Network[1]. BaP and UVPM have similar emission sources and a 2016 paper exploring the relationship between collocated Aethalometer UVPM measurements and Defra PAH Network BaP measurements[22], determined the following quadratic relationships between the two pollutants.

Equation 3

$$BaP = a.UV^2 + b.UV + c$$

Where

BaP = predicted BaP concentration in μg m^{-3}
UV = measured UVPM concentration in μg m^{-3}

Table 16 gives the coefficients a, b, and c for the different site types.

Table 16 - Coefficients for predicting BaP concentrations from measured UVPM concentrations

Site type	Class	a	b	c
Marylebone Road	MY	0.000	0.947	0.076
Northern Ireland	NI	0.285	0.934	0.000
Rural	R	0.902	0.293	0.000
Urban and Roadside	UR	2.369	0.107	0.000
All sites		**0.343**	**0.827**	**0.001**

Using this relationship, Table 17 shows the measured and predicted annual 2020 BaP concentration at each Aethalometer site based on the measured annual UVPM concentration. It can be seen that the predicted BaP concentration generally agrees well with the measured concentration.

Table 17 - Predicted 2020 annual BaP concentration based on measured UVPM concentrations

Site	Class	UVPM (μg m^{-3})	Predicted BaP, (μg m^{-3})	Measured BaP (μg m^{-3})
Auchencorth Moss	R	0.03	0.01	0.01
Ballymena Ballykeel	NI	0.34	0.35	0.47
Belfast Centre	NI	0.22	0.22	-
Birmingham A4540 Roadside	UR	0.23	0.15	-
Birmingham Ladywood	UR	0.17	0.09	0.09
Cardiff Centre	UR	0.21	0.13	-
Chilbolton Observatory	R	0.18	0.08	0.06
Detling	R	0.16	0.07	-
Glasgow High Street	UR	0.08	0.03	-
Glasgow Townhead	UR	0.08	0.02	0.06
Kilmakee Leisure Centre	NI	0.33	0.34	0.23
London Marylebone Road	MY	0.25	0.31	0.11
London N. Kensington	UR	0.23	0.16	-
Strabane 2	NI	1.03	1.27	-

Using the relationship above for Northern Ireland sites, Table 18 gives the predicted BaP concentrations at Strabane for the last decade. This site has the highest measured UVPM and is therefore the most likely of the sites to be close to the BaP target values. The 2016 data has been omitted because the incomplete data gives an average that is not representative.

Table 18 - Predicted BaP concentrations from UVPM concentration at Strabane for the period 2009 to 2020

Year	UVPM concentration ($\mu g\ m^{-3}$)	Predicted BaP concentration ($\mu g\ m^{-3}$)
2009	0.9	1.1
2010	1.3	1.7
2011	0.8	0.9
2012	1.1	1.4
2013	1.2	1.5
2014	1.1	1.4
2015	0.9	1.1
2016	-	-
2017	0.9	1.0
2018	0.8	1.0
2019	0.9	1.1
2020	1.0	1.3

Eight out of these 11 years had predicted BaP concentrations above the 1.0 $\mu g\ m^{-3}$ target value in the EC Directive 2004/107/EC[23] relating to ambient BaP concentrations. The average concentration over these 11 years is predicted to be 1.2 $\mu g\ m^{-3}$. There will, however, be significant uncertainty attached to these values.

4.6.8.3 Particle mass concentration

The annual average particulate mass concentration was compared with the Black Carbon concentration at co-located sites where automatic particulate mass instrumentation was installed. The results are shown in Table 19.

Table 19 - Comparison of Annual Black Carbon and Particulate Mass Concentrations

Site	BC ($\mu g\ m^{-3}$)	PM_{10} ($\mu g\ m^{-3}$)	$PM_{2.5}$ ($\mu g\ m^{-3}$)	BC as % of PM_{10} (%)	BC as % of $PM_{2.5}$ (%)
Auchencorth Moss	0.1	5 (FIDAS)	3 (REF.EQ)	3	4
Belfast Centre	0.9	12 (mixed)	7 (mixed)	8	13
Birmingham A4540 Roadside	1.9	14 (FIDAS)	8 (REF.EQ)	14	24
Birmingham Ladywood	0.8	12 (FIDAS)	7 (REF.EQ)	6	11
Cardiff Centre	0.7	14 (TEOM FDMS)	7 (TEOM FDMS)	5	10
Chilbolton Observatory	0.4	12 (FIDAS)	8 (REF.EQ)	3	5
Detling*	0.5	14 (GRAV)	-	4	-
Glasgow High Street	0.9	9 (FIDAS)	5 (REF.EQ)	10	18
Glasgow Townhead	0.6	9 (FIDAS)	5 (REF.EQ)	7	12
London Marylebone Road	1.4	16 (TEOM FIDAS)	9 (TEOM FIDAS)	9	16
London N. Kensington	0.8	13 (FIDAS)	8 (REF.EQ)	6	10
Strabane 2	1.6	15 (REF.EQ)	-	10	-

Notes:

- The techniques used for monitoring PM are:
  - (TEOM) – Tapered Element Oscillating Microbalance
  - (BAM) – Beta Attenuation Monitor
  - (GRAV) – Gravimetric Monitor
  - (FDMS) – Filter Dynamics Measurement System
  - (OLS) – Optical Light Scattering
  - (FIDAS) – Fine Dust Analysis System,
  - (REF.EQ) – the reference methods of measurement are defined in the relevant EU Directives
- * indicates a Local Authority run site for PM that may not have identical QA/QC procedures to AURN datasets.
- A dash indicates that no measurements were made.

The PM_{10} and $PM_{2.5}$ mass concentration measured at London Marylebone Road, Birmingham A4540 Roadside and Glasgow High Street sites had a higher percentage of Black Carbon than the other sites. Black Carbon therefore represented a large proportion of the total particulate mass at sites influenced by road traffic emissions.

At the rural background sites Black Carbon made up 5% or less of the PM mass.

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