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AIRBORNE PARTICLE CONCENTRATIONS, PARTICLE NUMBERS AND BLACK CARBON IN THE UNITED KINGDOM - ANNUAL REPORT 2021

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Airborne Particle Concentrations, Particle Numbers and Black Carbon in the United Kingdom - Annual report 2021

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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 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).

This annual report for 2021 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 2021.

And, where applicable:

- Plots of the diurnal, weekly and monthly trends in ratified network data in 2021
- 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 2021, the Network measured:

- Hourly particle number concentrations using a Condensation Particle Counter (CPC) at three sites
- 15-minute particle size distributions using a Scanning Mobility Particle Sizer (SMPS) at three sites
- Hourly aerosol mass and chemical speciation (ammonium, nitrate, sulfate and organic compounds) in $PM_{2.5}$ at London Honor Oak Park, and in PM_1 at London Marylebone Road using an aerosol chemical speciation monitor.
- Weekly measurements of the mass concentration of organic carbon and elemental carbon (OC/EC) in $PM_{2.5}$ at Auchencorth Moss. Daily $PM_{2.5}$ measurements of the mass concentration of OC/EC at Chilbolton Observatory, London Marylebone Road and London Honor Oak Park. For all sites, $PM_{2.5}$ 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 $PM_{2.5}$ using an Aethalometer at 14 sites.

The impact of the continuing Covid-19 pandemic on the operation of the Network was limited in 2021. There were however some delays for Equipment Support Units (ESUs) 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. Covid-19 restrictions at NPL meant that access to laboratories was restricted during early 2021, which resulted in a delay of the servicing and calibration of the network CPCs and SMPSs.

Fully ratified Network data can be downloaded from the Defra UK-AIR website[1]. Some notable features from the network data in 2021 are:

- Annual average particle number concentrations for 2021 at London Marylebone Road remained at levels similar to those measured since 2016. There were no significant changes in annual average particle number concentrations observed at London Honor Oak Park and Chilbolton Observatory from 2019 to 2021.

- Steady decreases in the annual averages of EC and OC mass concentrations at London Marylebone Road and London Honor Oak Park continued in 2021. By contrast, annual averages of EC and OC mass concentrations at Chilbolton Observatory and Auchencorth Moss have shown no significant changes over recent years. As weekly sampling at Chilbolton Observatory ended in June 2020 in favour of daily sampling, better clarity on composition during short-term pollution events or diurnal variations can now be obtained.

- Annual average mass concentrations of BC and UVPM were measured at all 14 sites in 2021 and the concentrations for both components were broadly similar to those measured in 2020. The largest decrease of UVPM was observed at Strabane 2 site from 1.03 µg m^{-3} in 2020 to 0.76 µg m^{-3} in 2021.

- The significant downward trend in measured black carbon mass concentrations observed at all the long-running sites in the network apart from Strabane 2 since 2009 continued into 2021. The relative decrease at London Marylebone Road remains much larger than that at other sites, whereas the highest concentration of BC among roadside sites is now measured at Birmingham A4540 Roadside.

The annual average data capture across all network sites was:

  - 65 % for particle number concentration measurements
  - 80 % for particle size distribution measurements
  - 61 % for aerosol mass and chemical composition measurements
  - 93 % for organic carbon and elemental carbon measurements
  - 94 % for black carbon measurements

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); and aerosol mass and chemical speciation.

Prior to 2020, these data were 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 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 shown 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 and Defra.

This report presents a summary of the 2021 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 2021)

The network in 2021 was structured in the same way as the previous year. There were no changes to site or equipment configurations.

Also of note are that:

- The CPC at the Birmingham Ladywood site continued to not be operational throughout 2021 due to the need to relocate the instrument – discussions continued to agree the best location for the instrument.
- The operation of the network was affected in 2021 by the continuing 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.
    - On a few occasions local site operators (LSOs) had Covid-19 and could not attend sites as planned. Specifically, some LSO *ad hoc* visits to diagnose and fix breakdowns or change Aethalometer tapes were delayed. In all other cases, however, either another LSO was able to attend, or the visit was delayed by a week.
    - Covid-19 restrictions at NPL meant that access to laboratories was restricted during early 2021, which resulted in a delay of the servicing and calibration of the network CPCs and SMPSs

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 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 2021 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. They also allow the benefit of the measurements made to be maximised, 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.

Fourteen of the 15 sites (all but Honor Oak Park) 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 2021. The colour key indicates the emissions sources representative of each site (as previously defined for the UK Black Carbon Network sites): Green = Glasgow urban area; Red = Birmingham urban area; Blue = London Urban area; Orange = solid fuel use / domestic emissions.

Site Name	Site Classification	Hourly $PM_{2.5}$ or PM_1 aerosol mass and speciation	Daily $PM_{2.5}$ OC/EC	Weekly $PM_{2.5}$ OC/EC	Hourly particle number concentration	15-minute 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		X	X	X	6
London North Kensington	Urban background						X	7
London Marylebone Road	Urban roadside	X [1]	X		X	X	X	8
London Honor Oak Park	Urban background	X [2]	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] The London Marylebone Road ACSM samples PM_1
[2] The London Honor Oak Park ACSM samples $PM_{2.5}$

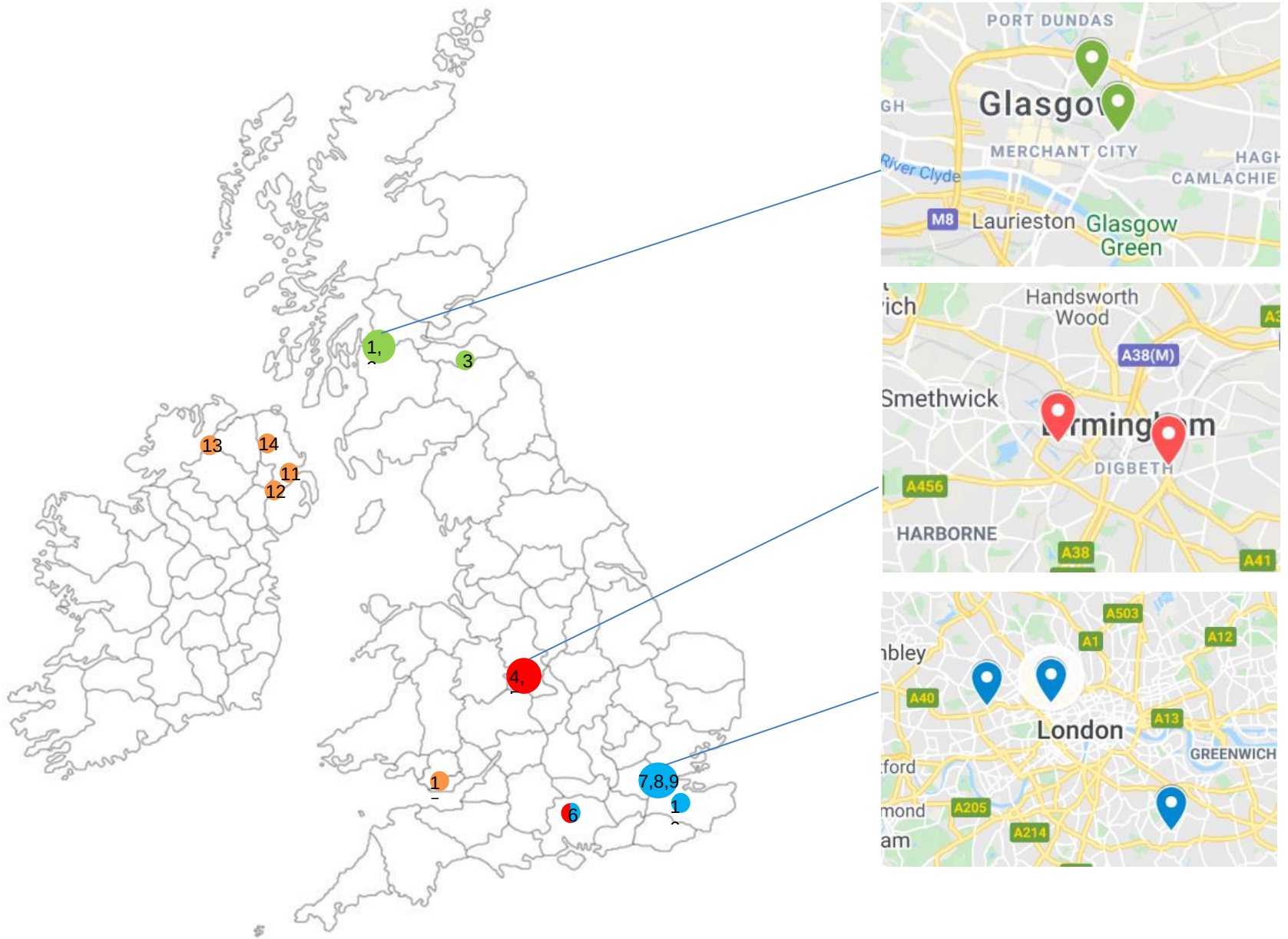

Figure 1 - Network sites in 2021. The colour key indicates the emissions sources representative of each site (as previously defined for the Black Carbon Network sites): Green = Glasgow urban; Red = Birmingham Urban; Blue = London Urban; Orange = solid fuel use / domestic emissions.

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 Environment Agency.

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, ACSMs 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 2021 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 were CPC butanol leaks at London Honor Oak Park and London Marylebone Road due to instruments flooding with butanol as a result of internal blockages. In the case of London Marylebone Road these blockages were in both the CPC and the drier system.

Table 2 - Data capture for particle number concentration measurements

Site Name	Data capture [%]
Chilbolton Observatory	82 (75)
London Marylebone Road	48 (44)
London Honor Oak Park	66 (60)
Average	**65 (59)**

Note: Figures in Table 2 are the data capture calculated when three weeks of Covid-19 delays are removed from the planned time coverage. The data capture without the removal of these three weeks are in brackets in Table 2.

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 Chilbolton Observatory. This was sent to the instrument manufacturer for repair.

Table 3 - Data capture for particle size distribution measurements

Site Name	Data capture [%]
Chilbolton Observatory	67 (61)
London Marylebone Road	85 (78)
London Honor Oak Park	88 (80)
Average	**80 (73)**

Note: Figures in Table 3 are the data capture calculated when three weeks of Covid-19 delays are removed from the planned time coverage. The data capture without the removal of these three weeks are in brackets in Table 3.

2.3.3 Aerosol mass and chemical composition

The ACSM at London Honor Oak Park ran for the majority of the year. The main cause of data loss occurred due to the need to replace an aging detector in the quadrupole, which was sent back to the manufacturer in the US in February. The ACSM at London Marylebone Road suffered several major breakdowns due to problems with the temperature control module and replacement parts causing instability in the 24V supply to the electronic motherboard, which in turn caused the vaporizer power and bias voltage to also drift. The entire instrument was returned to the manufacturer for diagnosis and repair in December 2021.

Table 4 - Data capture for aerosol mass and chemical composition measurements

Site Name	Data capture [%]
London Marylebone Road	43
London Honor Oak Park	79
Average	**61**

2.3.4 Organic carbon and elemental carbon

The common causes of data loss at the London Marylebone Road sampler were due to filter exchange errors and instrument breakdowns arising from various part failures.

Table 5 - Data capture for OC/EC measurements

Site Name	Data capture [%]
Auchencorth Moss	96
Chilbolton Observatory	100
London Marylebone Road	78
London Honor Oak Park	97
Average	**93**

2.3.5 Black carbon

The main cause of data loss was electric fuse failure and delays in servicing sites due to the COVID-19 situation. At the Chilbolton Observatory site there was no data in July and August due to instrument failure and issues with accessing the roof to clean and seal the inlet.

Table 6 - Data capture for black carbon measurements

Site Name	Data capture [%]
Auchencorth Moss	98
Ballymena Ballykeel	91
Belfast Centre	100
Birmingham A4540 Roadside	86
Birmingham Ladywood	100
Cardiff Centre	93
Chilbolton Observatory	81
Detling	97
Glasgow High Street	99
Glasgow Townhead	94
Kilmakee Leisure Centre	95
London Marylebone Road	97
London N. Kensington	99
Strabane 2	90
Average	**94**

2.4 INSTRUMENTATION

2.4.1 Particle number concentration

Particle number concentrations are measured using TSI model 3772-CEN Condensation Particle Counters (CPC), 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[3]. At all concentrations each particle is counted individually. CEN/TS 16976:2016[3] 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 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, sulfate 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 4 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.

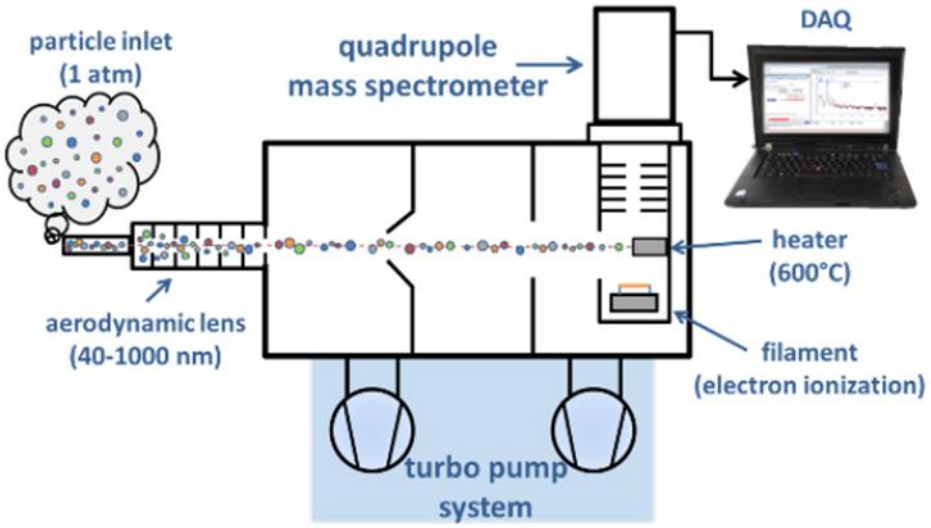

Figure 4 - ARI Aerosol Speciation Chemical Monitor schematic.
(DAQ = Data acquisition (control)).

2.4.4 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 $PM_{2.5}$ was sampled using a Thermo Partisol 2025 sequential air sampler (Figure 5) at London Marylebone Road and London Honor Oak Park. The original PM_{10} sampling heads were changed to $PM_{2.5}$ heads at London Honor Oak Park and London Marylebone Road in February 2019 and October 2019, respectively. At Chilbolton Observatory, the Partisol (daily, PM_{10}) was removed in October 2019.

Weekly measurements of $PM_{2.5}$ continued to be made at Auchencorth Moss throughout 2021, using a Leckel SEQ47/50 sequential sampler (Figure 5). The Chilbolton Observatory 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 6). 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[4]. 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.

Figure 5 - (a) Thermo Partisol 2025 sampler (b) Leckel SEQ47/50 sampler

Figure 6 - Sunset Laboratory Inc. thermal/optical carbon analyser

2.4.5 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 7).

Figure 7 Aethalometer model AE33

This 7-wavelength instrument operates at 950 nm, 880 nm, 660 nm, 590 nm, 520 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 rate, 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*.[5]. 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.

The results from the 880 nm channel give the quantitative concentration of 'black' carbon and those from 370 nm channel 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 both Aethalometers (model AE22 and AE33) were sampling in parallel from the same inlet at traffic and urban background sites in London (July 2021). Additional comparison campaign has been planned in 2022 to show continuity of data and quantify any differences in measurements. Preliminary results, however, suggest that concentrations measured by the AE33 model are approximately 35% higher than from the AE22 model. Although the methodology, in principle, is the same, both models use different algorithms and factors to calculate the final black carbon mass concentration. These are: 1) multiple scattering factor, C, used in both models as a fixed value, and 2) Mean Ratio factor used only in early-model aethalometers (including the AE22) to correct surface area of the filter spot where particles are collected.

Thus, all results provided in this report should be treated with caution especially when comparing 2020 and 2021 data from the AE33 model with earlier years when the AE22 model was used. A note to this effect was added to the Black Carbon Network page of the UK AIR website[6] 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[7]. NPL is accredited in accordance with International Standard ISO/IEC 17025:2017[8] 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 instrument type 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 Reports 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 Environment Agency 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 particle number concentration of a test sample being produced by a well characterised aerosol generator. The results 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 particle 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 a broad sized distribution of the background mineral peak of the water used to generate the polystyrene latex nanosphere aerosols used for calibration.

3.1.3 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 bi-annually by trained technical users. Particles of ammonium sulfate 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 different ratios of 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.

3.1.4 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.

3.1.5 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 data handling 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 in 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"[9].

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 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 Attenuation Monitor (BAM) 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 (α) 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 the 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 sulfate and 36 % for chloride.

3.2.4 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 is 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.

3.2.5 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 ± 0.10 µg m^{-3} for hourly means, compared to the network BC mean concentration of 0.85 µg m^{-3}. Converting this into a standard uncertainty represents an average contribution of 11.4 %.

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 a planned additional comparison campaign with the AE22 model in 2022.

Hourly	24.1%
Monthly	7.8%
Annual	7.8%

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 then.

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.

3.3.3 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 sulfate and ammonium nitrate standards.

3.3.4 Partisol and Leckel sequential Air Samplers

The Partisol 2025 samplers were serviced by the Environment Agency's Ambient Air Monitoring (AAM) Team, during 2021. 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.

3.3.5 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. 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.

3.3.6 Aethalometer

The AE33 Aethalometer instruments were serviced by ACOEM UK Ltd during 2021. 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 2021 time series

Time series of hourly particle number concentrations (between approximately 7 nm and 3 µm in diameter) measured at network sites during 2021 are shown in Figure 8.

4.1.2 2021 diurnal, weekly, and monthly profiles

The diurnal, weekly, and monthly profiles for particle number concentrations in 2021 are shown for the London Honor Oak Park, London Marylebone Road, and Chilbolton Observatory sites in Figure 9, Figure 10 and Figure 11 respectively (plots generated using the OpenAir Tools run on the R software platform[12,13]). 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 London Honor Oak Park during the evening that is larger than at the other two sites. This may be due to domestic wood-burning.

4.1.3 Long-term trends

Figure 12 and Figure 13 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 12 (the London sites) after the dramatic drop at the end of 2007 due to the introduction of sulfur-free diesel fuel and of the LEZ (Low Emission Zone)[14].

UK-wide legislation[15] enacted in June 2007 required that diesel and super-unleaded petrol sold by retailers in the UK for use in road vehicles should be “sulfur free” (less than 50 ppm sulfur)[16] from 4 December 2007, with all UK road vehicle fuel being “sulfur free” (less than 10 ppm sulfur) 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 “sulfur free” and the commencement of enforcement of the London LEZ. Measurements of airborne particle number concentrations at the two sites in London and the site in Birmingham show that over a period of few months in late 2007, concentrations were reduced by between 30% and 59 %[1.] Given the simultaneous drop of concentration at Birmingham centre (which would not be affected by the London LEZ), it is probable that the reduction at London sites is a combination of change in fuel composition and the introduction of the London LEZ.

For the London Ultra Low Emission Zone (ULEZ) that was introduced in April 2019 (and expanded further October 2021) however, the effects on annual particle concentrations for 2020 and 20211 are currently difficult to determine, predominately due to the potential influence of the Covid-19 lockdown in those years.

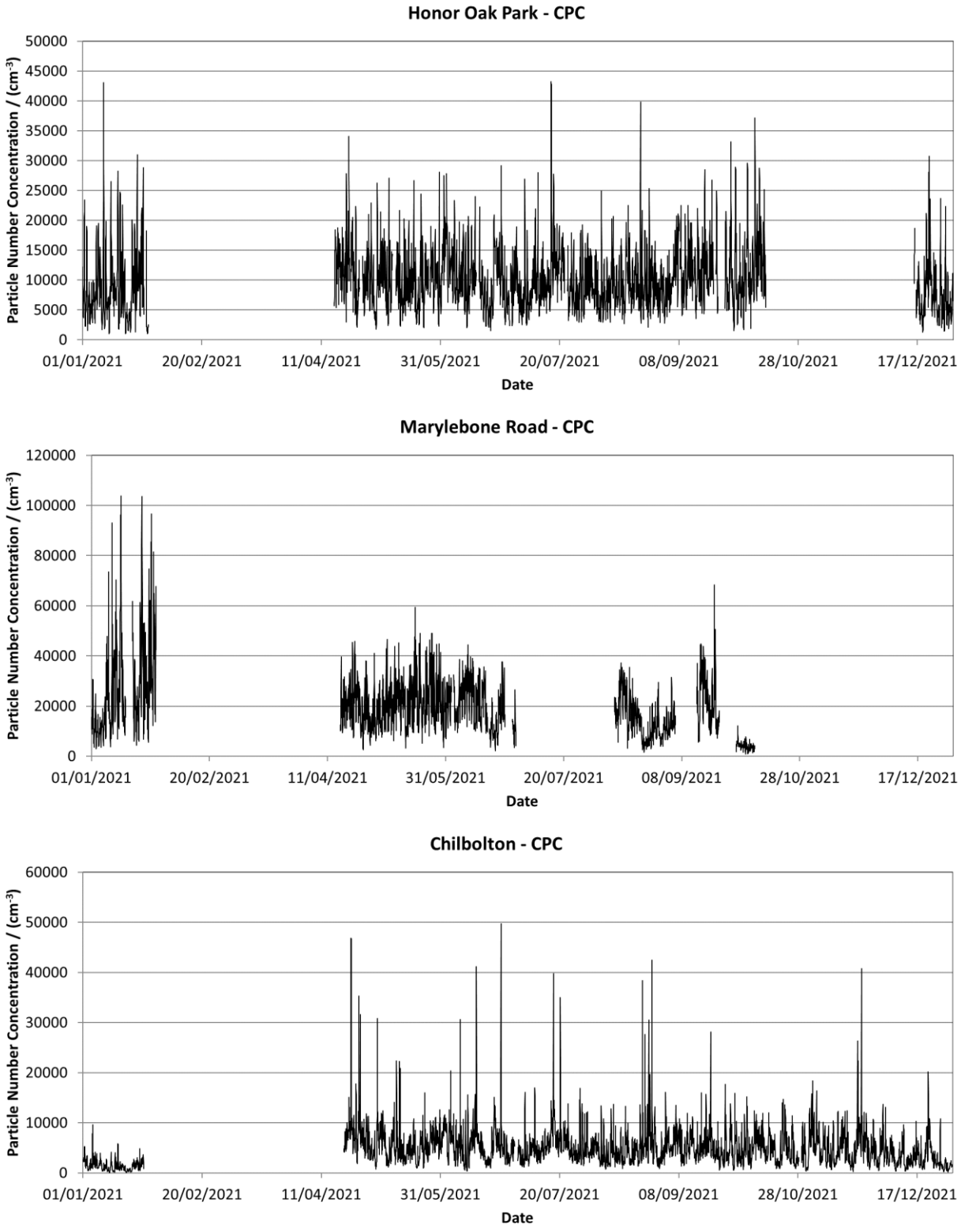

Figure 8 - Hourly particle number concentrations at London Honor Oak Park, London Marylebone Road and Chilbolton Observatory in 2021.

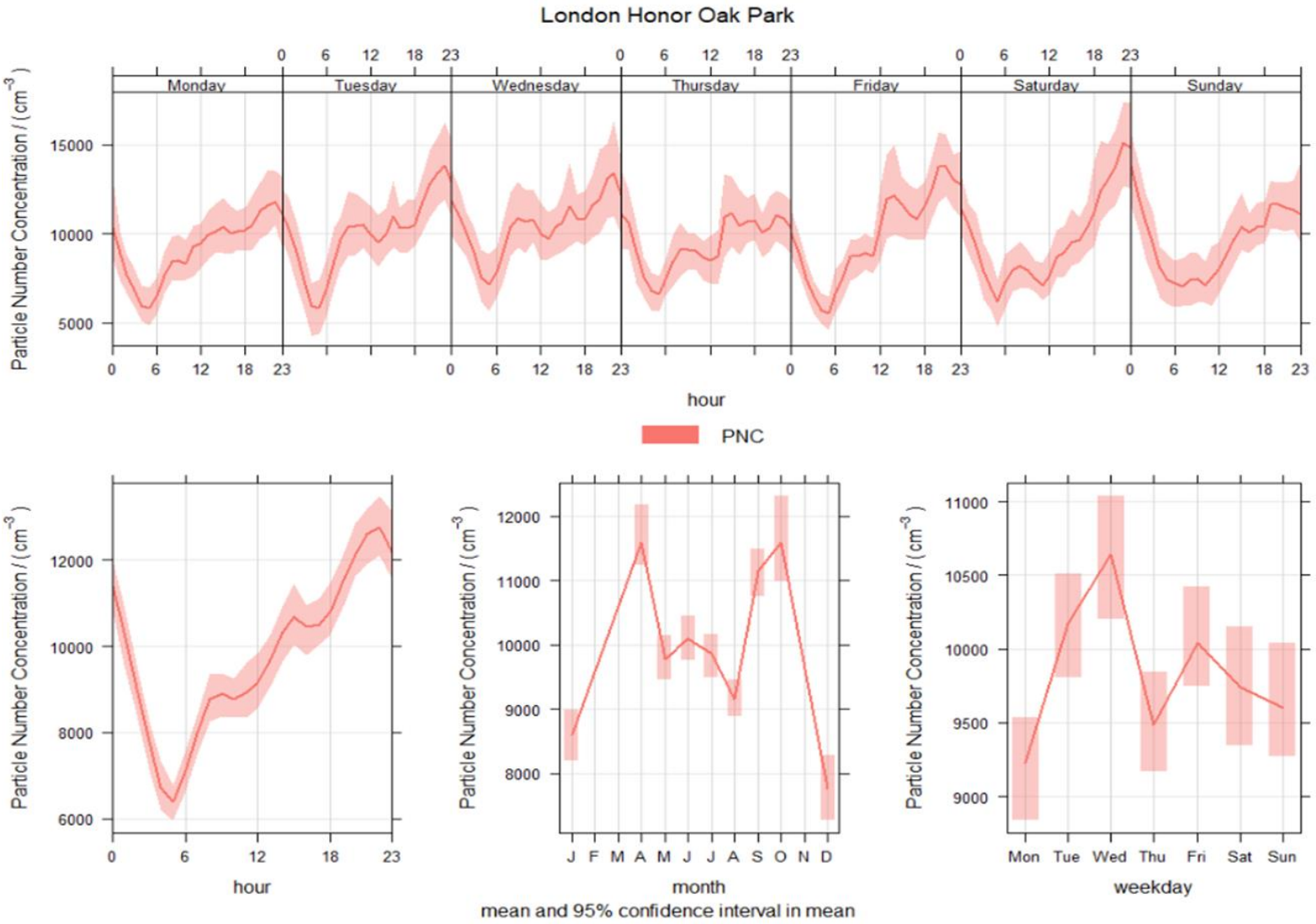

Figure 9 - Temporal variations of Particle number concentrations (PNC) in 2021 at London Honor Oak Park.

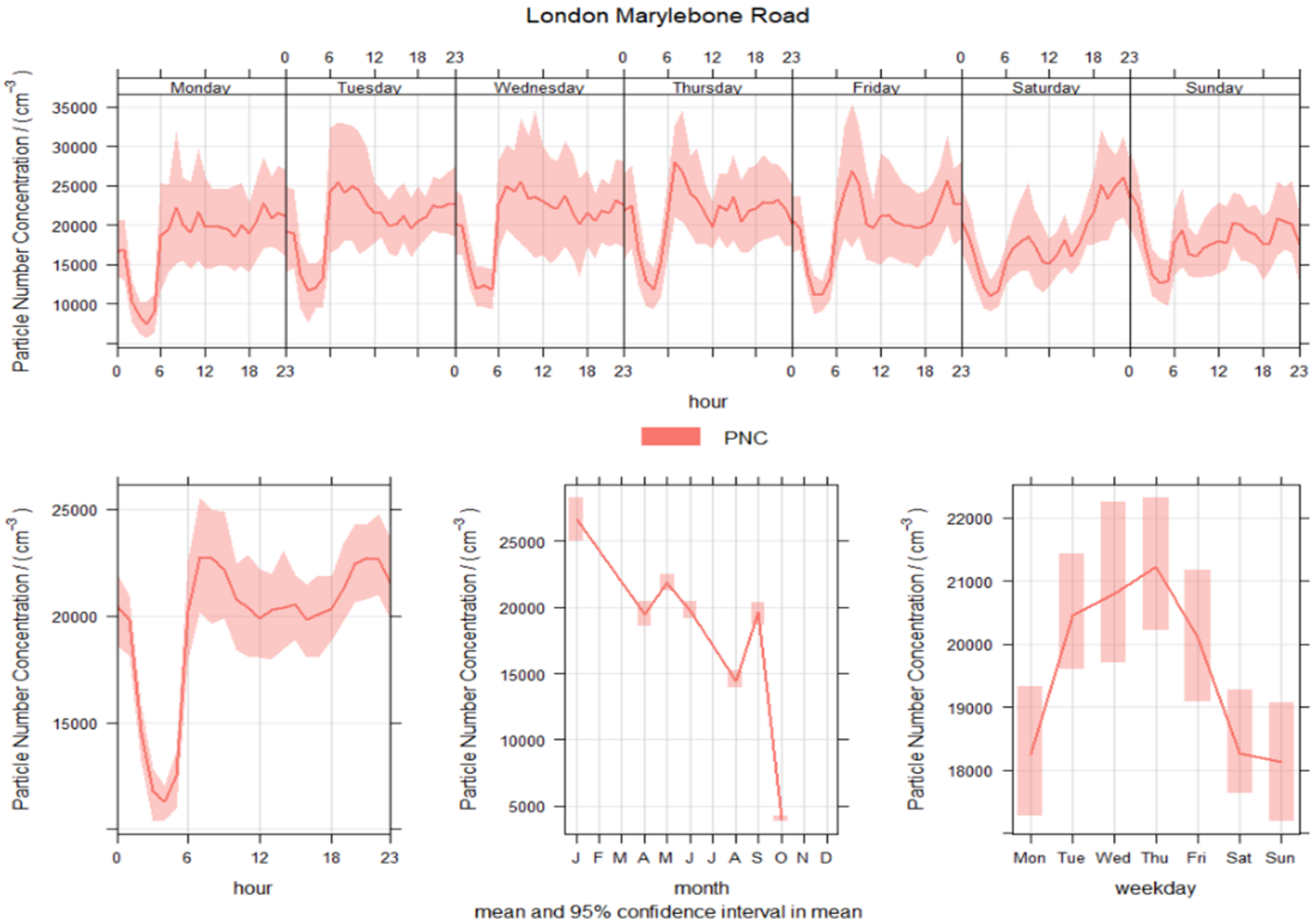

Figure 10 - Temporal variations of particle number concentrations (PNC) in 2021 at London Marylebone Road. Note: October has low data capture, which accounts for the low particle number concentration.

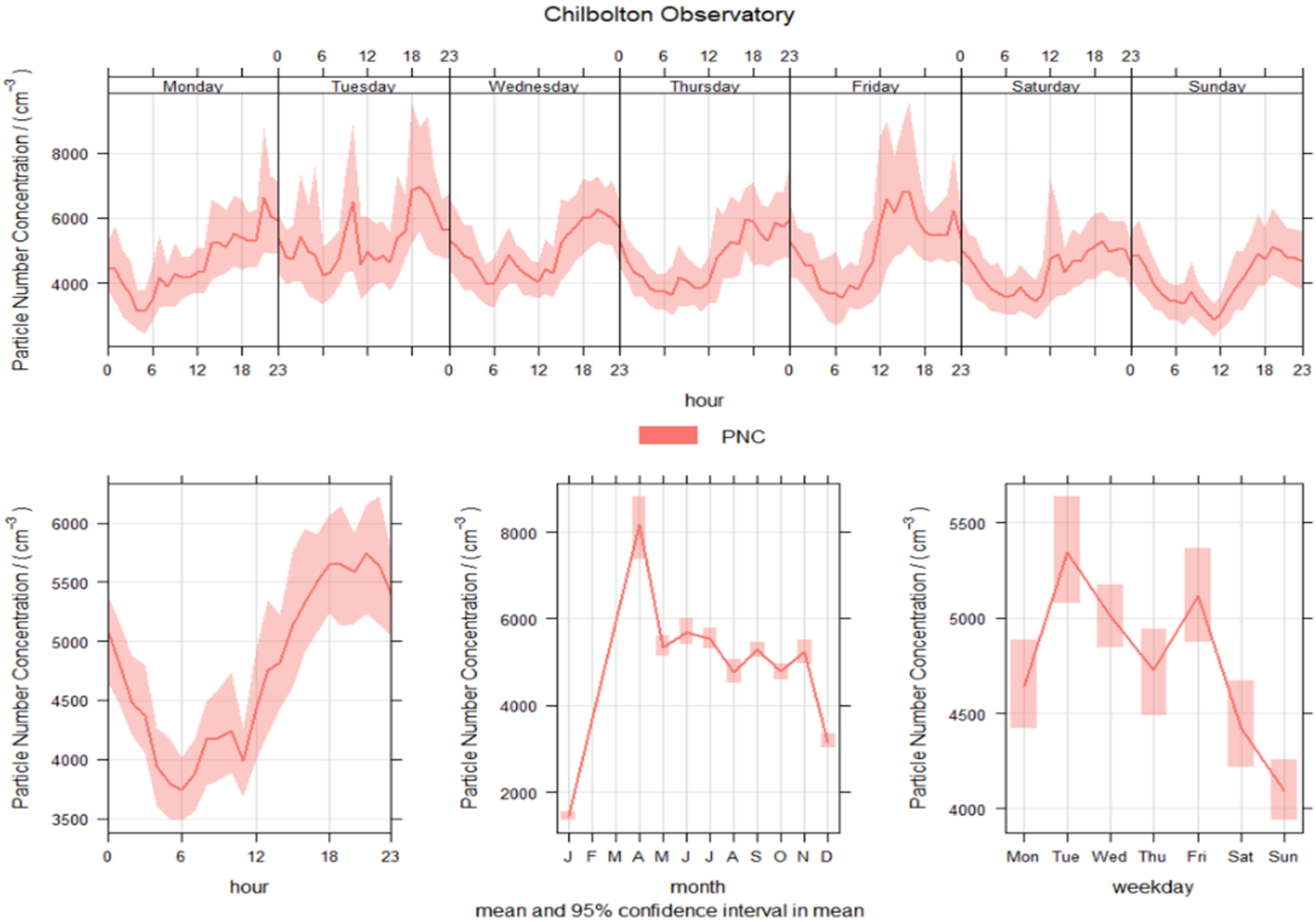

Figure 11 - Temporal variations of particle number concentrations (PNC) in 2021 at Chilbolton Observatory. Note: January has lower data capture than other winter months, which accounts for the low particle concentration.

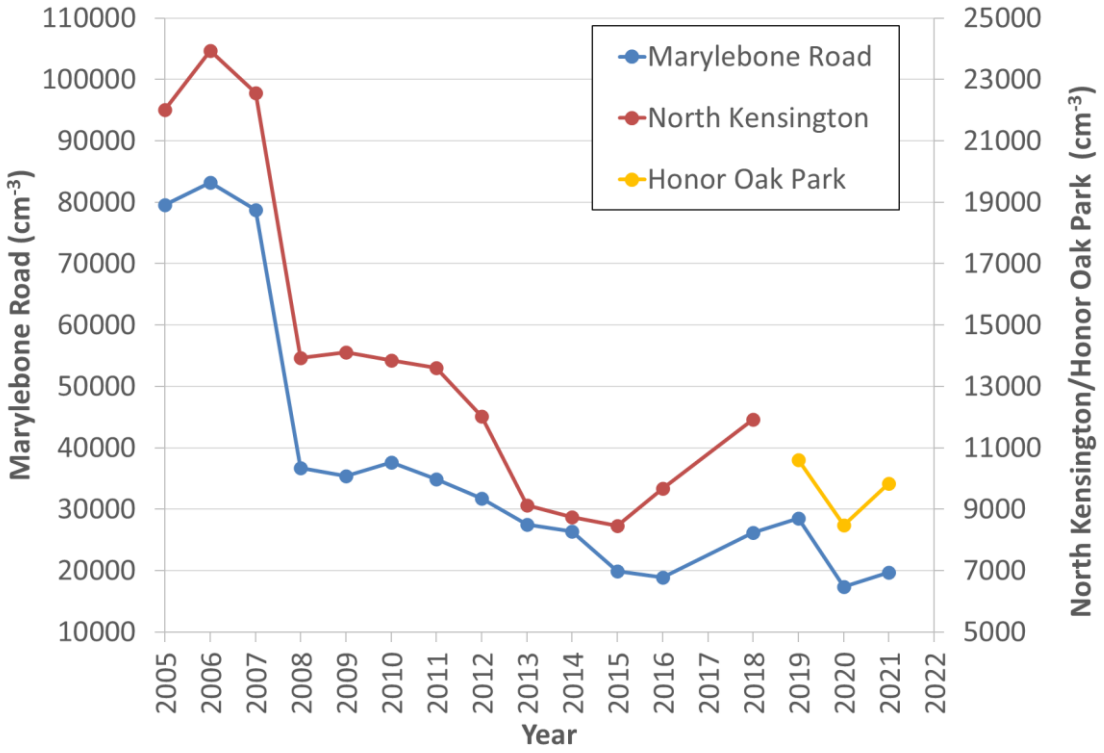

Figure 12 - Historical long-term particle number concentration annual trends at all London sites. The London North Kensington site moved to London Honor Oak Park in mid-November 2018.

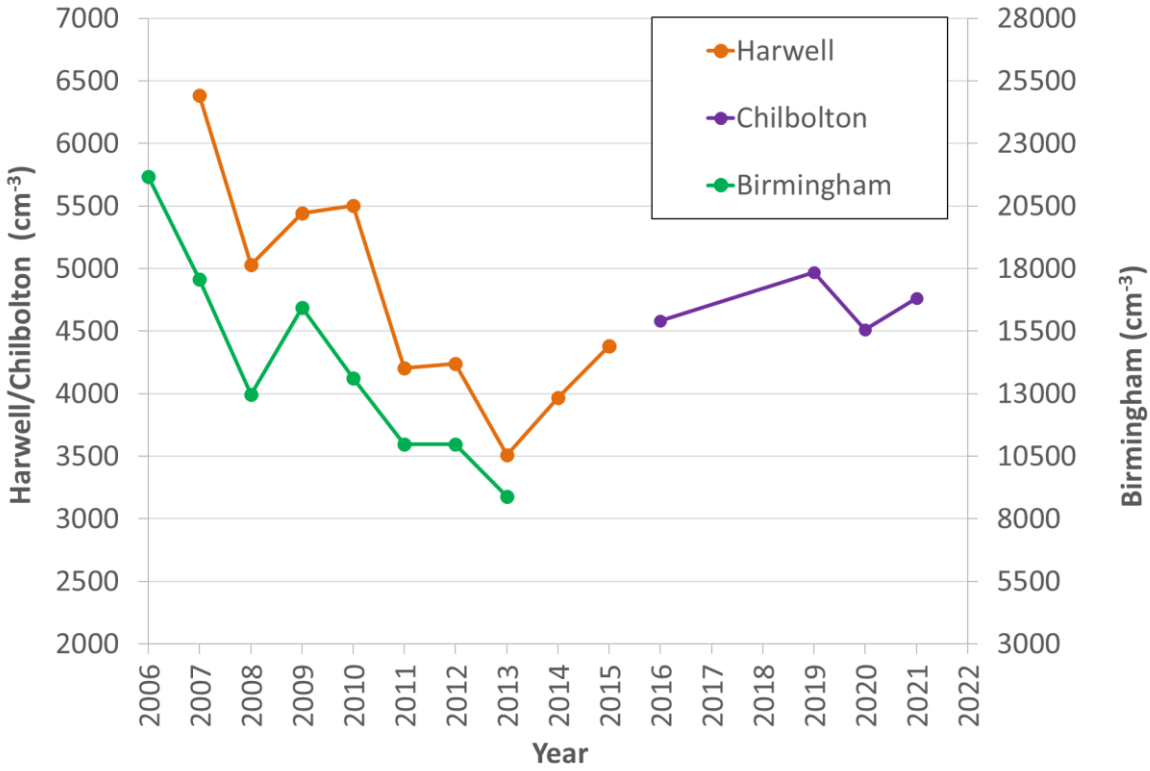

Figure 13 - Historical long-term particle number concentration annual trends at all non-London sites. The Harwell site moved to Chilbolton Observatory in 2016. The 2016 data uses an adjusted SMPS total number concentration due to low time coverage. Insufficient data was available from Chilbolton Observatory 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 2021 time series

Time series of monthly particle size distributions measured at network sites during 2021 are shown in Figure 14. The plots show both the variation in particle number concentration and the shape of the particle size distribution across 2021 at each site.

4.2.2 Long-term trends

Time series of annual particle size distributions measured at network sites from 2010 to 2021 are shown in Figure 15. The plots show both the variation in particle number concentration and particle size distribution.

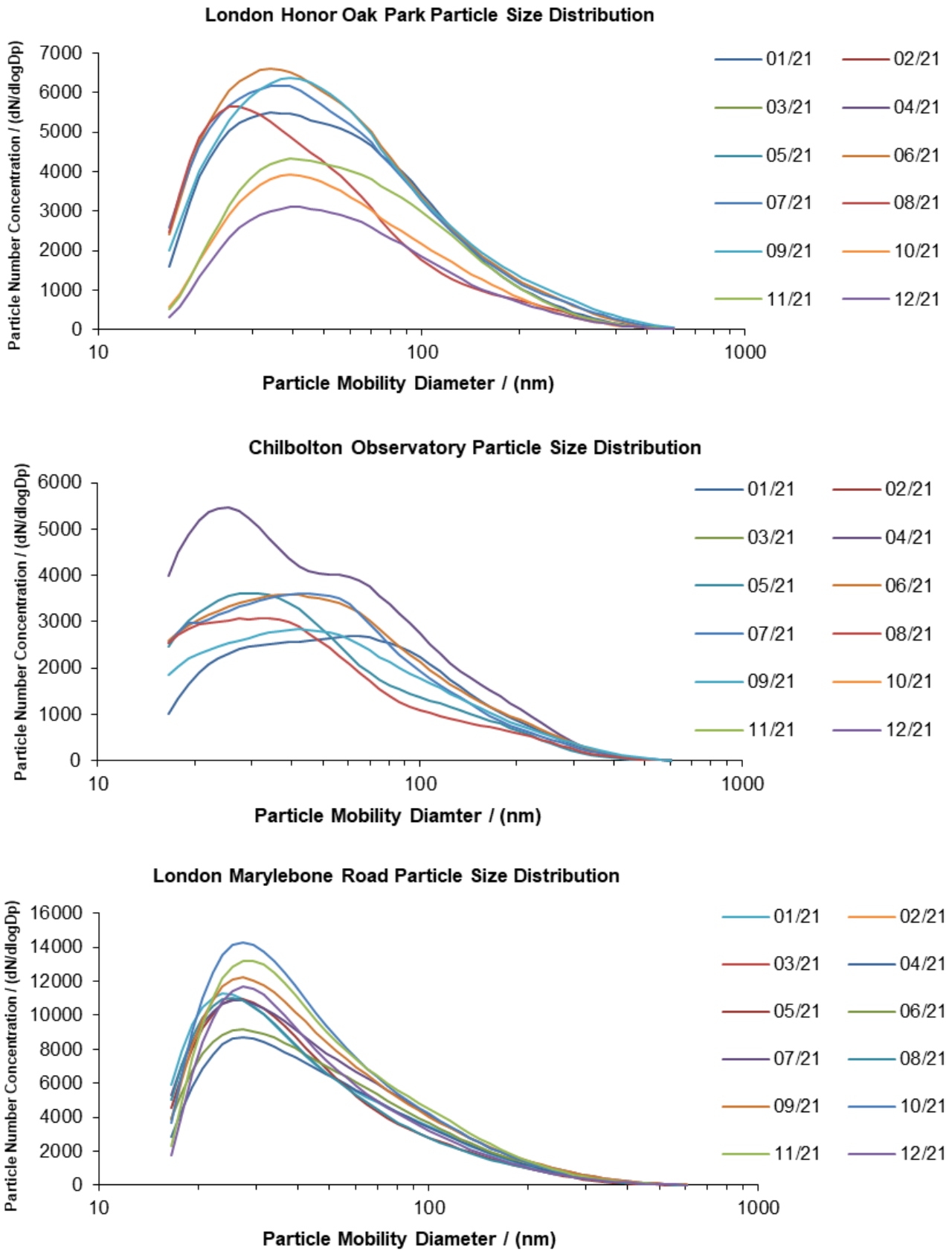

Figure 14 - Monthly averaged particle size distributions at the Network sites for each month during 2021

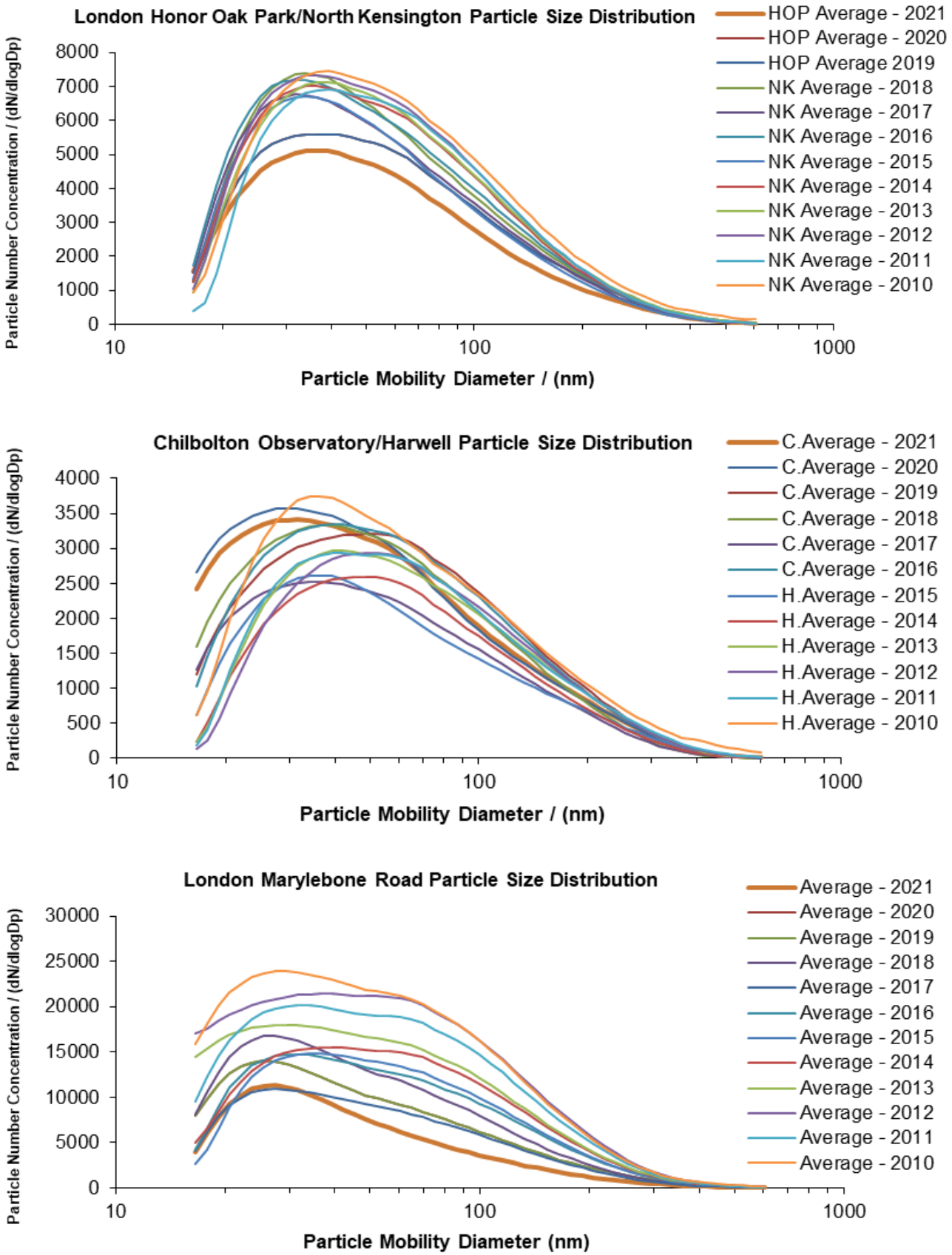

Figure 15 - Comparison of the 2010 to 2021 annual-averaged size distribution

4.3 AEROSOL MASS AND CHEMICAL COMPOSITION

4.3.1 2021 time series

Figure 16 (plots generated using the OpenAir Tools run on the R software platform[12,13]) shows the time series of monthly concentrations of organics, nitrate, sulfate and ammonia at Honor Oak Park and Marylebone Road during 2021.

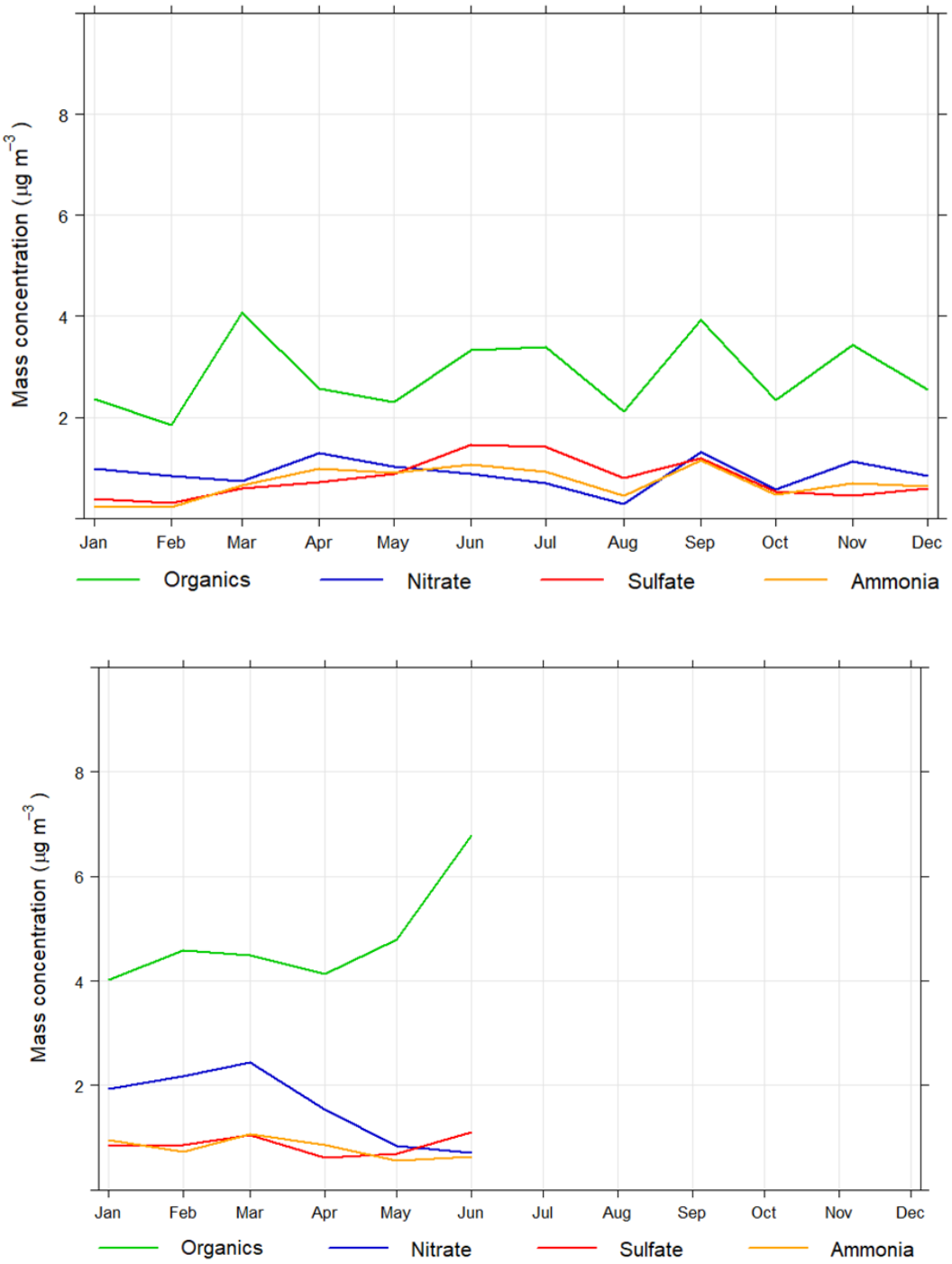

Figure 16 - Monthly average mass concentrations of organics, nitrate, sulfate and ammonia measured by ASCM in 2021 at London Honor Oak Park (top) and London Marylebone Road (bottom)

4.3.2 Long-term trends

An ACSM instrument was installed at London North Kensington in 2013 measuring the PM_1 size fraction. 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, sulfate, and ammonia in the $PM_{2.5}$ size fraction.

The new ACSM instrument measuring the PM_1 size fraction was installed at London Marylebone Road in mid-July 2020.

Figure 17 and Figure 18 (plots generated using the Open-Air Tools run on the R software platform[12,13]) show the long-term trends (using monthly averages) of the four components measured using the ACSM instrument at London North Kensington / London Honor Oak Park and London Marylebone Road.

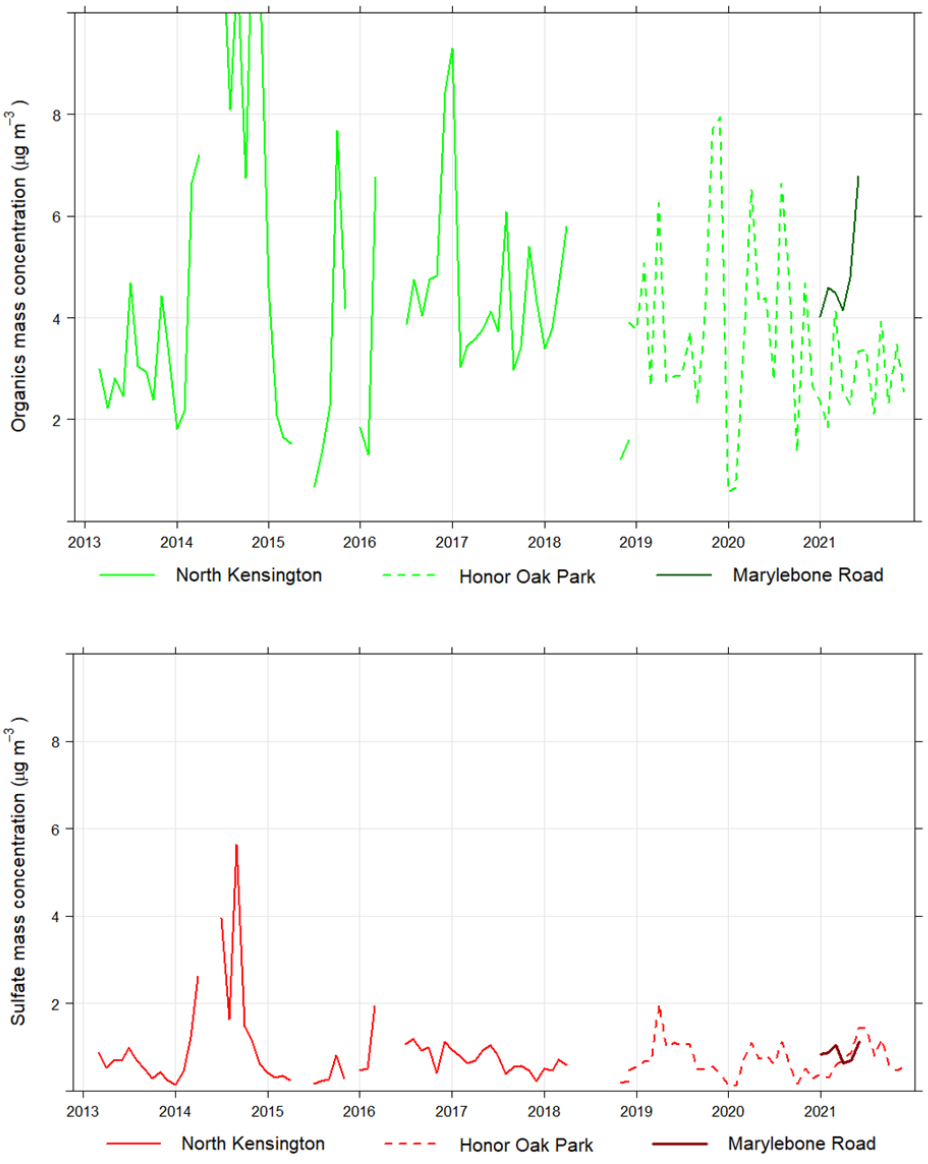

Figure 17 - Long-term mass concentration trends of organics and sulfate at the Urban Background site London Honor Oak Park (London North Kensington before 2019) and Roadside site London Marylebone Road

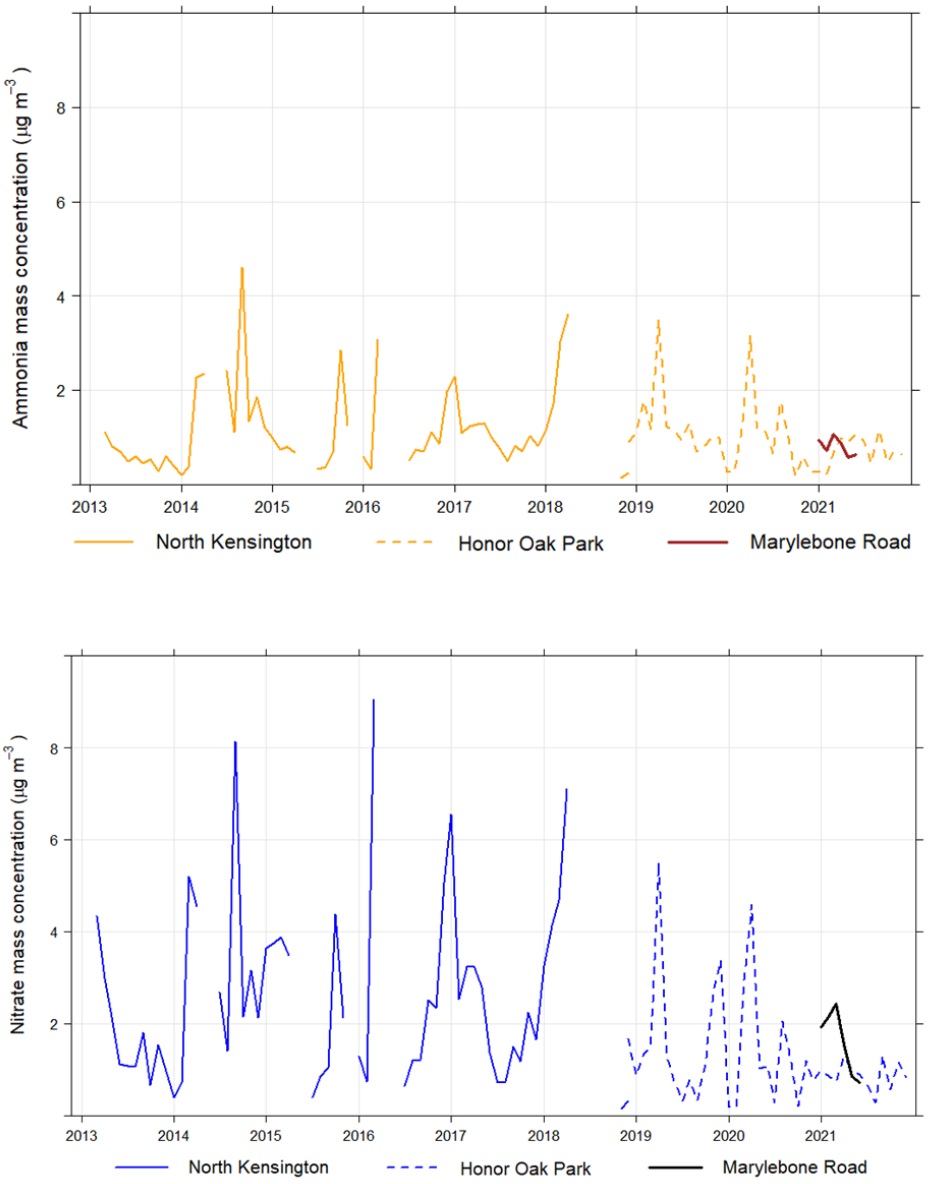

Figure 18 - Long-term mass concentration trends of ammonia and nitrate at the Urban Background site London Honor Oak Park (London North Kensington before 2019) and Roadside site London Marylebone Road

4.4 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 carried out 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 (from 1 September 2011) was moved to Chilbolton Observatory and has operated there since 4 February 2016. The sampler at Auchencorth Moss has been operational since 17 November 2011.

4.4.1 2021 time series

The time series of OC, EC and TC (Total Carbon – the sum of OC and EC) are displayed in Figure 19, Figure 20, Figure 21 and Figure 22 for each site. The plots for London Marylebone Road, London Honor Oak Park and Chilbolton Observatory comprise daily data; the plot for Auchencorth Moss comprises weekly data.

4.4.2 Long-term trends

Figure 23 and Figure 24 show the long-term time series for the measurements since the installation of the Leckel samplers at Harwell / Chilbolton Observatory and Auchencorth Moss. The data from Chilbolton Observatory (February 2016 - December 2021) is plotted continuously with the data from the former Harwell site and its daily data is plotted continuously with the former weekly data.

Figure 25 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).

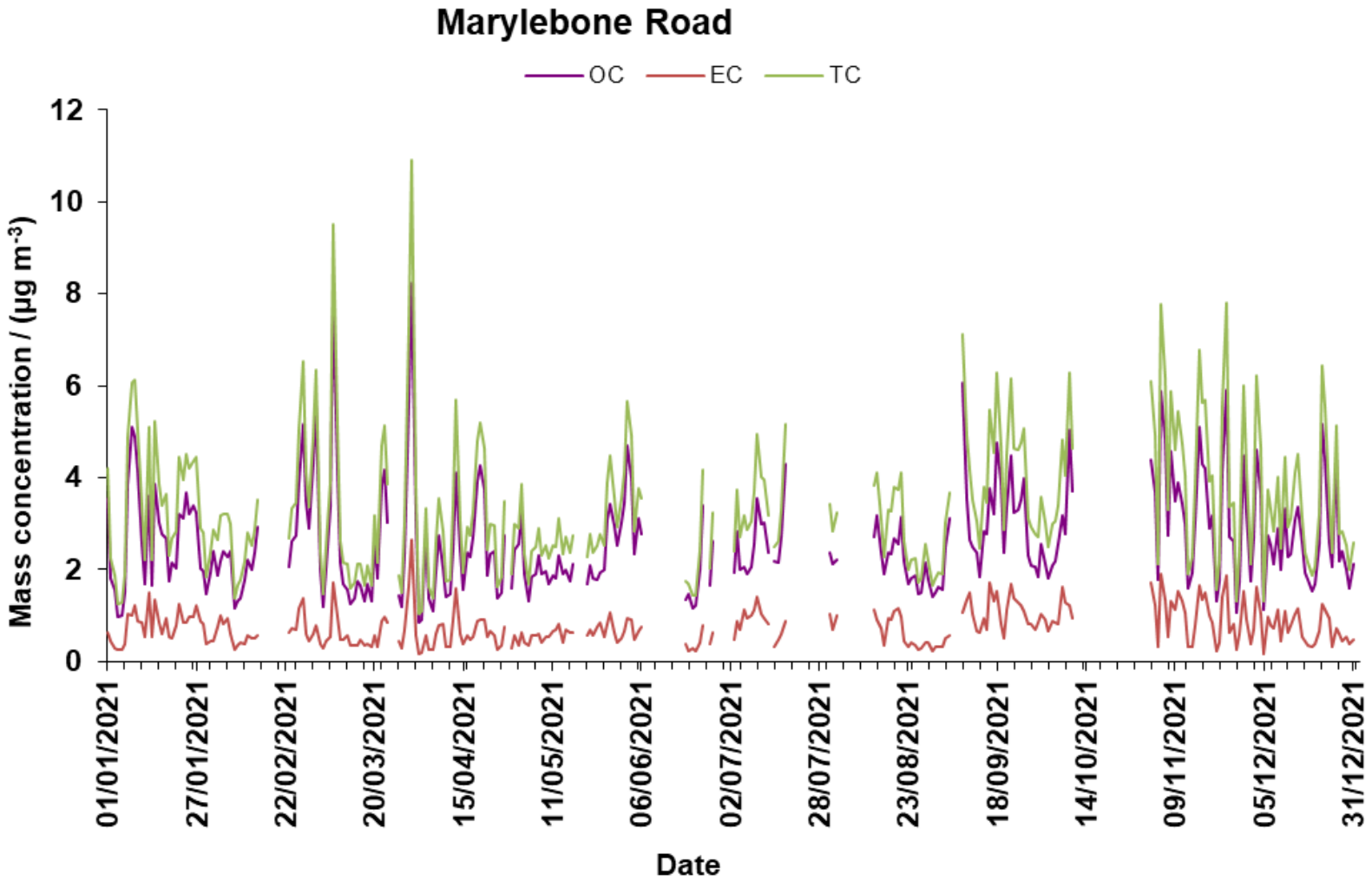

Figure 19 - $PM_{2.5}$ OC, EC, and TC mass concentrations (µg m^{-3}) at London Marylebone Road during 2021

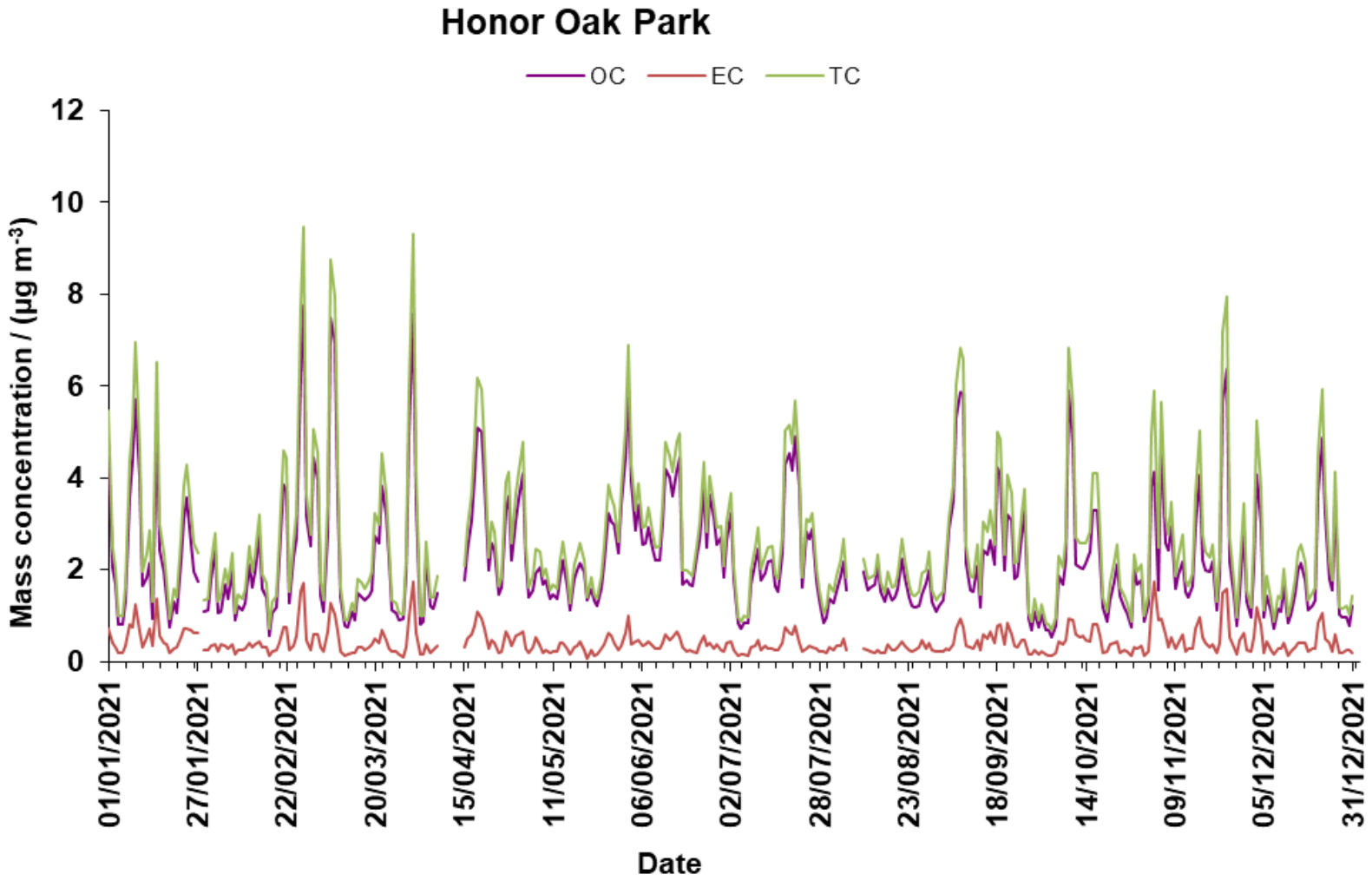

Figure 20- $PM_{2.5}$ OC, EC, and TC mass concentrations (µg m^{-3}) at London Honor Oak Park during 2021

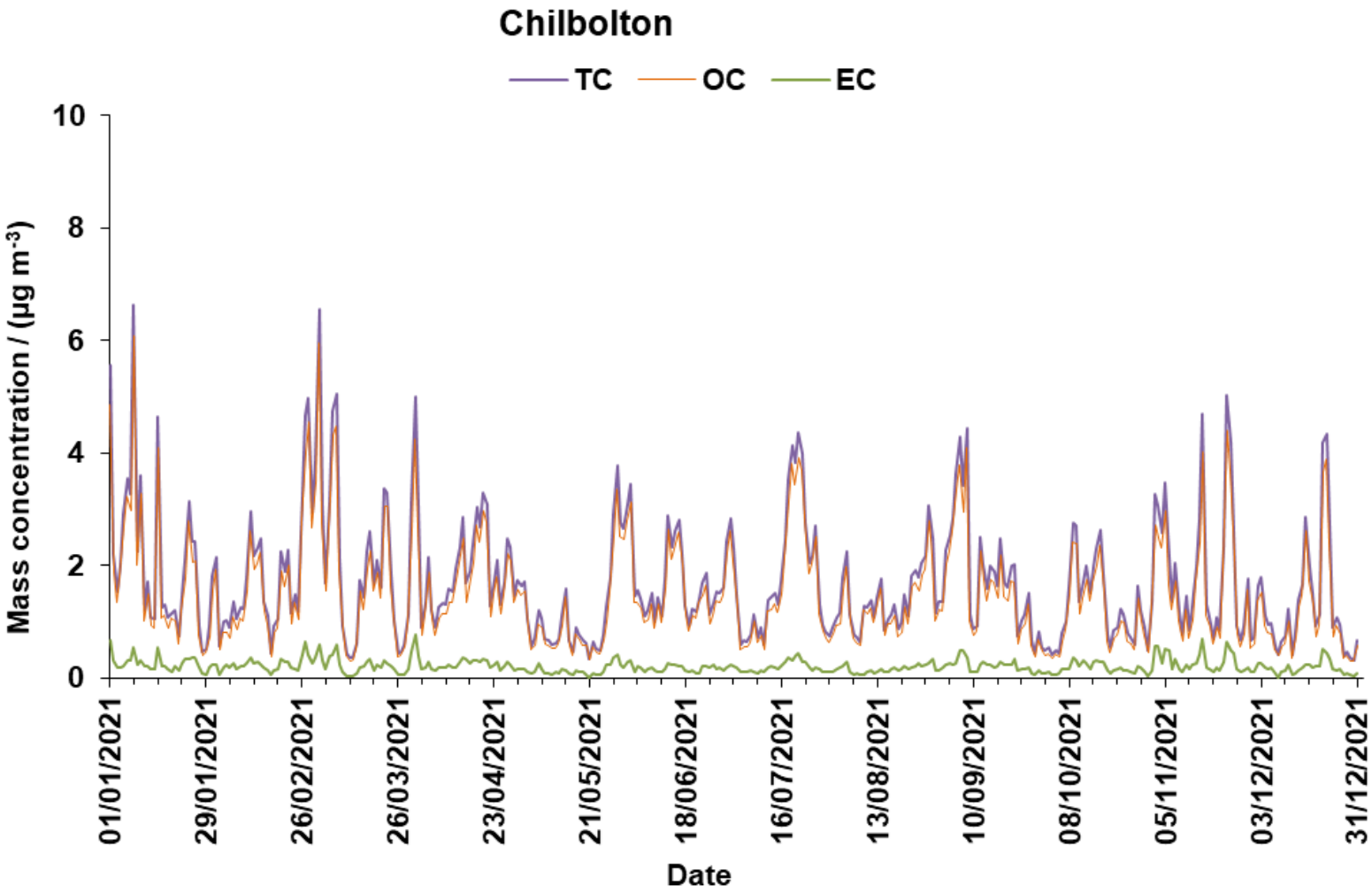

Figure 21 - $PM_{2.5}$ OC, EC, and TC mass concentrations (µg m^{-3}) at Chilbolton Observatory during 2021

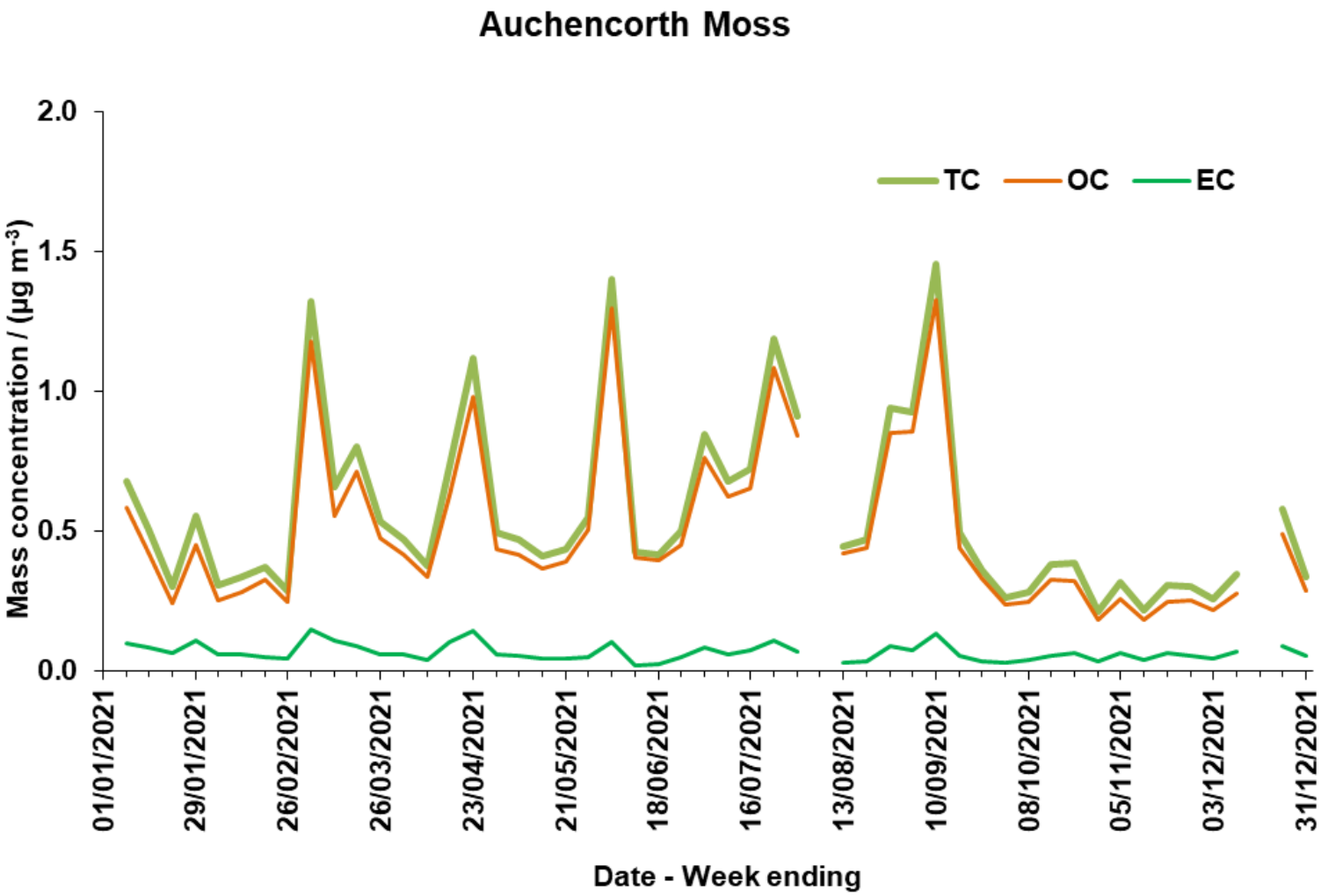

Figure 22 - $PM_{2.5}$ OC, EC, and TC mass concentrations (µg m^{-3}) at Auchencorth Moss during 2021

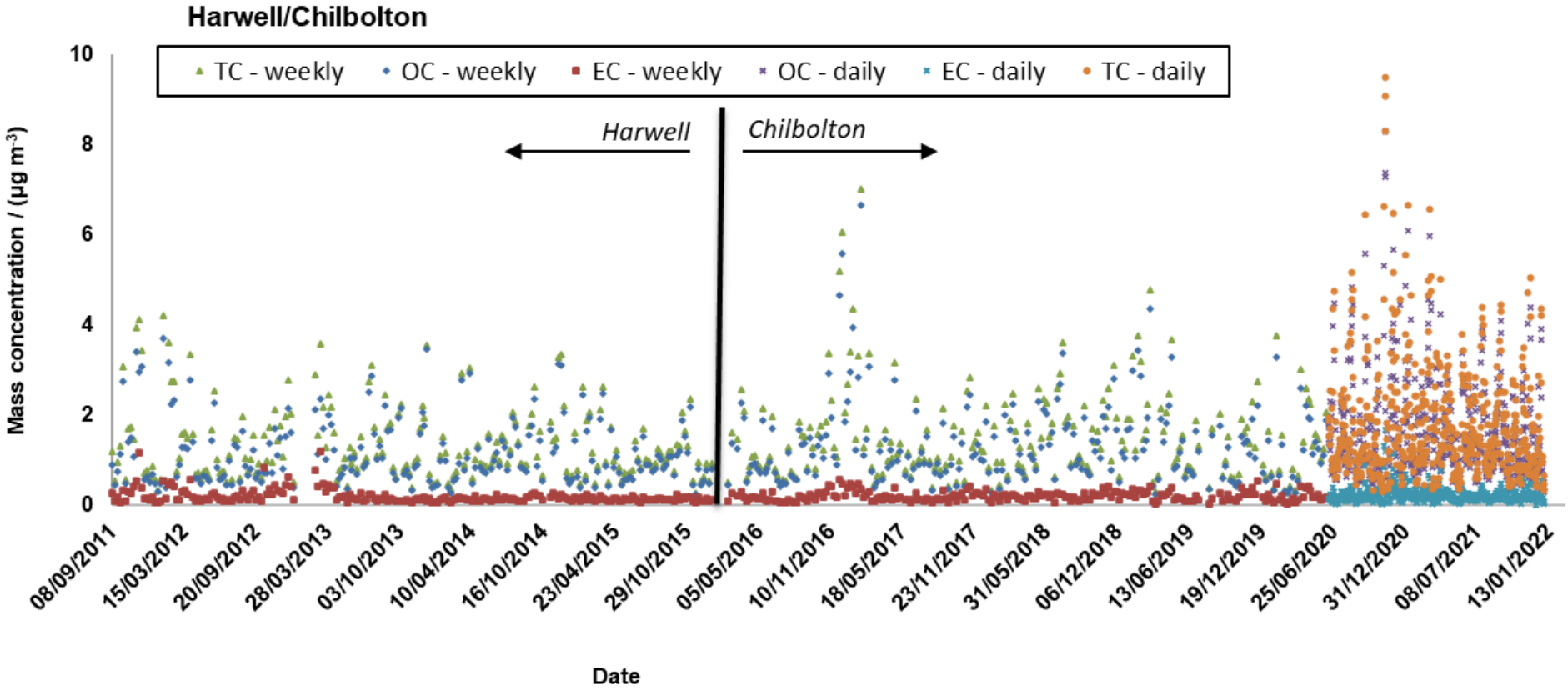

Figure 23 - Time series of the weekly OC, EC, and TC mass concentrations in the $PM_{2.5}$ fraction at Harwell/Chilbolton Observatory since the installation of the sampler up to June 2020 and daily mass concentrations from 11 June 2020

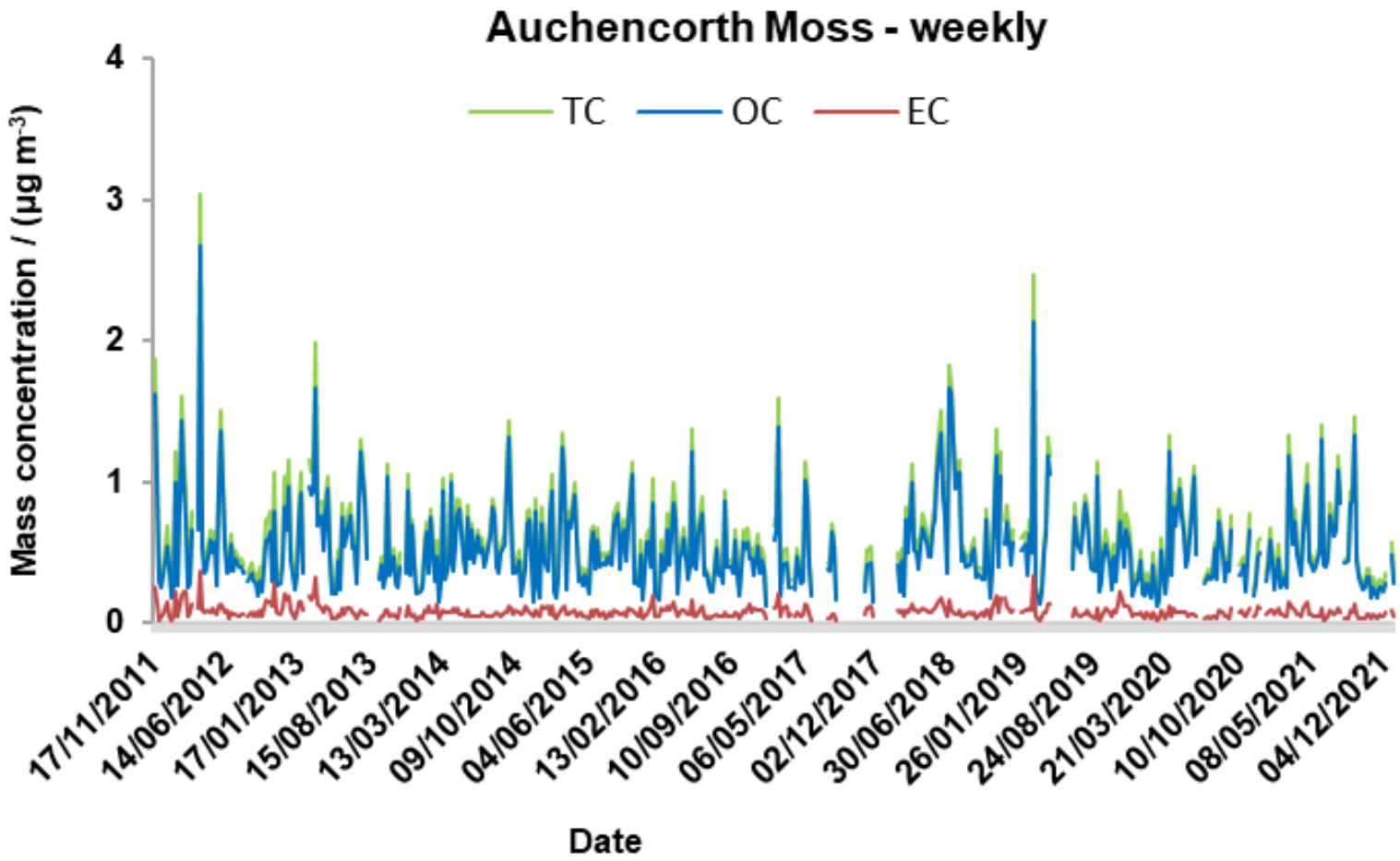

Figure 24 - Time series of weekly OC, EC, and TC in the $PM_{2.5}$ fraction at Auchencorth Moss to the end of 2021

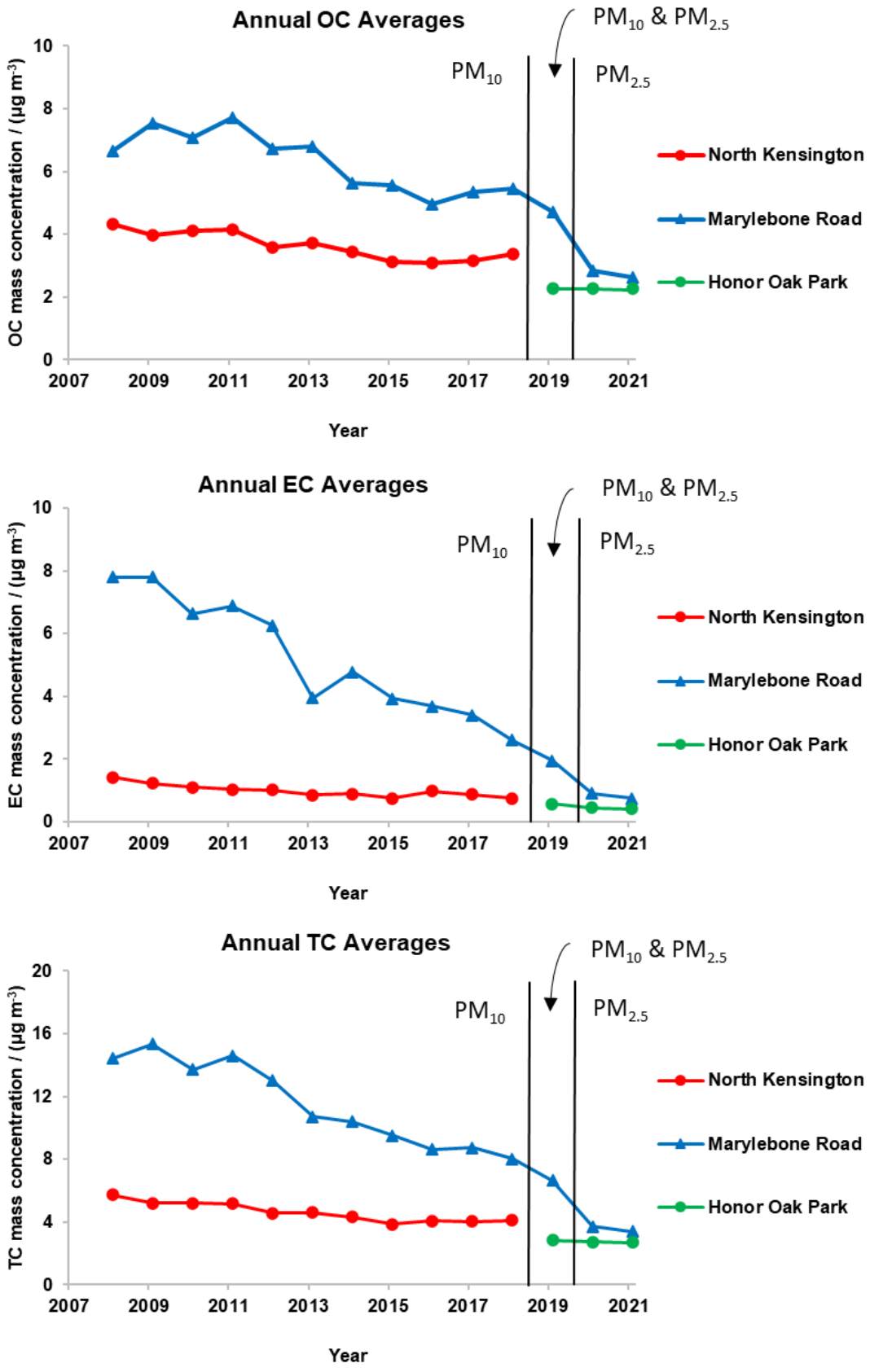

Figure 25 - Annual trends for OC, EC, and TC measurements. PM_{10} sampling heads were changed to $PM_{2.5}$ heads at London Honor Oak Park and London Marylebone Road in February 2019 and October 2019, respectively.

4.5 BLACK CARBON AND UV-ABSORBING PARTICULATE MATTER

4.5.1 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. Theoretically 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 2.4.5. 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 7. These Aethalometer measurements can be used in source apportionment studies and to determine the particle absorption wavelength dependence.

Table 7 - Annual mean of particulate matter concentrations measured at specific wavelength (indicated in nm in brackets) by the AE33 Aethalometer in 2021. UVPM is calculated by subtracting the BC mass concentration from the UV mass concentration

	PM mass concentration (µg m^{-3})							
Site	**UV**	**Blue**	**Green**	**Yellow**	**Red**	**BC**	**IR-2**	**UVPM**
	(370)	(470)	(520)	(590)	(660)	(880)	(950)	
Auchencorth Moss	0.18	0.18	0.16	0.16	0.15	0.15	0.15	0.03
Ballymena Ballykeel	1.10	1.01	0.93	0.89	0.85	0.80	0.80	0.30
Belfast Centre	1.21	1.16	1.08	1.07	1.02	0.98	0.96	0.22
Birmingham A4540 Roadside	2.00	2.04	1.93	1.89	1.82	1.79	1.63	0.21
Birmingham Ladywood	0.92	0.91	0.86	0.84	0.80	0.77	0.80	0.14
Cardiff Centre	0.93	0.88	0.82	0.80	0.76	0.73	0.83	0.20
Chilbolton Observatory	0.58	0.50	0.45	0.43	0.41	0.38	0.40	0.20
Detling	0.72	0.66	0.61	0.60	0.57	0.55	0.55	0.16
Glasgow High Street	1.05	1.06	1.01	1.00	0.96	0.95	0.94	0.09
Glasgow Townhead	0.69	0.69	0.65	0.64	0.62	0.61	0.62	0.08
Kilmakee Leisure Centre	1.05	0.94	0.86	0.83	0.78	0.73	0.76	0.31
London Marylebone Road	1.46	1.44	1.39	1.33	1.29	1.25	1.26	0.20
London N. Kensington	0.94	0.89	0.83	0.80	0.76	0.74	0.75	0.20
Strabane 2	2.29	2.02	1.83	1.74	1.63	1.53	1.31	0.76
Average	**1.08**	**1.03**	**0.96**	**0.93**	**0.89**	**0.85**	**0.84**	**0.22**

BC and UVPM concentration data for 2021 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. Thus, all results provided in this report should be treated with caution especially when comparing 2020 and 2021 with earlier years when the AE22 model was used (see details in section 2.4.5).

4.5.2 2021 time series – black carbon

Figure 26 to Figure 30 show the black carbon concentrations measured in 2021. The time resolution of the measurements is hourly. Data has been split into regions of the UK for presentation purposes.

Very high BC mass concentrations (above 40 µg m^{-3}) were measured at Cardiff Centre on 05/06/2021 and at Detling site on 21/02/2021 and 24/03/2021. These pollution episodes have been also measured by the PM_{10} and $PM_{2.5}$ instruments on the AURN (Automatic Urban and Rural Network), so were retained as valid data.

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

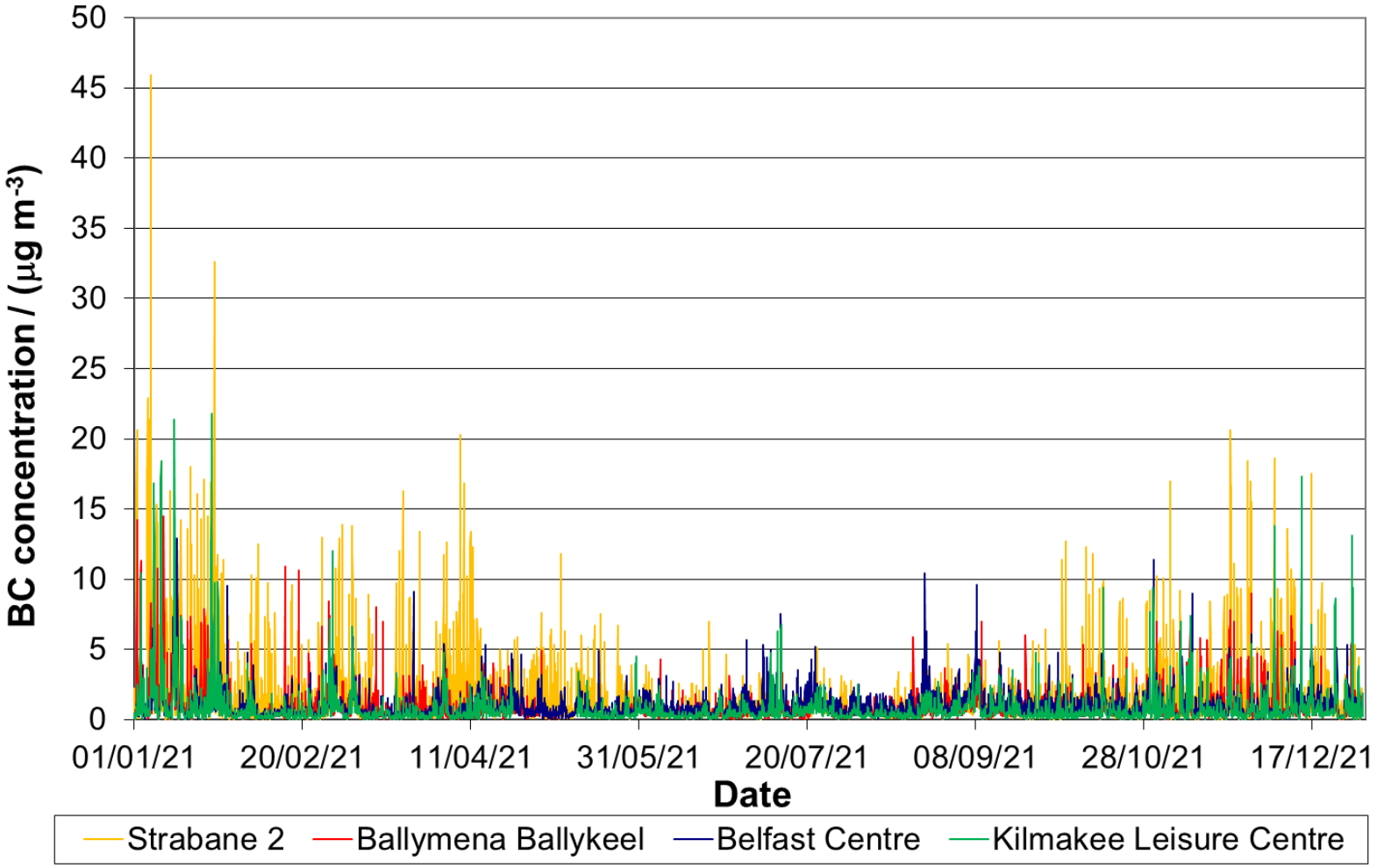

Figure 26 - Black carbon concentrations during 2021 in Northern Ireland

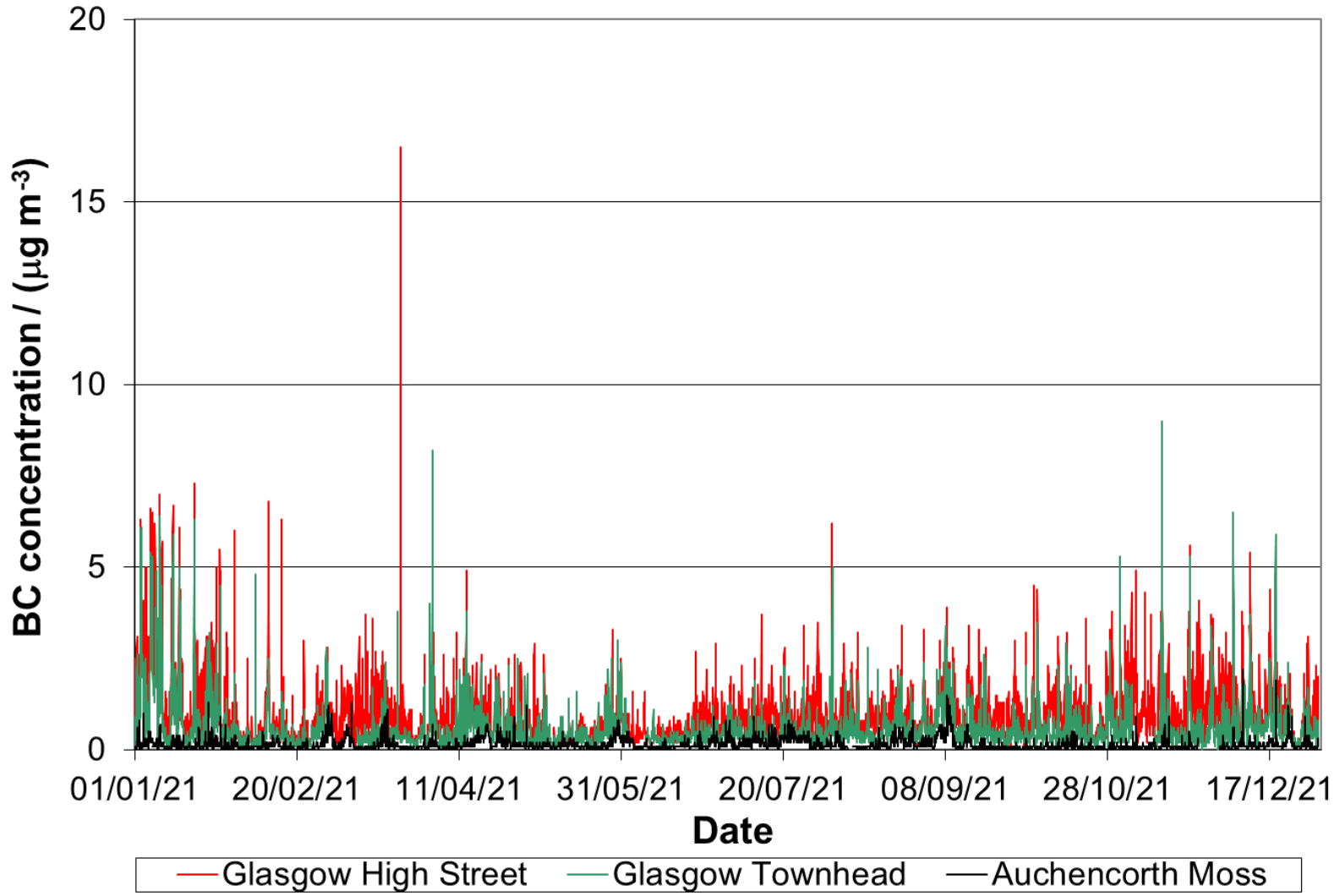

Figure 27 - Black carbon concentrations during 2021 in Scotland

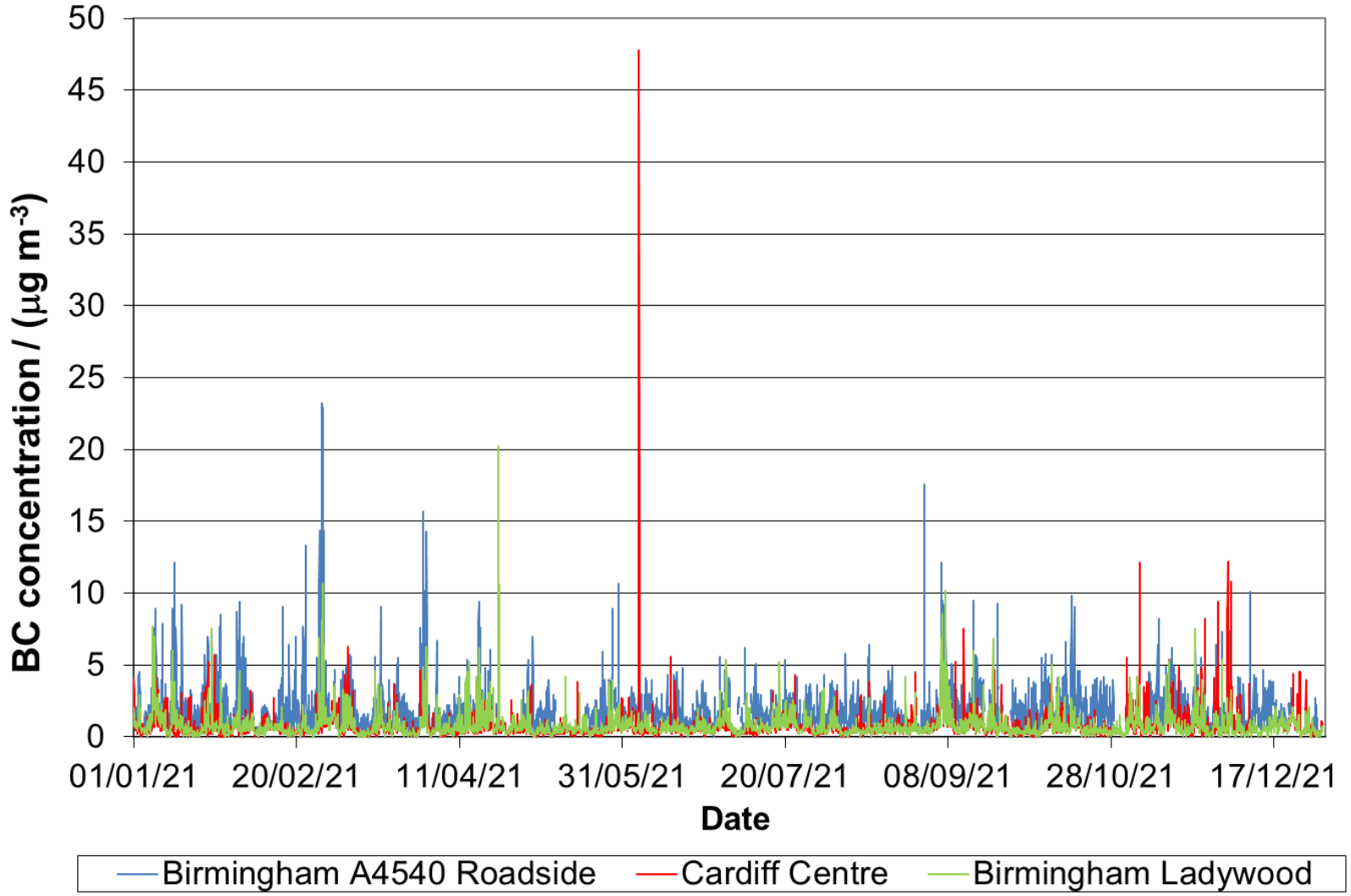

Figure 28 - Black carbon concentrations during 2021 in Wales and the Midlands

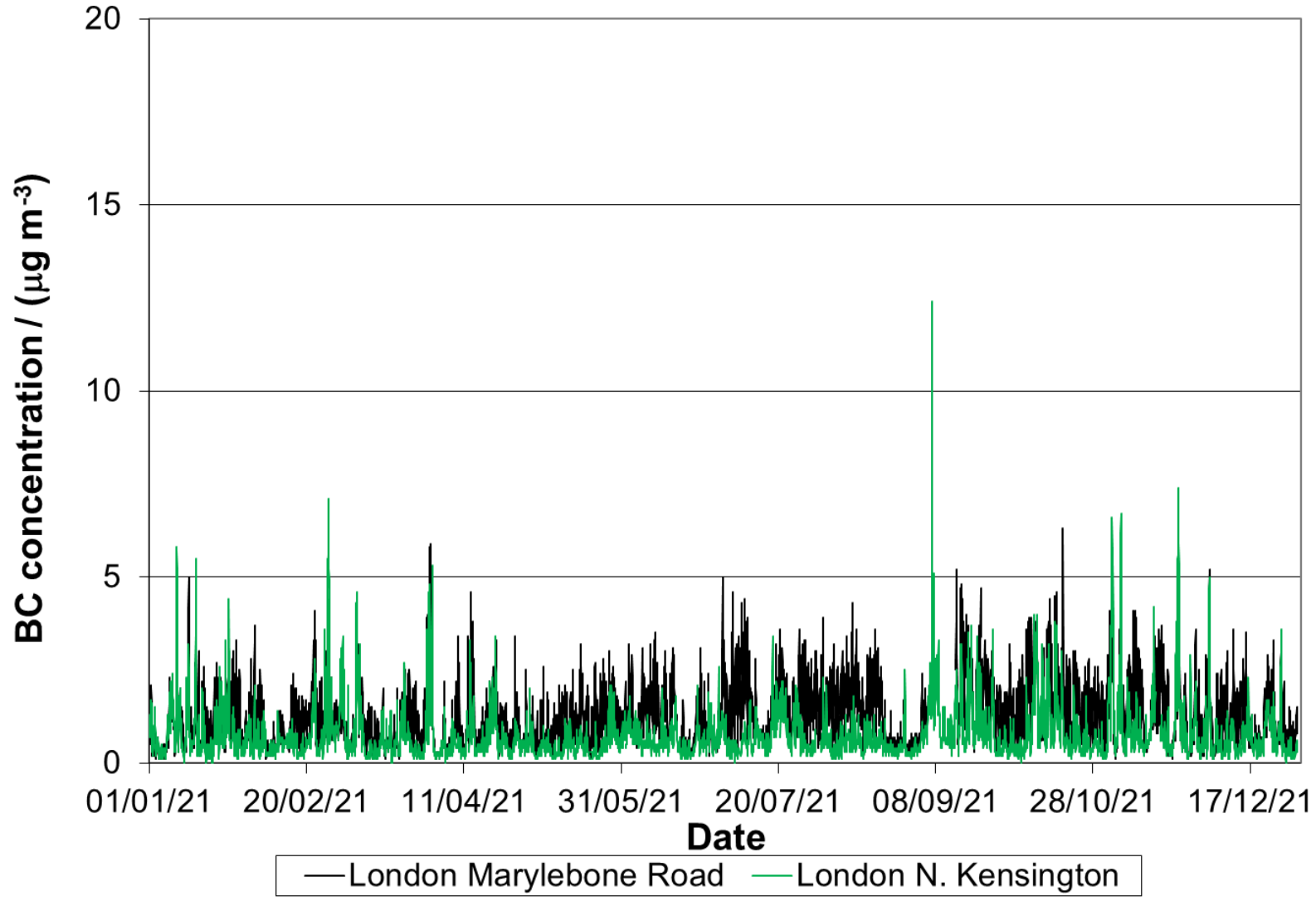

Figure 29 - Black carbon concentrations during 2021 in London

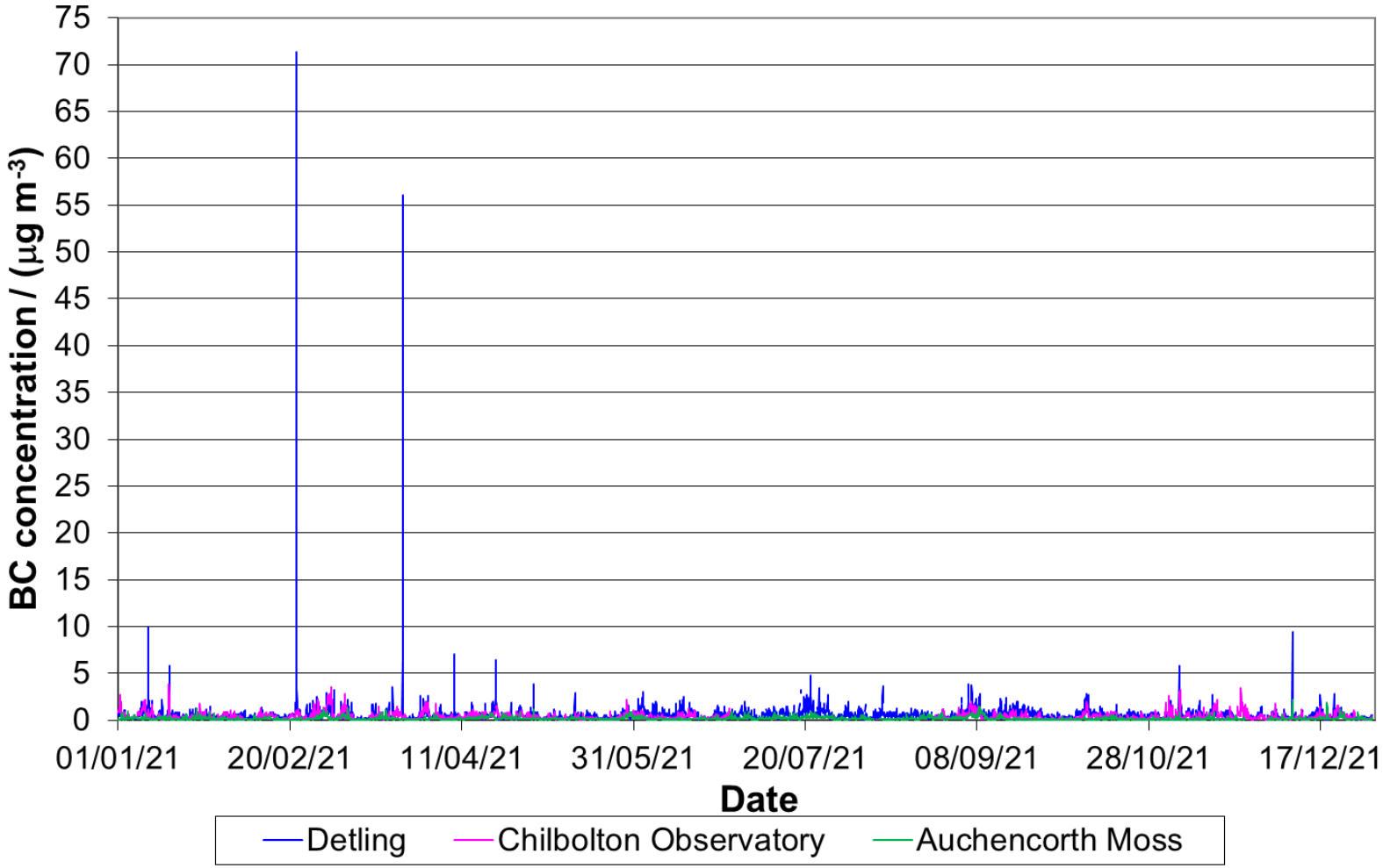

Figure 30 - Black carbon concentrations during 2021 at Rural Locations

4.5.3 2021 times series – UVPM

Figure 31 to Figure 35 show the UVPM concentrations measured in 2021. 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 mid-April (Figure 31).

Monthly averages for 2020 and 2021 at these sites are shown in Figure 36. In general, data for both sites follow the same pattern (U-shape) with the lowest level of UVPM concentrations in summer months.

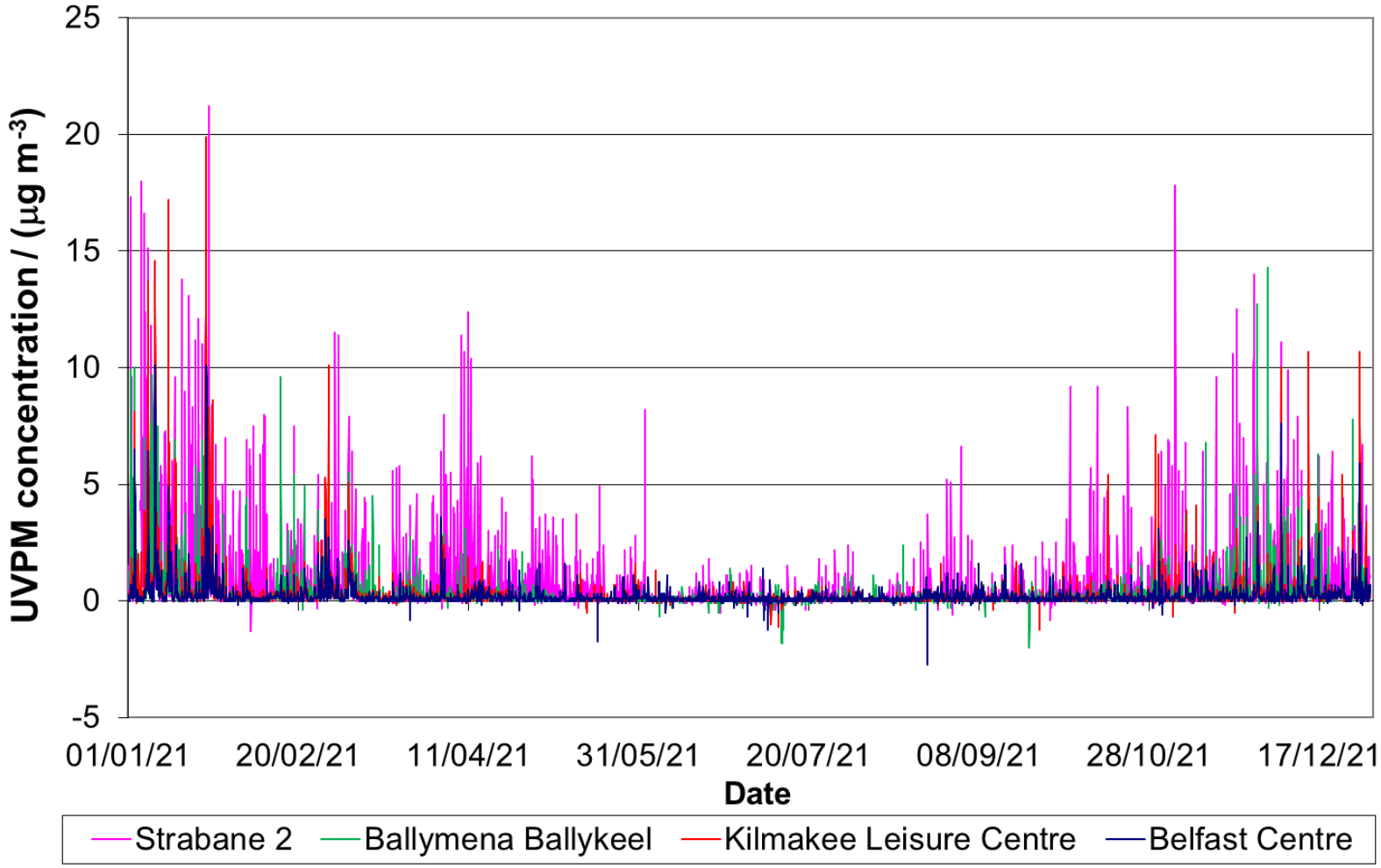

Figure 31 - UVPM concentrations during 2021 in Northern Ireland

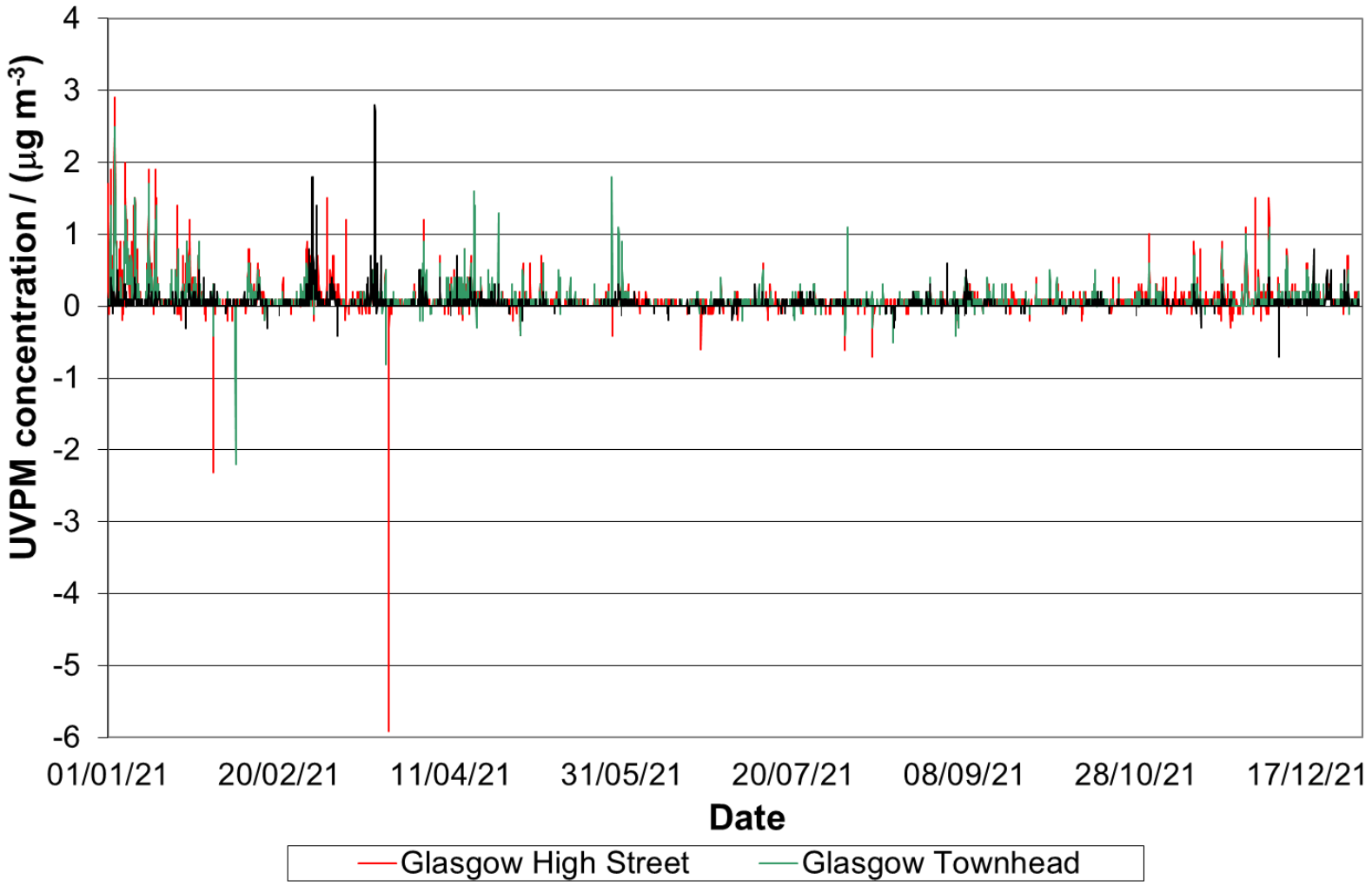

Figure 32 - UVPM concentrations during 2021 in Scotland

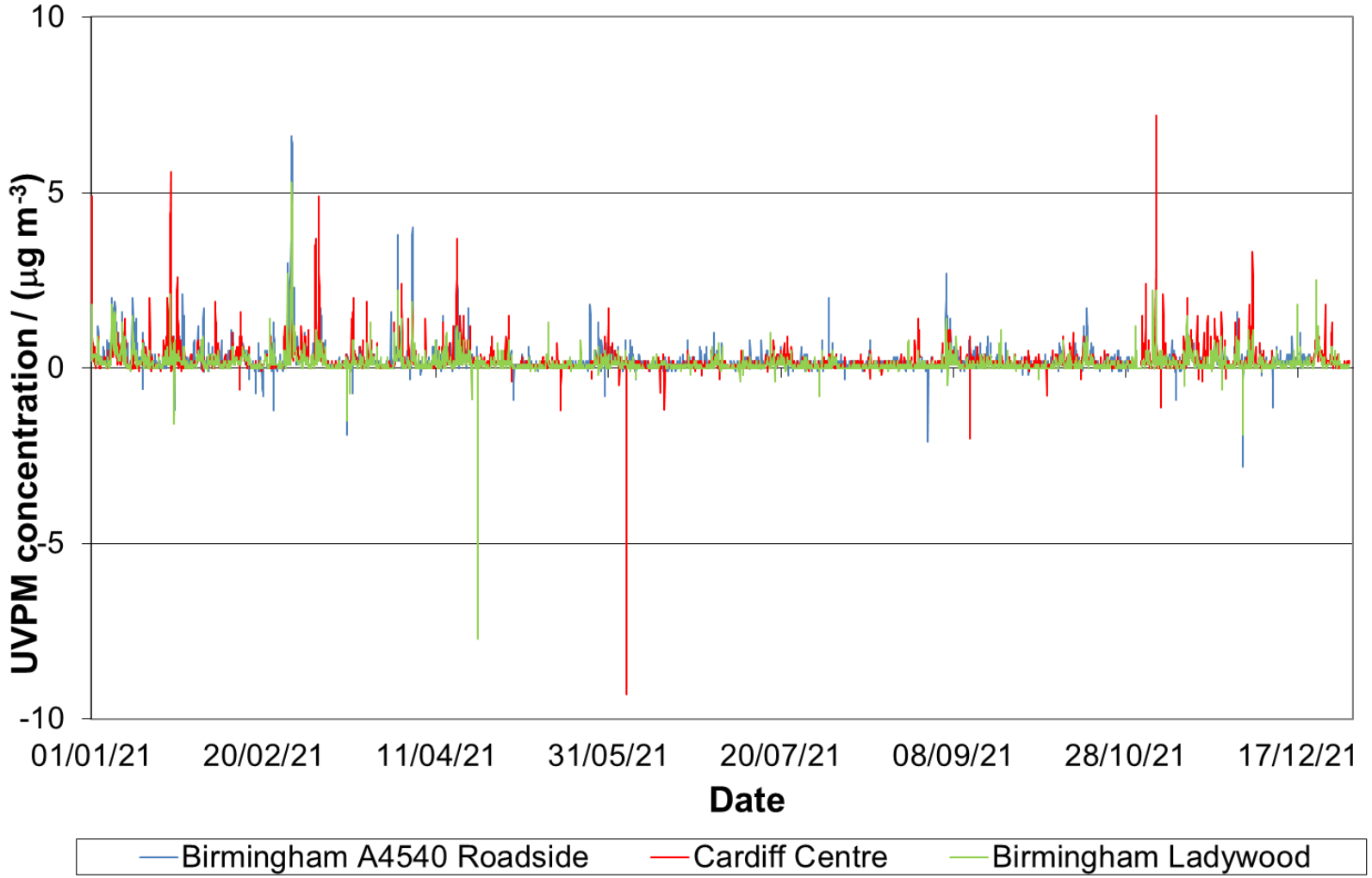

Figure 33 - UVPM concentrations during 2021 in Wales and the Midlands

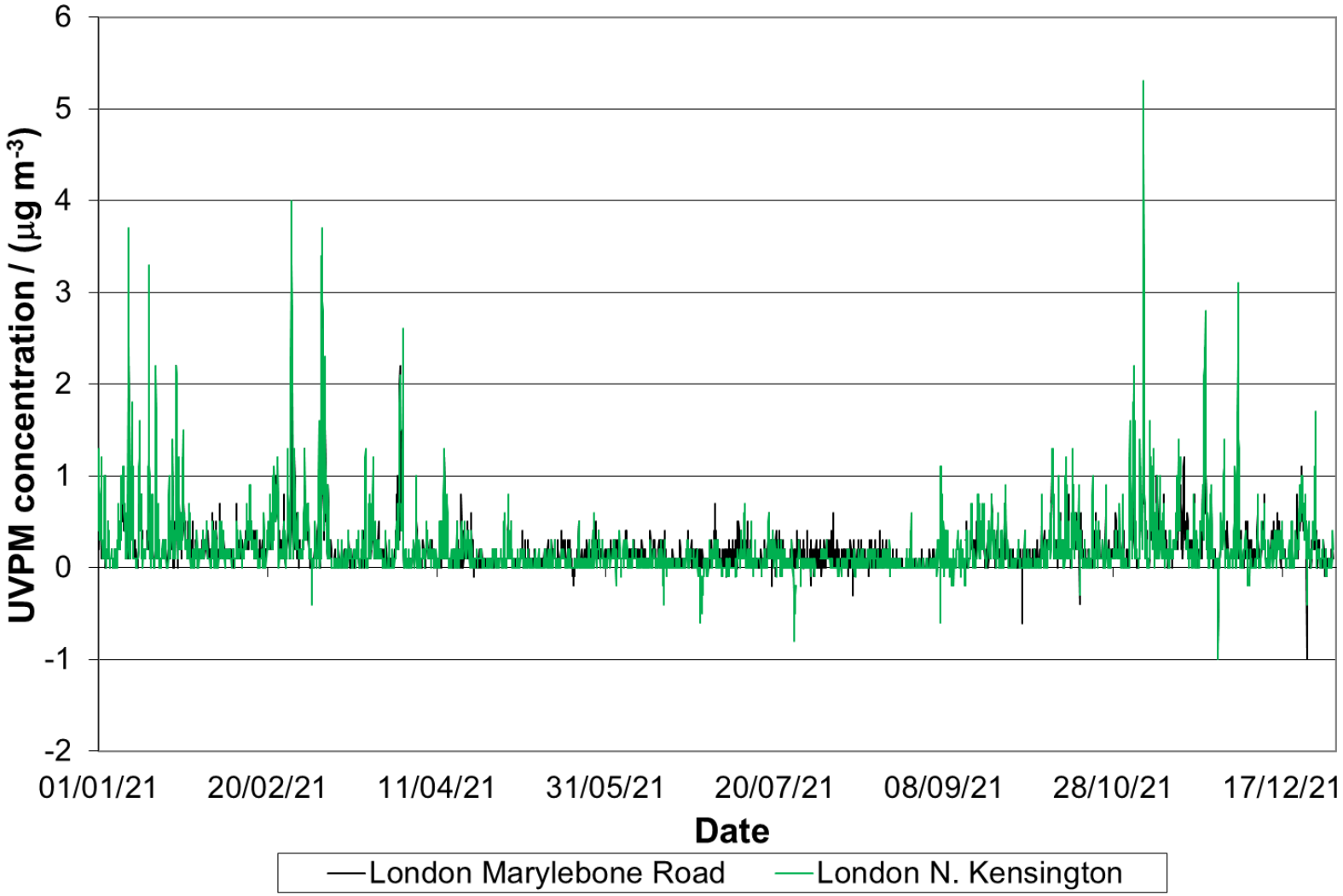

Figure 34 - UVPM concentrations during 2021 in London

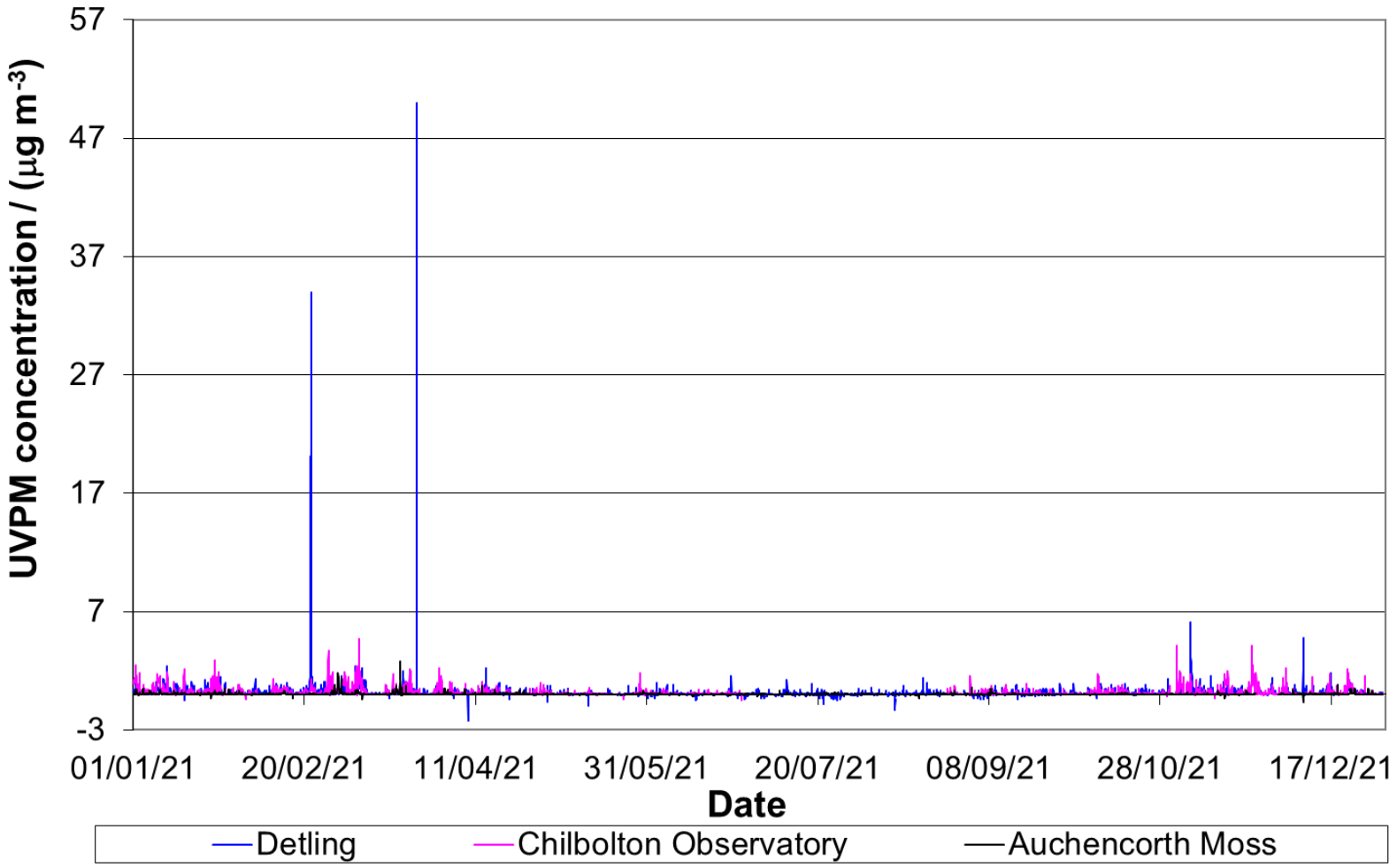

Figure 35 - UVPM concentrations during 2021 at Rural Locations

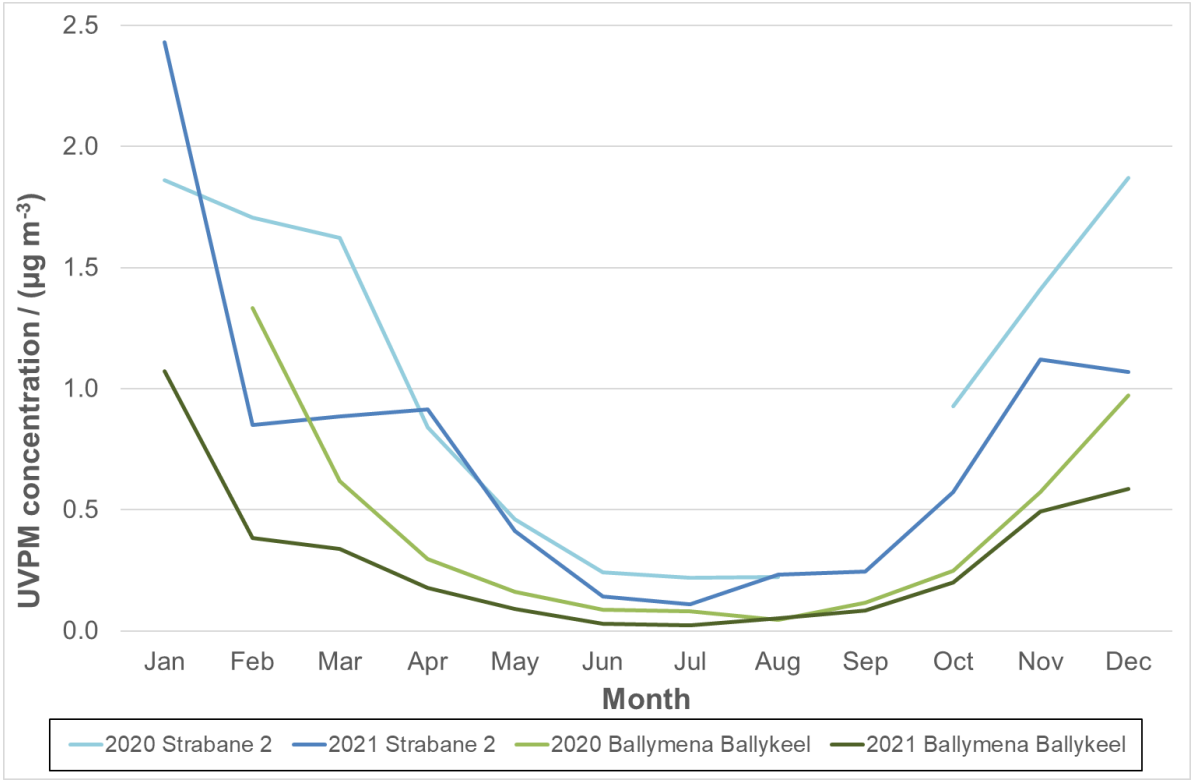

Figure 36 - UVPM concentrations at Strabane 2 and Ballymena Ballykeel sites, shown as monthly averages for 2020 and 2021

4.5.4 2021 annual averages – black carbon

The annual mean concentrations are presented as a bar graph (Figure 37) to aid the comparison of sites:

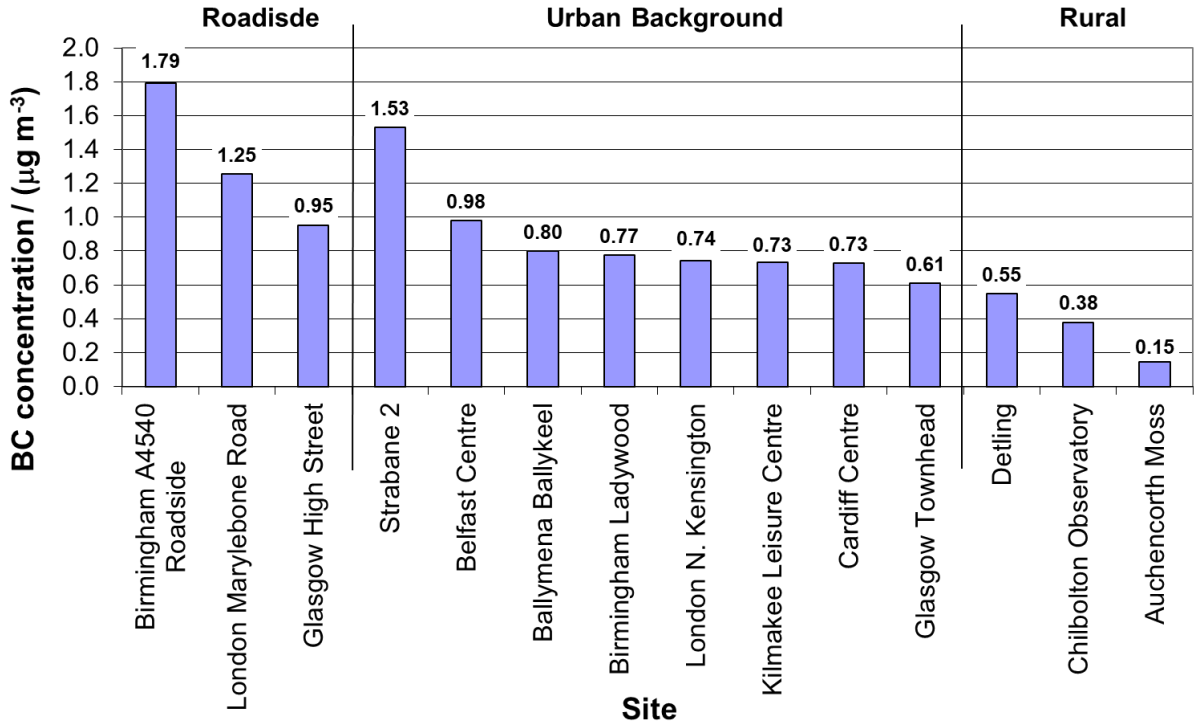

Figure 37 - Annual mean black carbon concentrations for 2021

Black carbon urban and roadside increments for London, Birmingham and Glasgow have been calculated by subtracting rural background measurements. Table 8 shows these calculated urban and roadside increment results for London, Birmingham, and Glasgow conurbations.

Table 8 - Urban and Roadside increments in black carbon concentrations in 2021

	BC increment / (µg m^{-3})	
Conurbation	**Urban**	**Roadside**
London	0.29	0.47
Birmingham	0.42	1.05
Glasgow	0.46	0.34

The urban increments for London, Birmingham and Glasgow were all similar in 2021. The roadside increment for Birmingham was larger than that for London, where it has dropped from 0.7 µg m^{-3} in 2020.

Figure 38 shows how the urban and roadside increments in London have changed over the period 2012 to 2021. The average urban increment (UB) is roughly stable, with increases during the cold periods indicating the contribution from domestic heating. The roadside increment (RS) for London has clearly dropped steadily over the period and is currently at the similar level as urban increment. 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, 2018 and 2021 which caused the gaps in Figure 38.

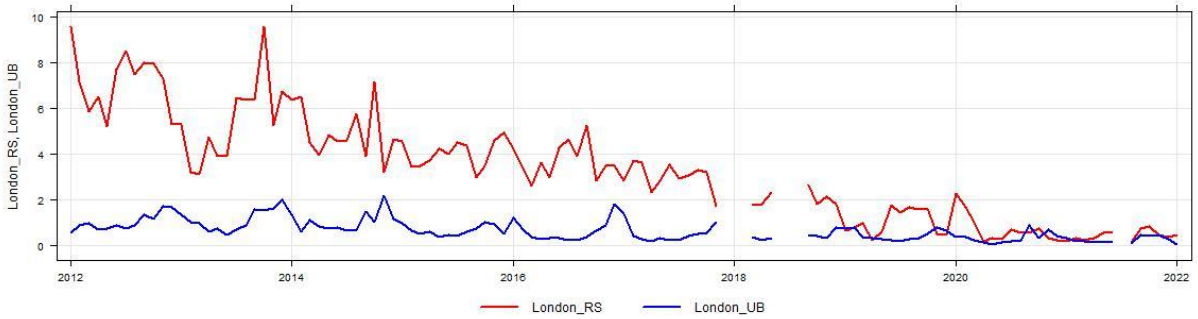

Figure 38 - Urban (UB) and roadside (RS) increments in London for the period 2012 to 2021

4.5.5 2021 annual averages – UVPM

The annual mean concentrations are presented as a bar graph (Figure 39) to aid the comparison of sites:

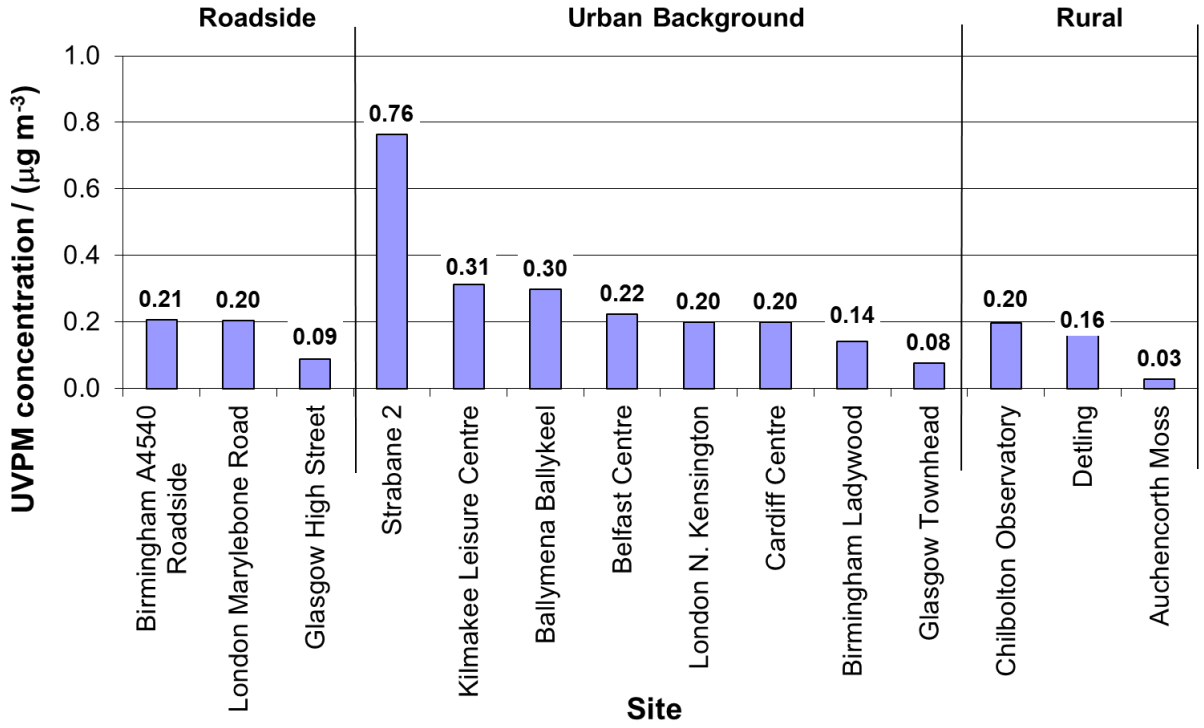

Figure 39 - Annual Mean UVPM concentrations for 2021

UVPM urban and roadside increments for London, Birmingham and Glasgow have been calculated by subtracting rural background measurements. Table 9 shows increment results for London, Birmingham, and Glasgow conurbations.

Table 9 - Urban and Roadside increments in UVPM concentrations in 2021

	UVPM increment / (µg m^{-3})	
Conurbation	**Urban**	**Roadside**
London	0.04	-0.01
Birmingham	-0.04	0.07
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 2020 and 2021.

Using the same method, the urban increment in UVPM concentration in Northern Ireland has been calculated relative to Belfast Centre where gas heating has largely displaced oil and coal since 2000. The results are shown in Table 10.

Table 10 - Increment in UVPM concentration in Northern Ireland

	Increment compared to Belfast Centre (µg m^{-3})	Increment compared to Belfast Centre (%)
Dunmurry	0.07	33
Ballymena Ballykeel	0.09	38
Strabane 2	0.55	244

The increments at Dunmurry (Kilmakee Leisure Centre), Ballymena Ballykeel and Strabane 2 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 2. Changes in the UVPM increment in Northern Ireland over the last ten years are summarised in Figure 40.

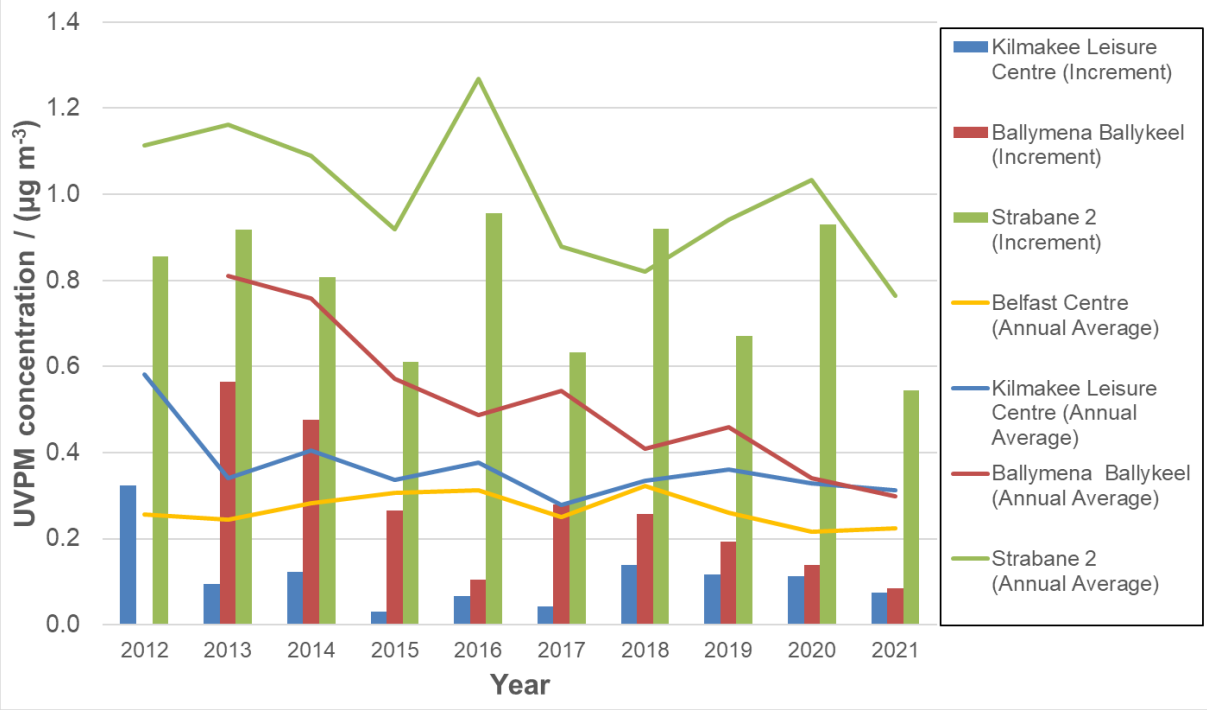

Figure 40 - Annual Mean UVPM concentrations and increments compared to Belfast Centre for 2012-2021

4.5.6 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 2021 data are presented in Figure 41 to Figure 54.

Data from 2009-2021 are presented in Figure 55 to Figure 59. These 13-year average plots only include those sites which have been operating for the whole of this period. The Chilbolton Observatory site was seen to record 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 – 2021, are considered to be less biased when compared to the single year (2021) measurements presented in Figure 41 to Figure 54.

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 calculated through bootstrap sampling, expressed with a level of confidence of 95%. It is not the overall measurement uncertainty. The shaded area on the x-axis in Figure 41 to Figure 54 is for display purposes only, to allow the uncertainty in the mean value to be seen more clearly. Figure 41 to Figure 59 are generated using the OpenAir Tools run on the R software platform[12,13].

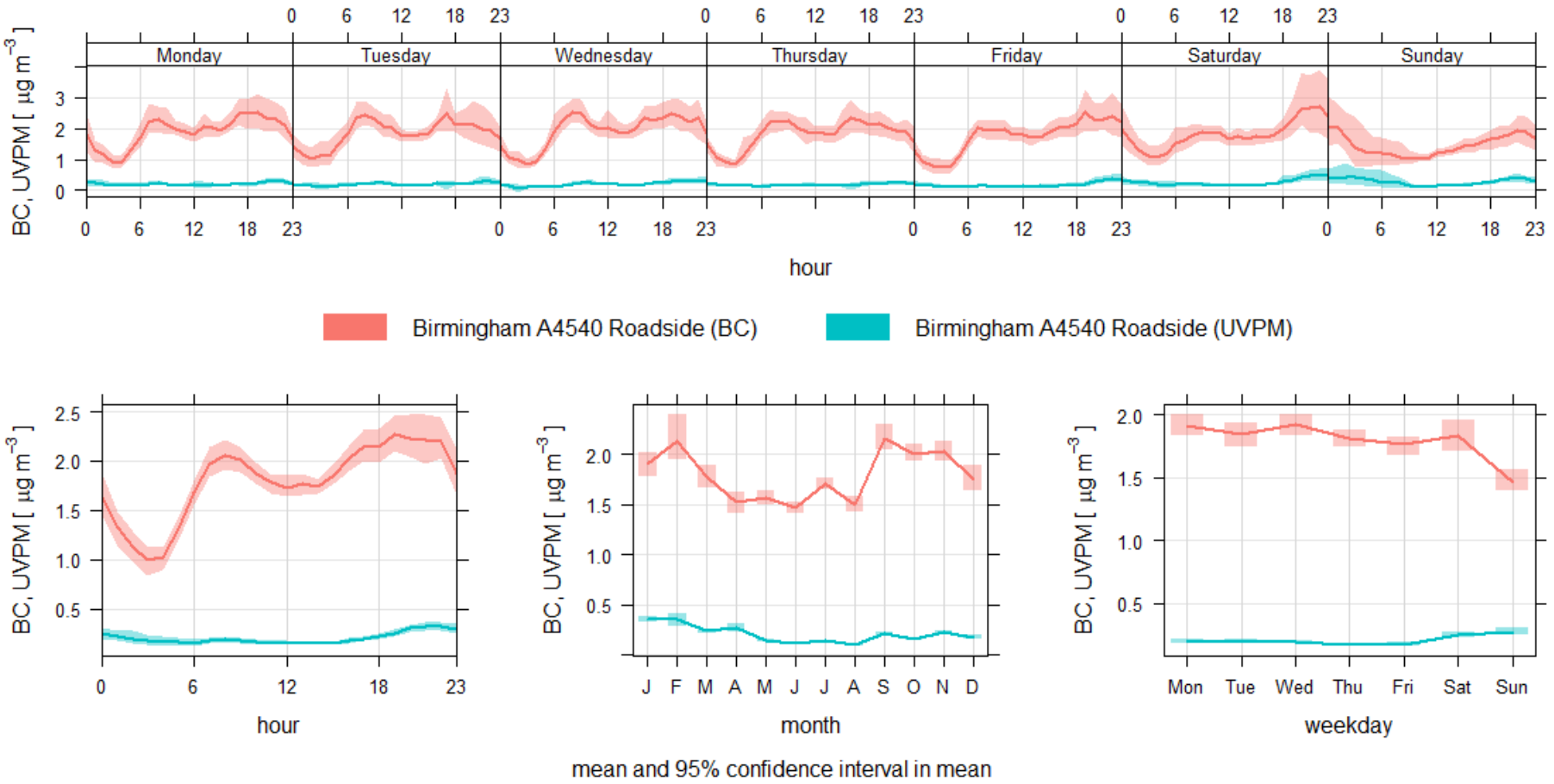

Figure 41 - Temporal variations of BC and UVPM concentrations at Birmingham A4540 Roadside for 2021

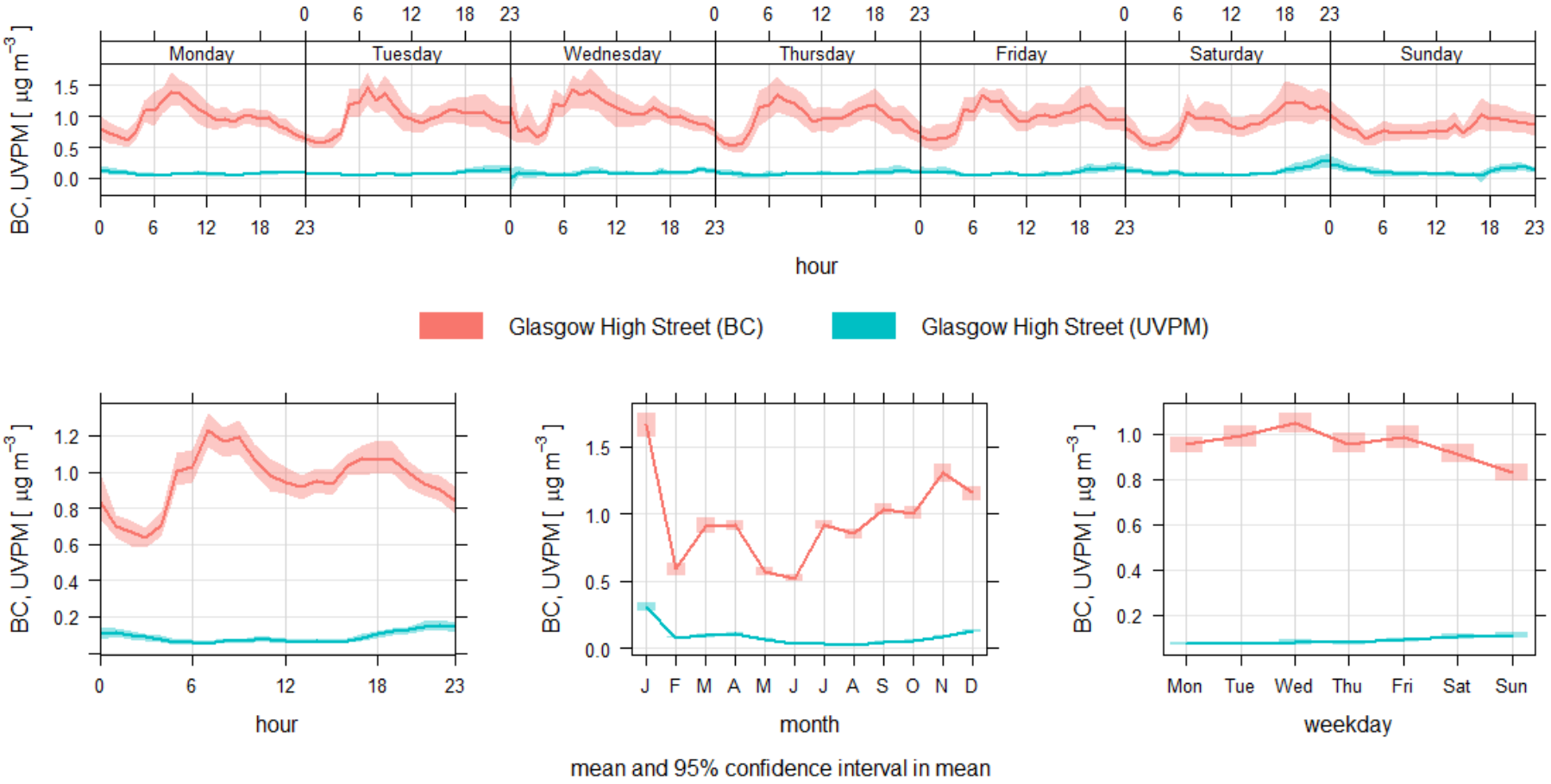

Figure 42 - Temporal variations of BC and UVPM concentrations at Glasgow High Street for 2021

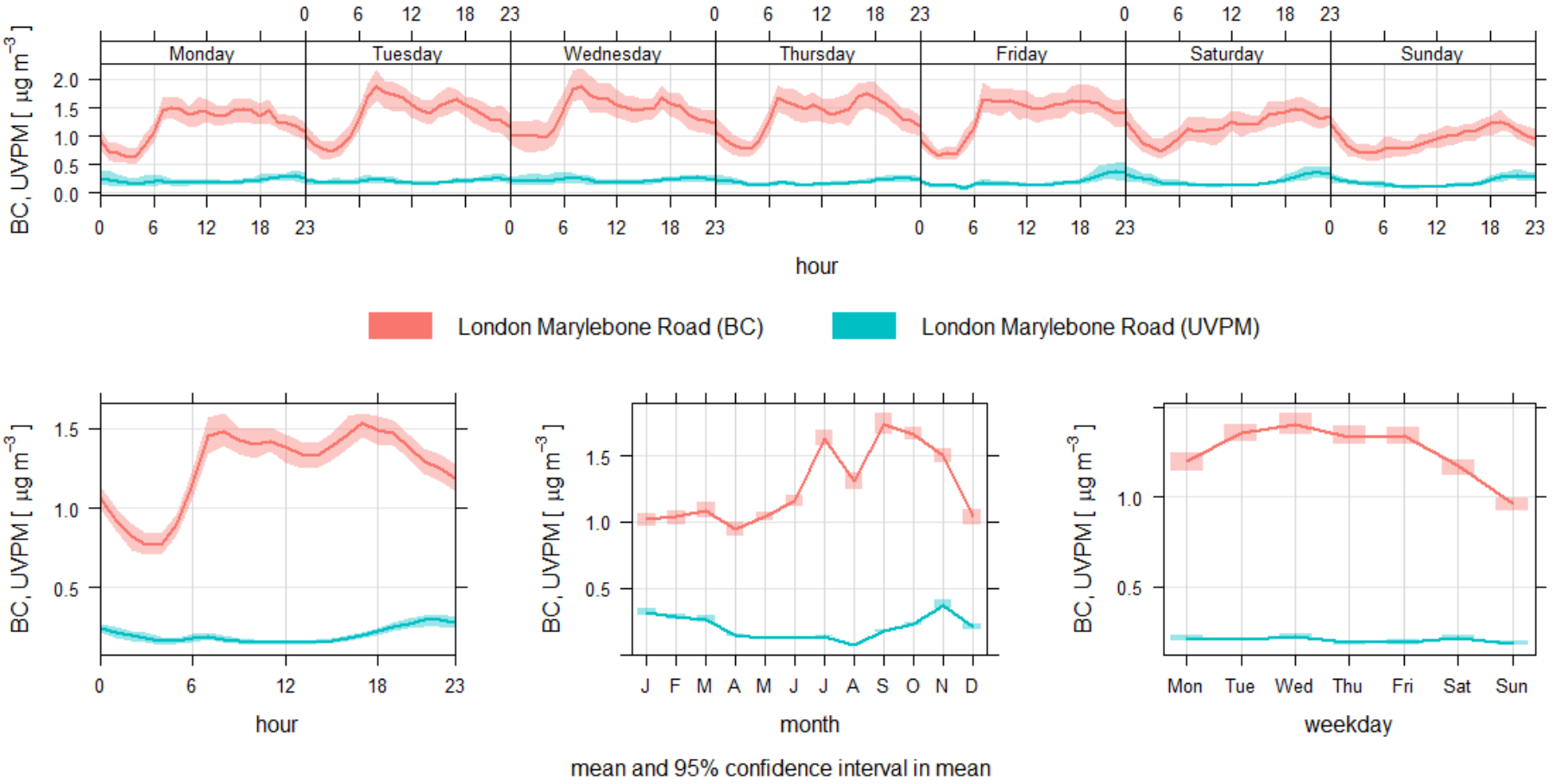

Figure 43 - Temporal variations of BC and UVPM concentrations at London Marylebone Road for 2021

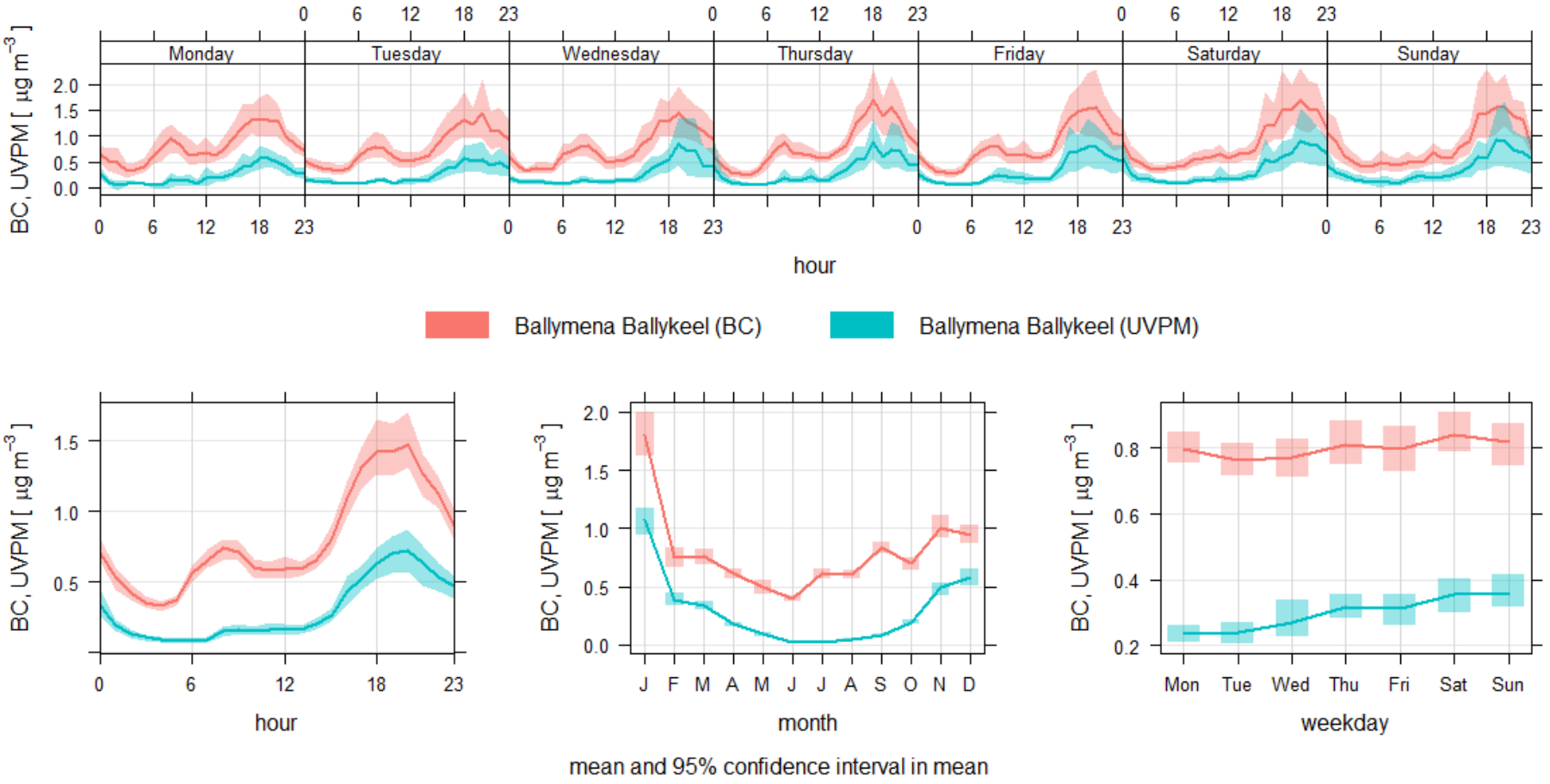

Figure 44 - Temporal variations of BC and UVPM concentrations at Ballymena Ballykeel for 2021

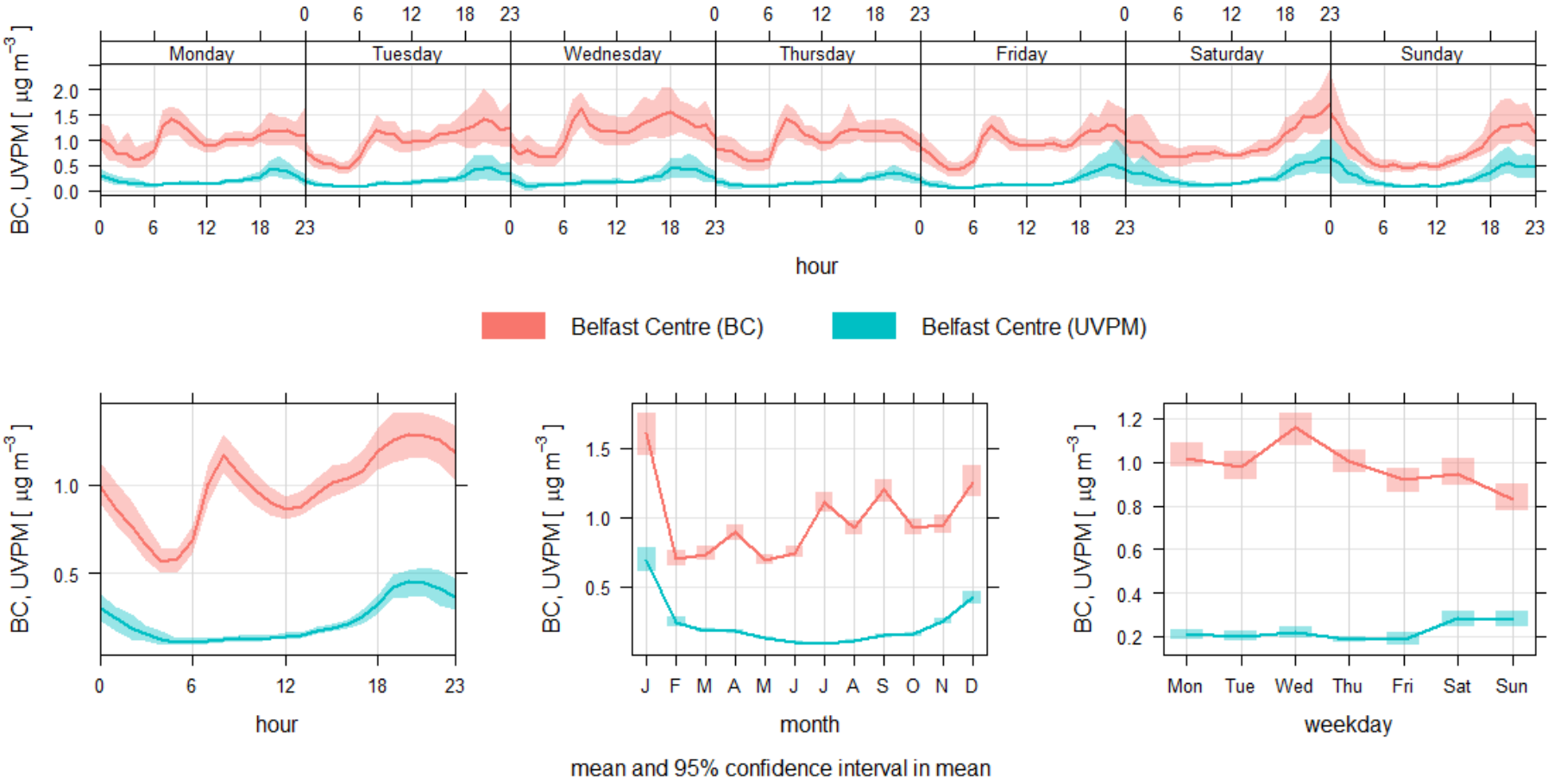

Figure 45 - Temporal variations of BC and UVPM concentrations at Belfast Centre for 2021

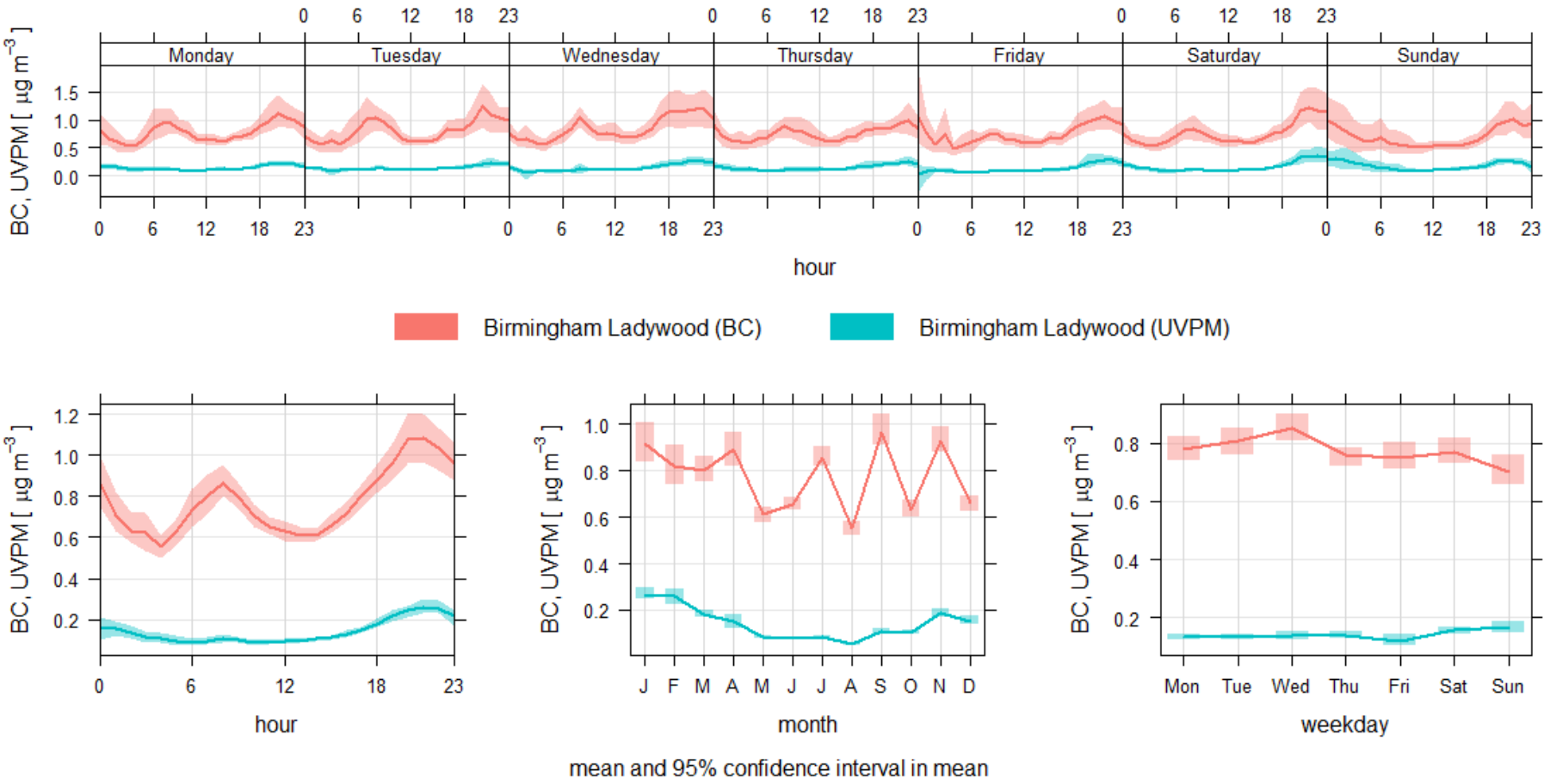

Figure 46- Temporal variations of BC and UVPM concentrations at Birmingham Ladywood for 2021

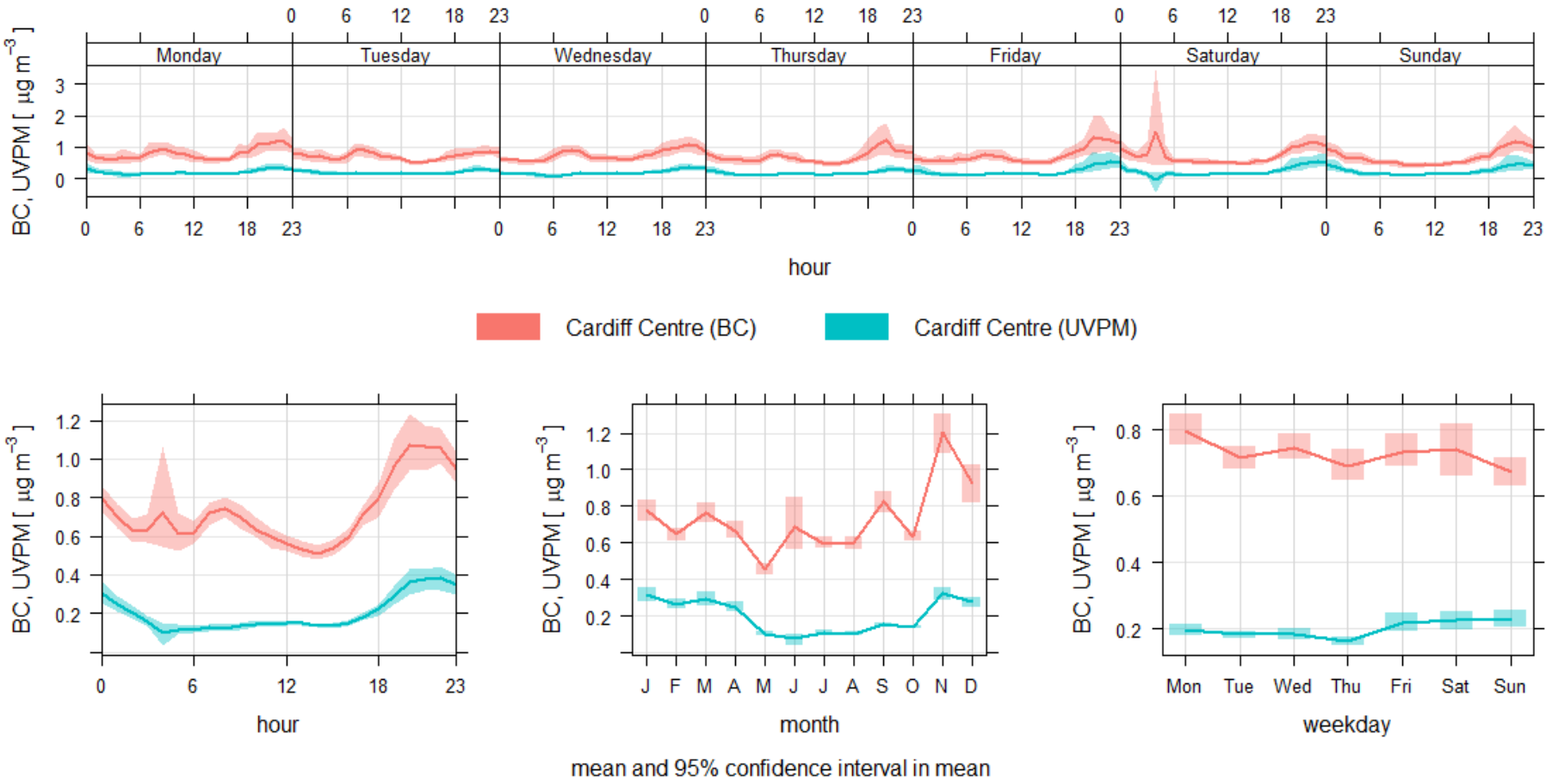

Figure 47 - Temporal variations of BC and UVPM concentrations at Cardiff Centre for 2021

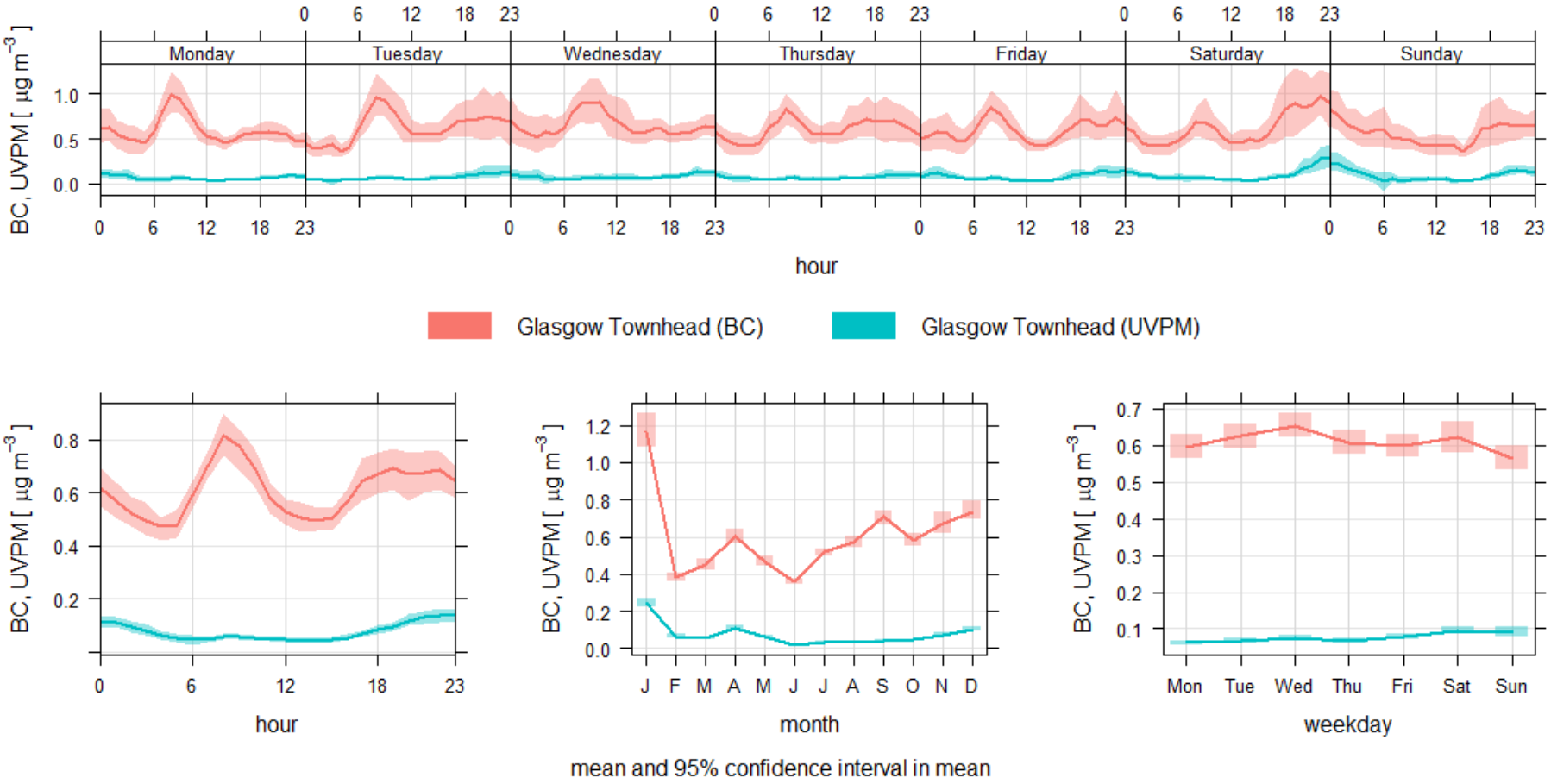

Figure 48 - Temporal variations of BC and UVPM concentrations at Glasgow Townhead for 2021

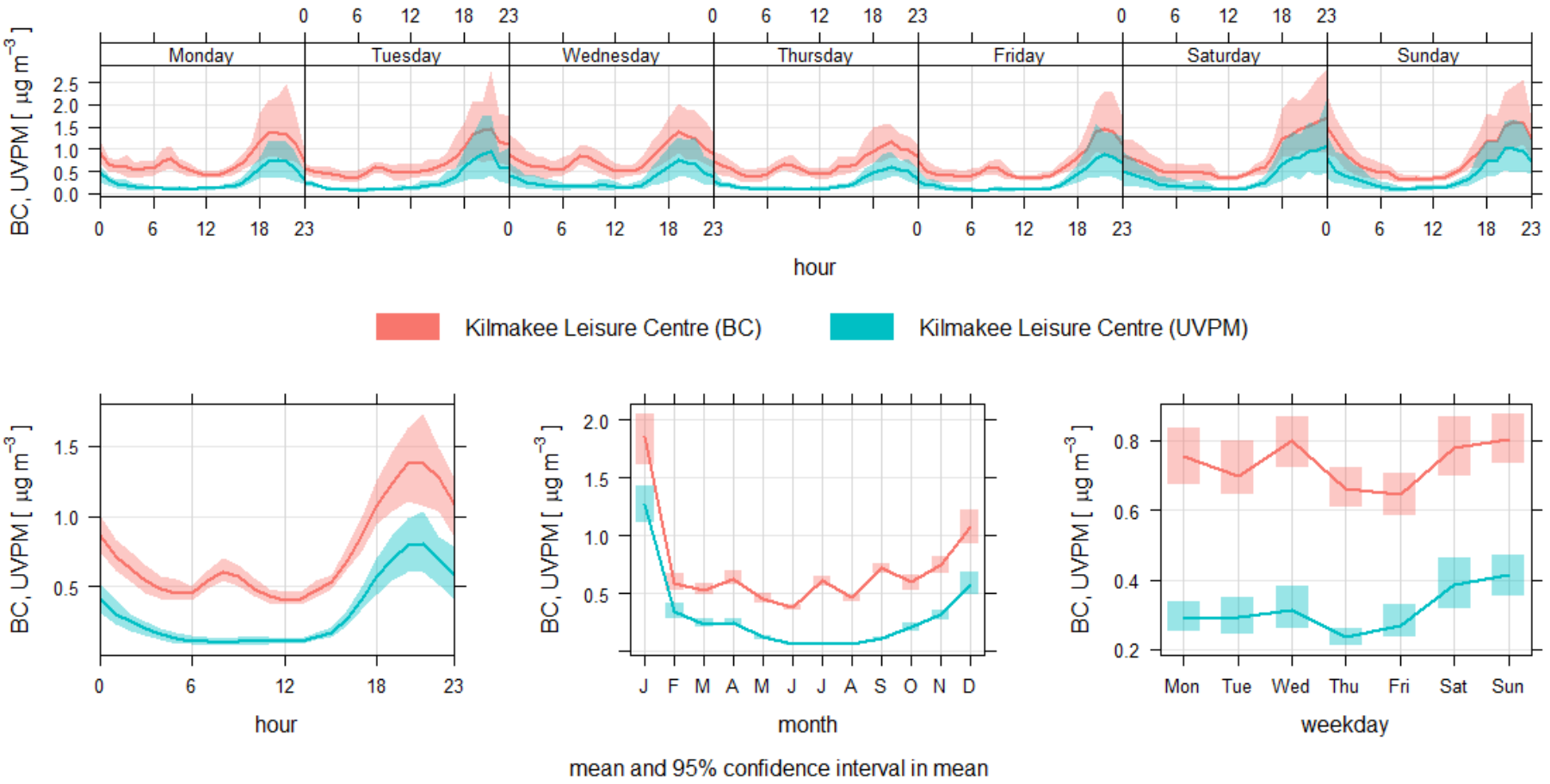

Figure 49 - Temporal variations of BC and UVPM concentrations at Kilmakee Leisure Centre for 2021

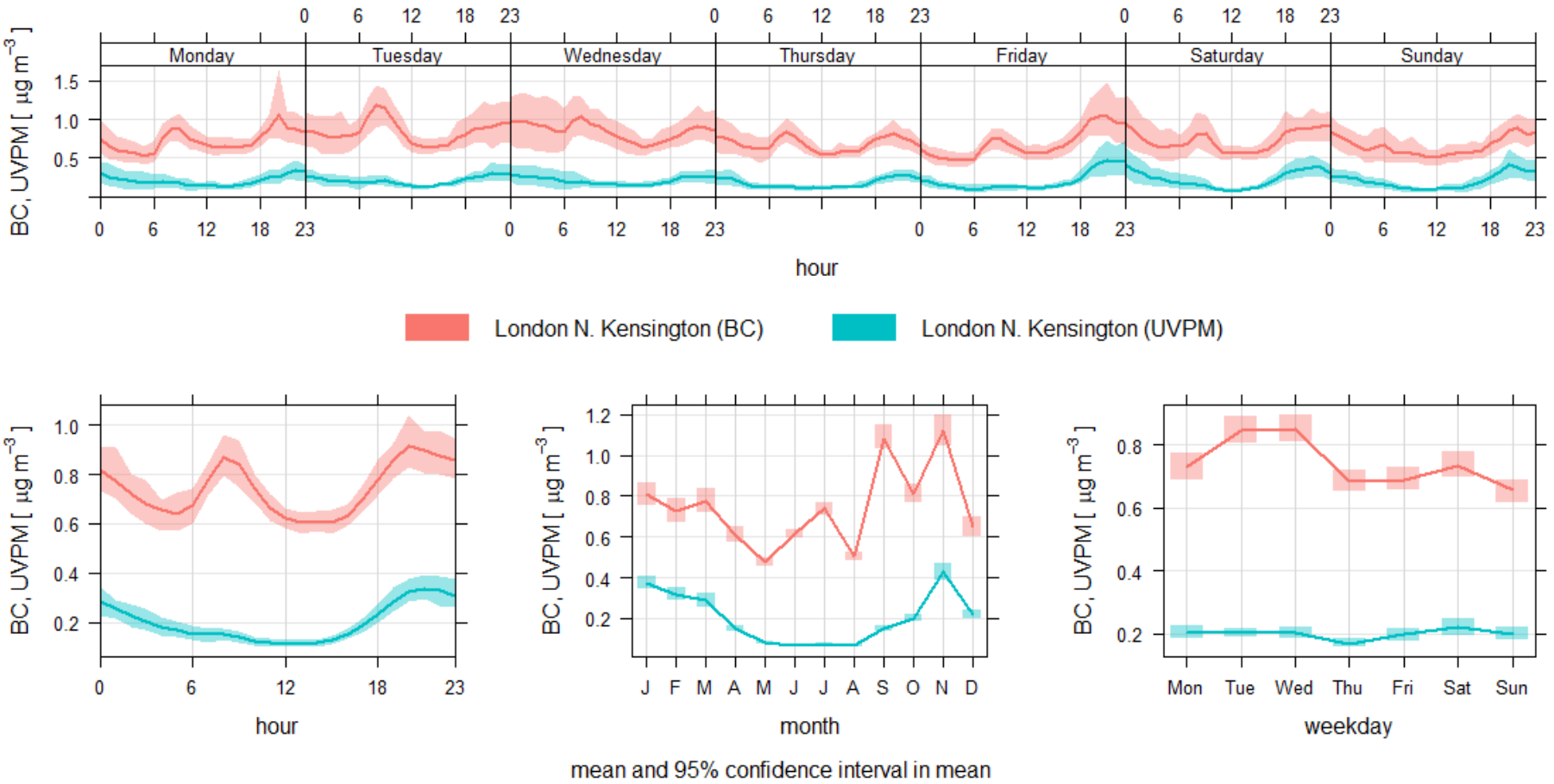

Figure 50 - Temporal variations of BC and UVPM concentrations at London N. Kensington for 2021

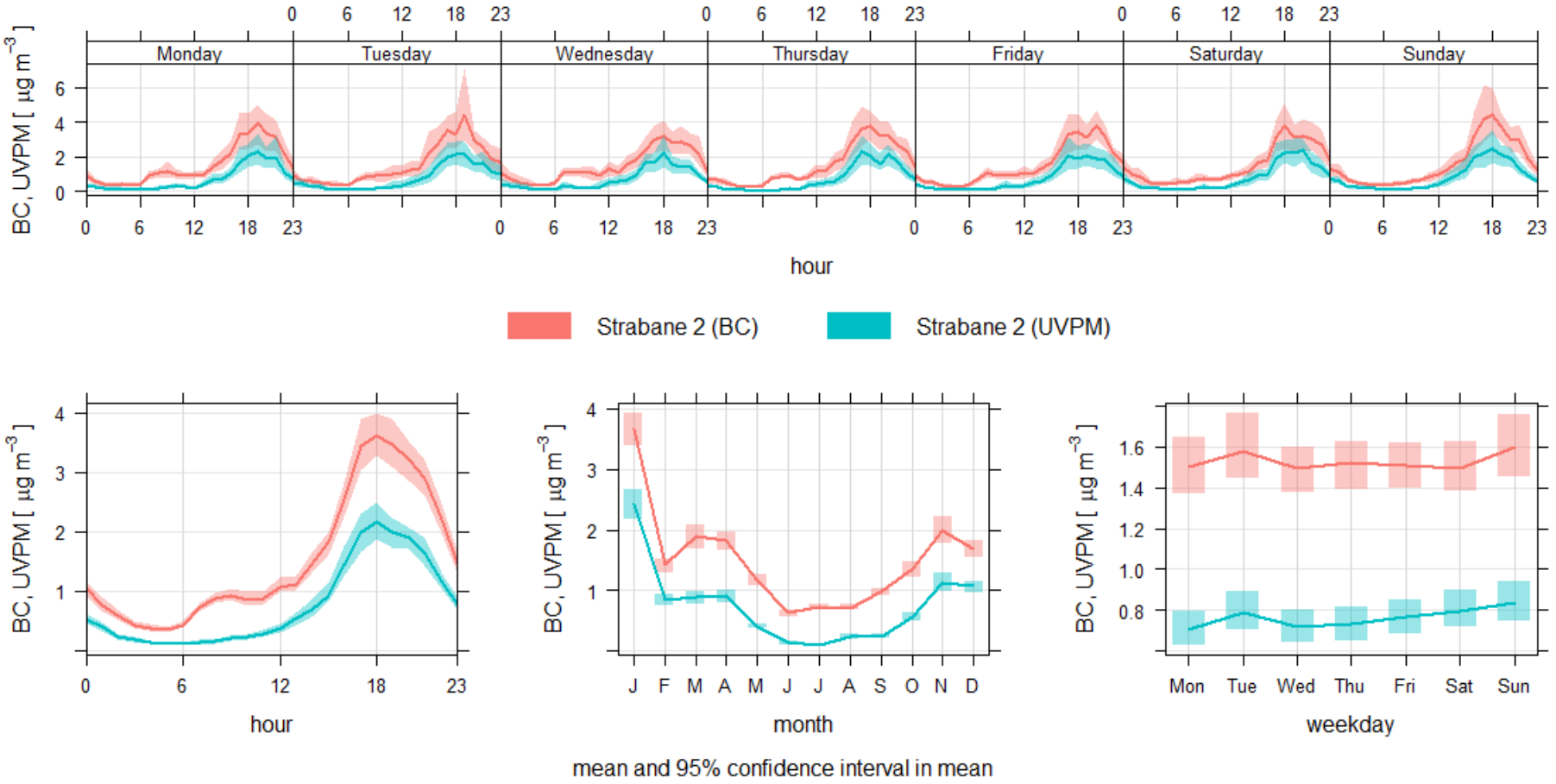

Figure 51 - Temporal variations of BC and UVPM concentrations at Strabane 2 for 2021

BC and UVPM data at Rural Background sites for 2021

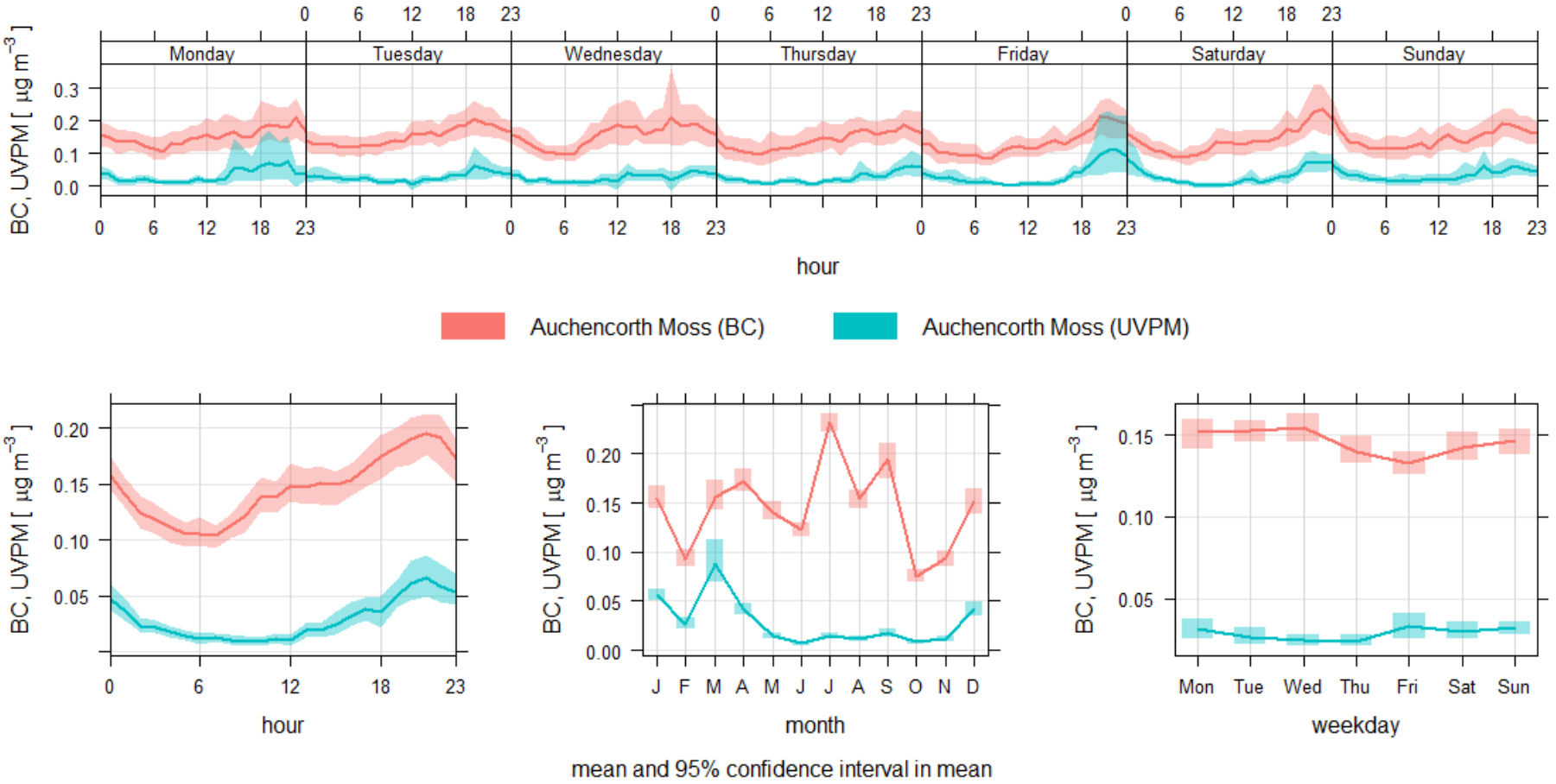

Figure 52 - Temporal variations of BC and UVPM concentrations at Auchencorth Moss for 2021

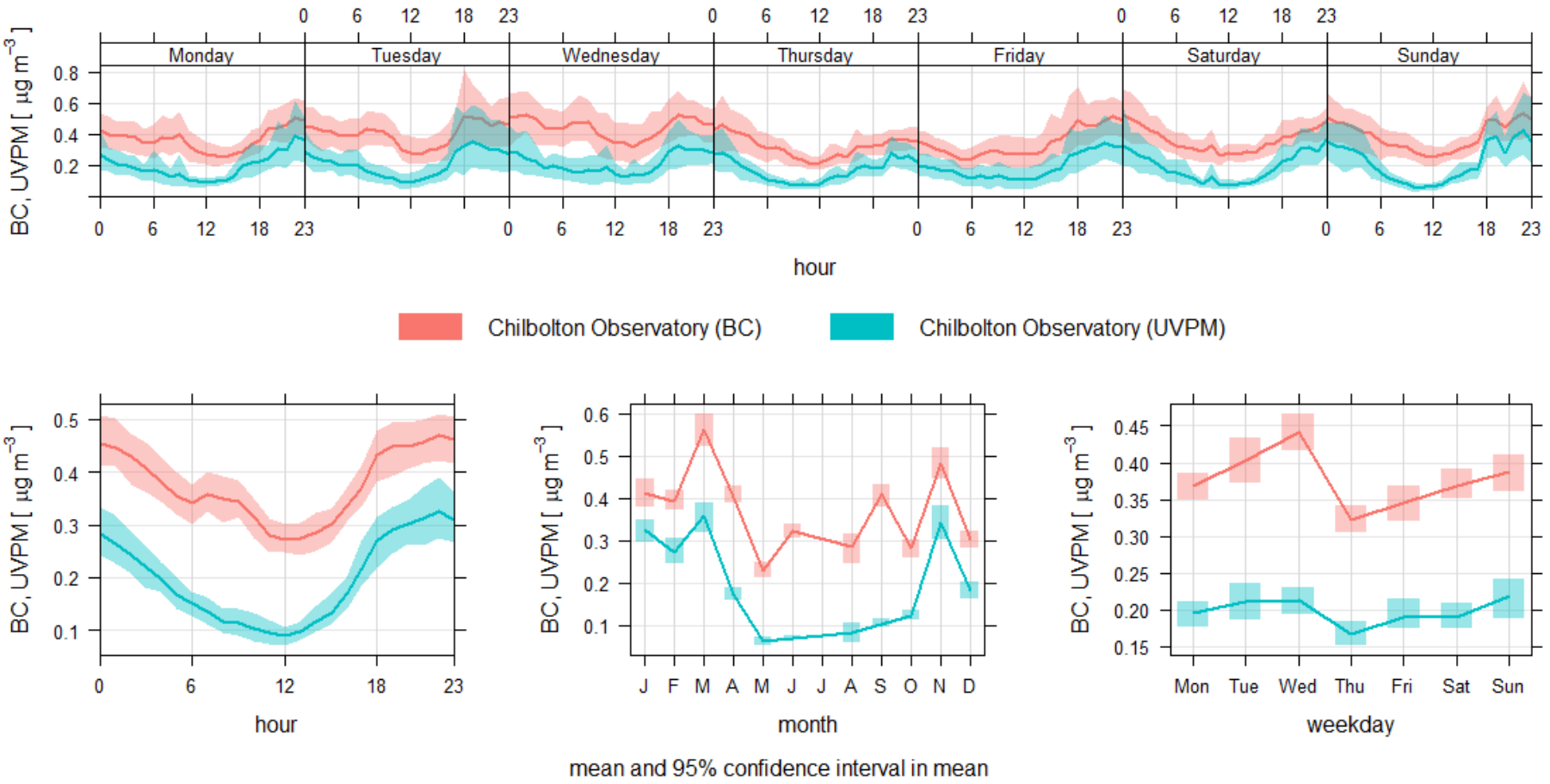

Figure 53 - Temporal variations of BC and UVPM concentrations at Chilbolton Observatory for 2021

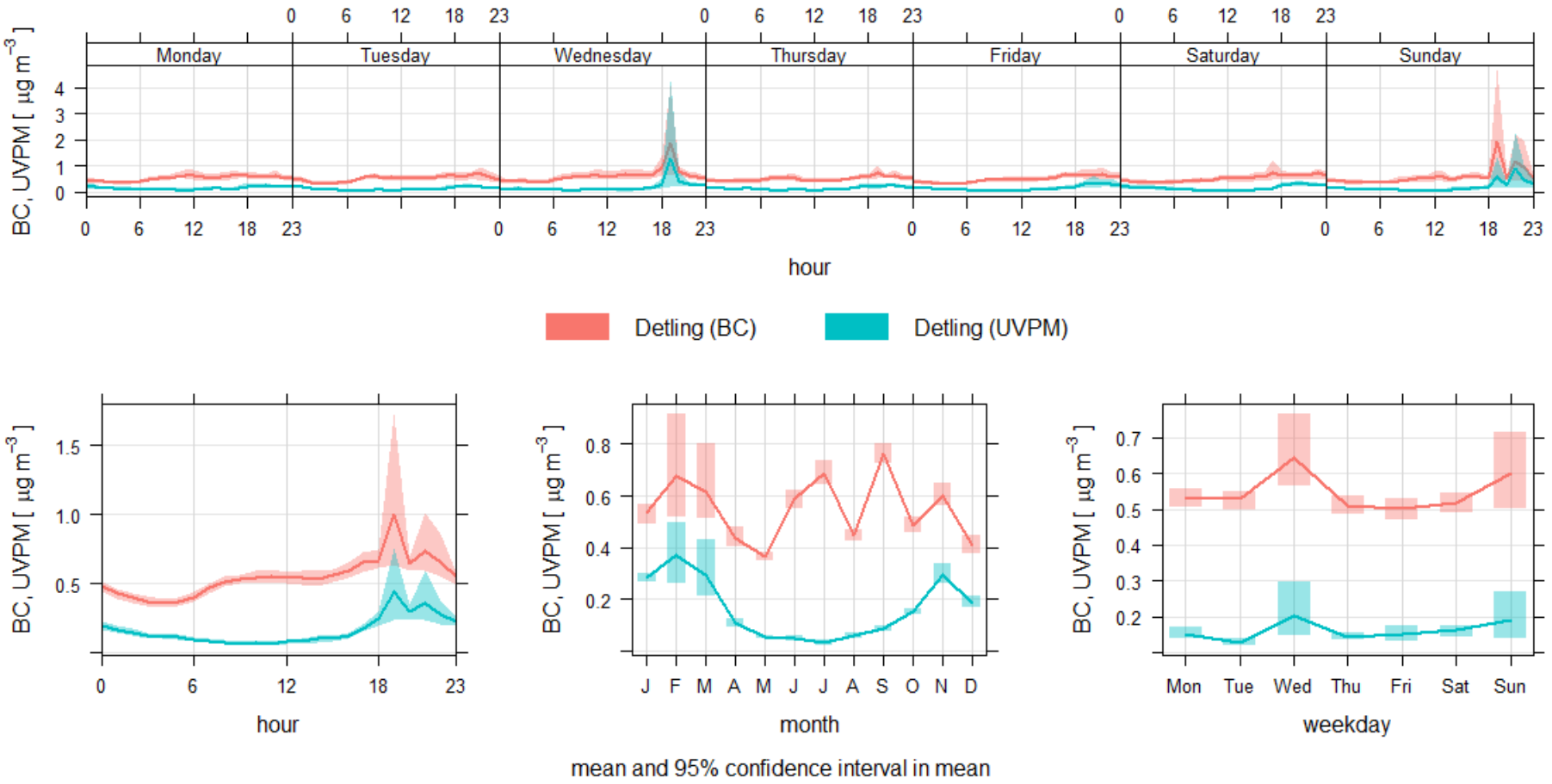

Figure 54 - Temporal variations of BC and UVPM concentrations at Detling for 2021

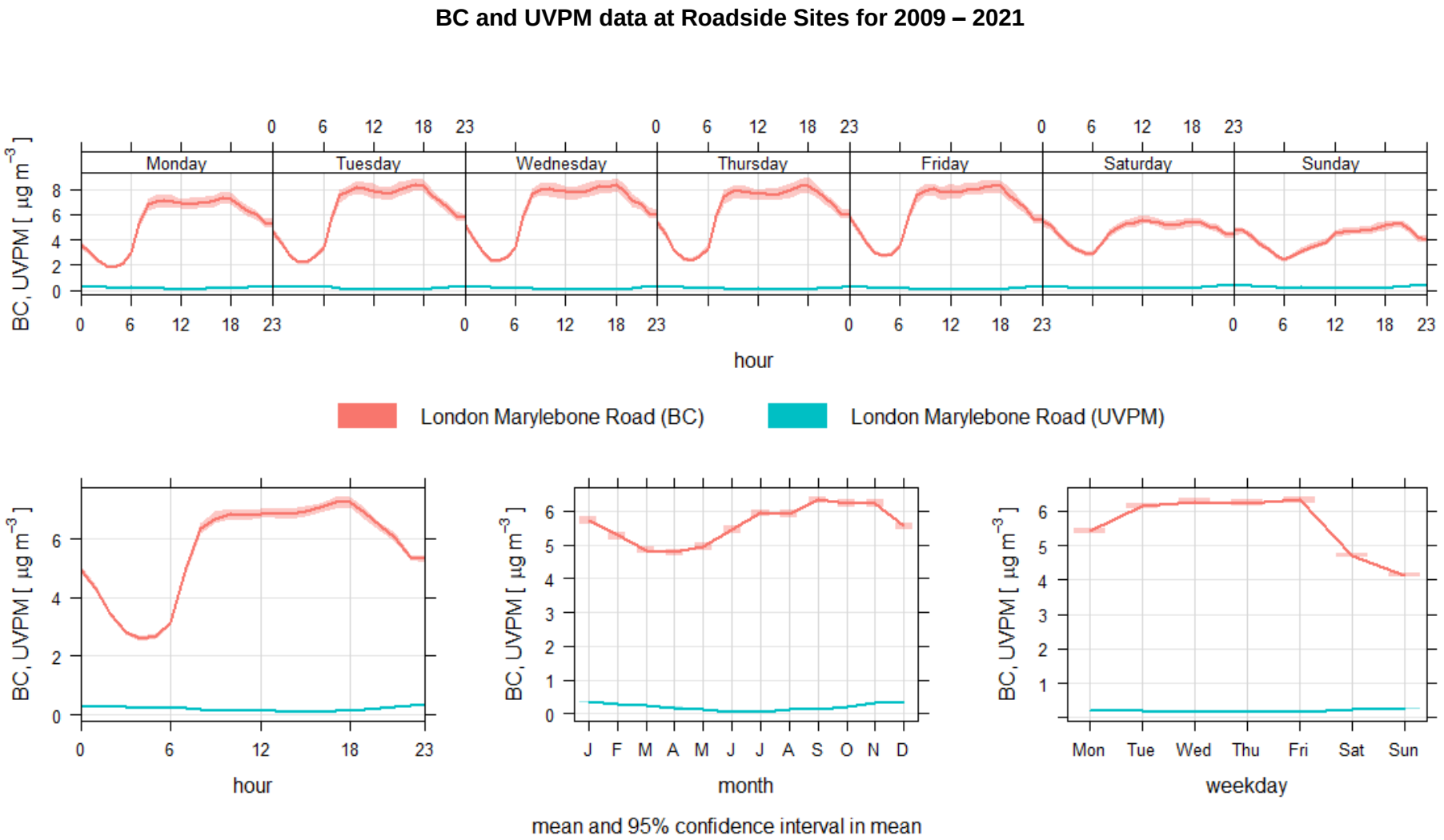

Figure 55 - Temporal variations of BC and UVPM concentrations at London Marylebone Road for 2009-2021

BC and UVPM data at Urban Background Sites for 2009 – 2021

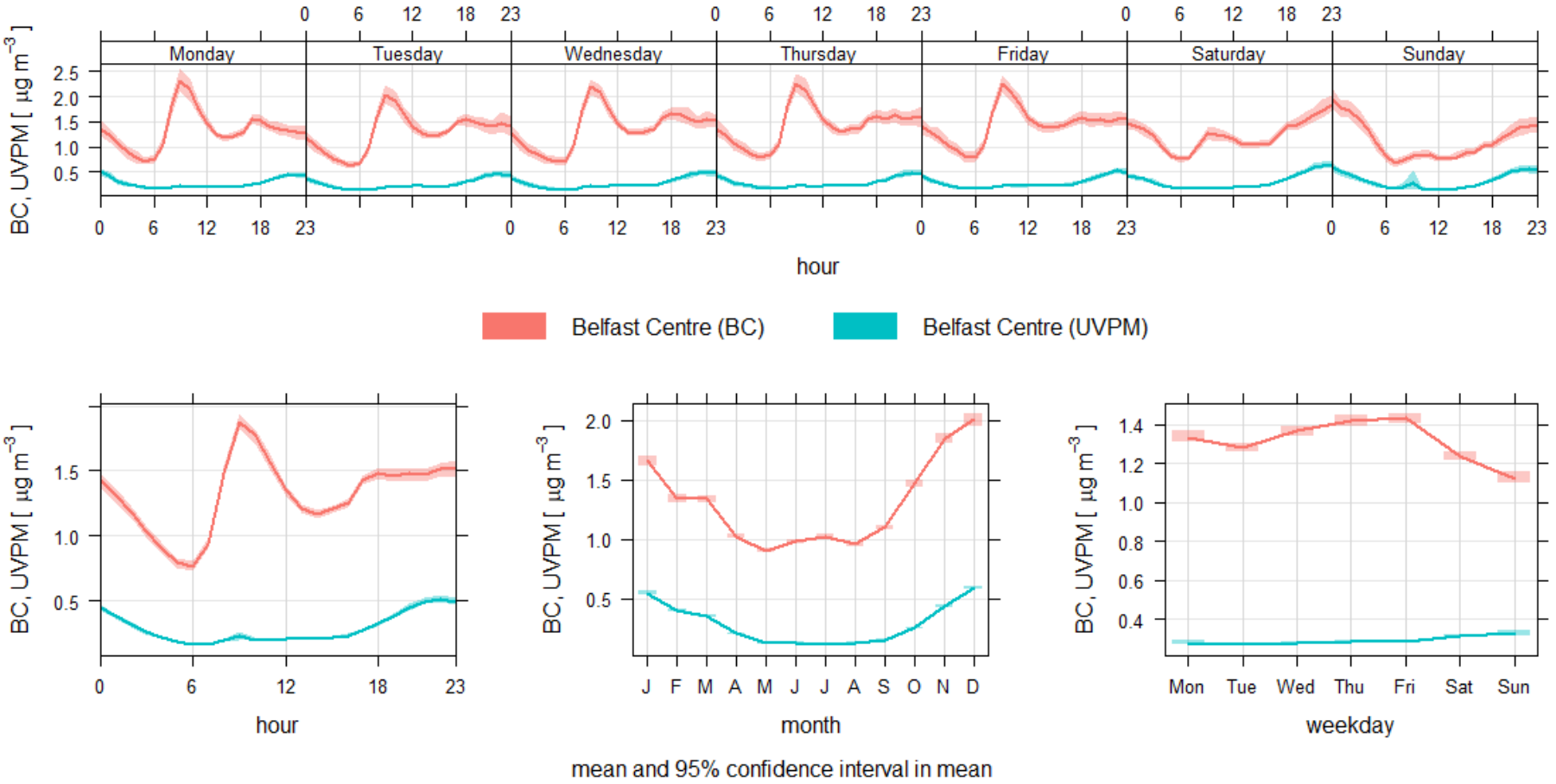

Figure 56 - Temporal variations of BC and UVPM concentrations at Belfast Centre for 2009-2021

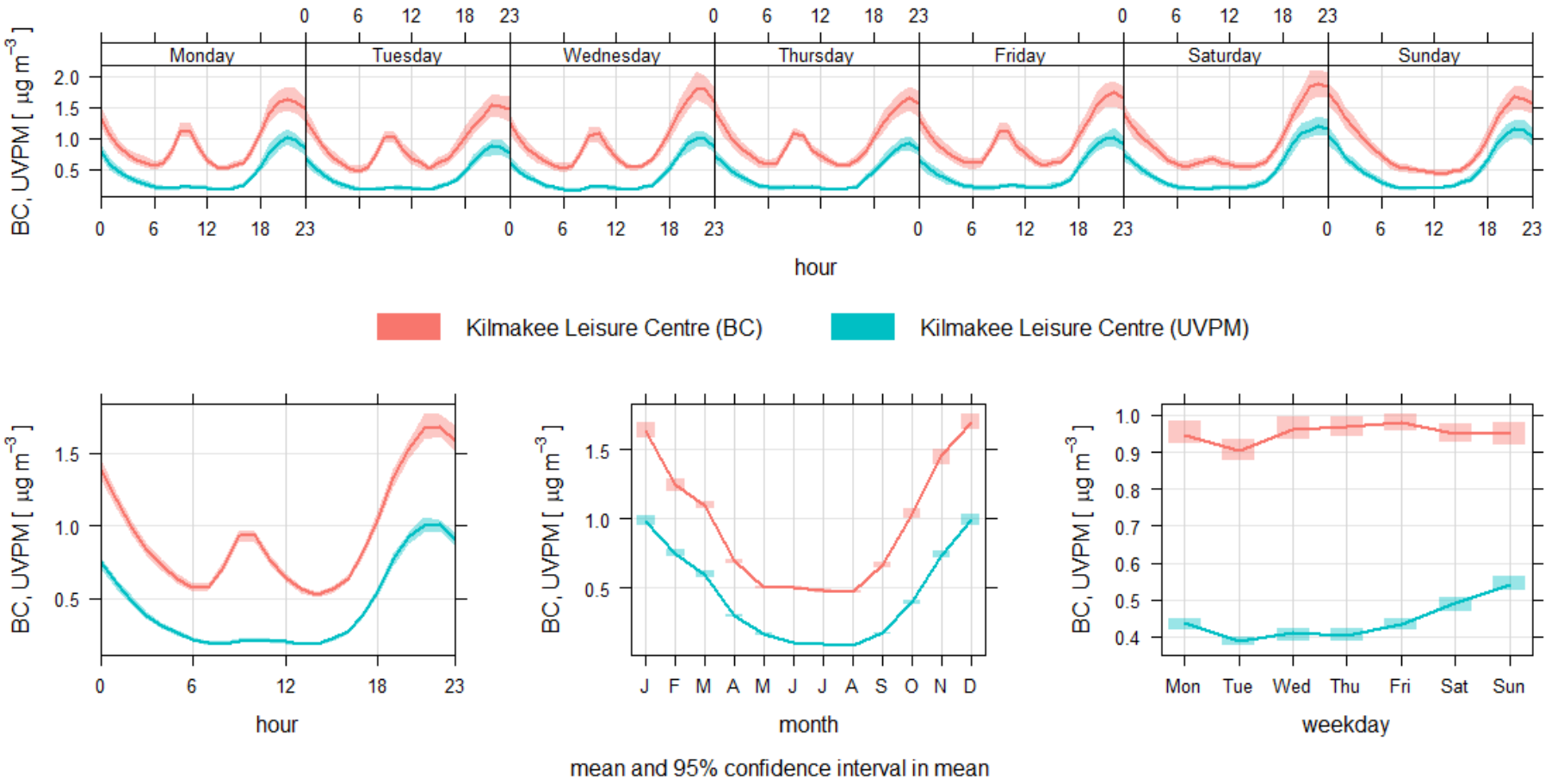

Figure 57 - Temporal variations of BC and UVPM concentrations at Kilmakee Leisure Centre for 2009-2021

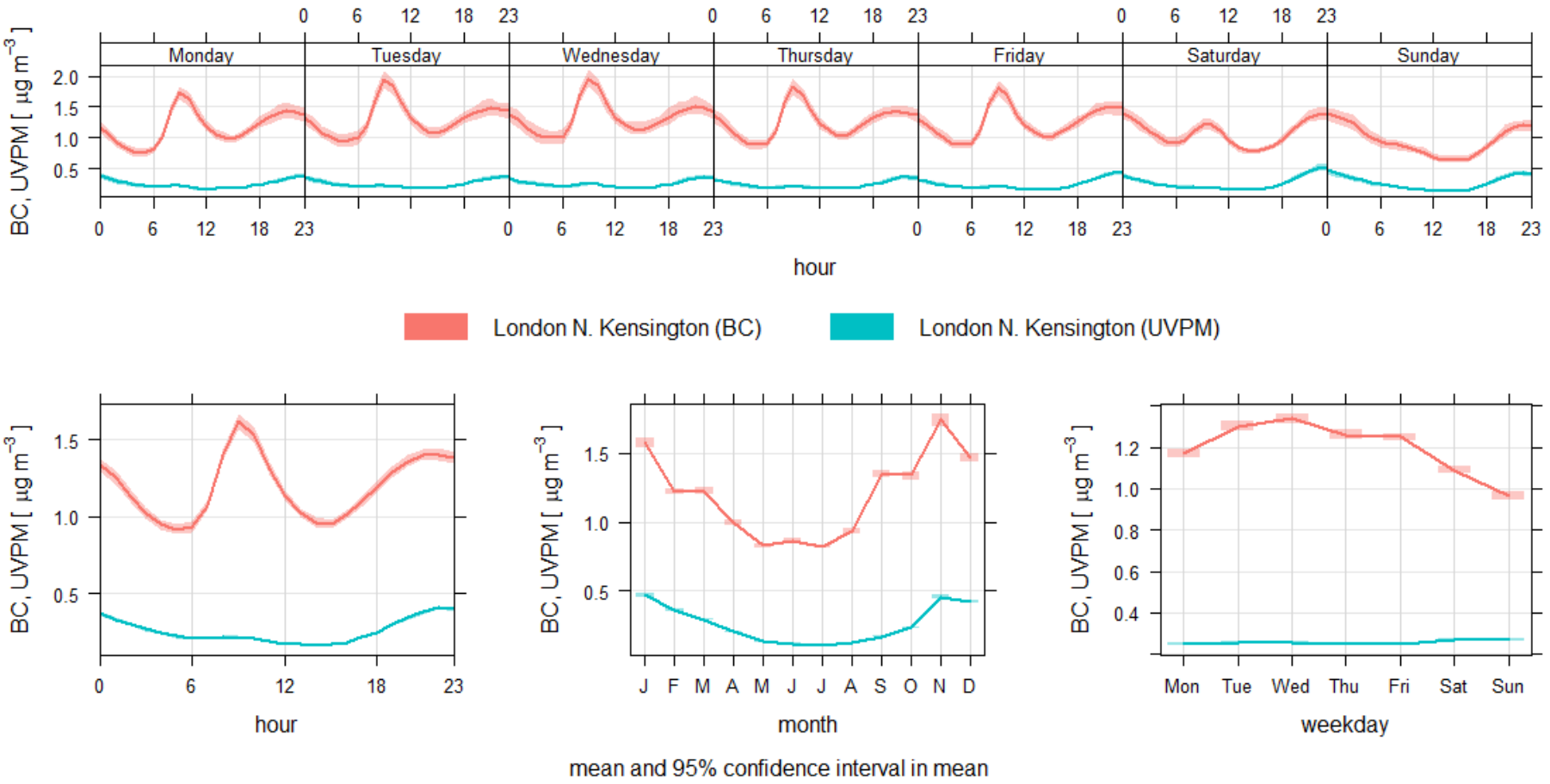

Figure 58 - Temporal variations of BC and UVPM concentrations at London N. Kensington for 2009-2021

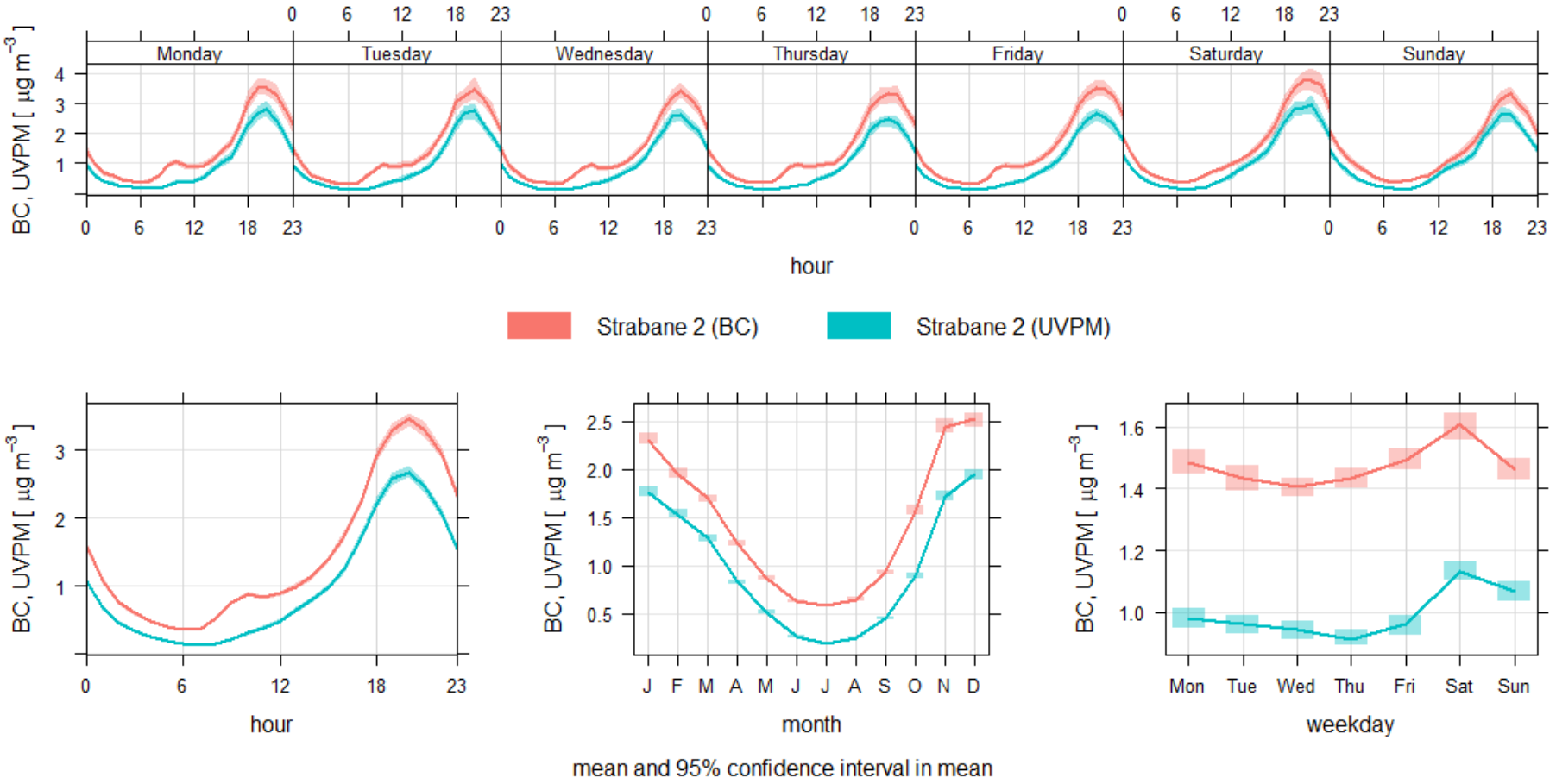

Figure 59 - Temporal variations of BC and UVPM concentrations at Strabane 2 for 2009-2021

Roadside sites

On weekdays the black carbon concentrations at 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 Covid-19 restrictions and reduced traffic some variations have been observed at all three roadside sites.

There was little UVPM signature in any of the roadside sites.

Urban Background sites

Black carbon 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 2009-2021 show 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 and 2021 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 60, using Belfast Centre as an example.

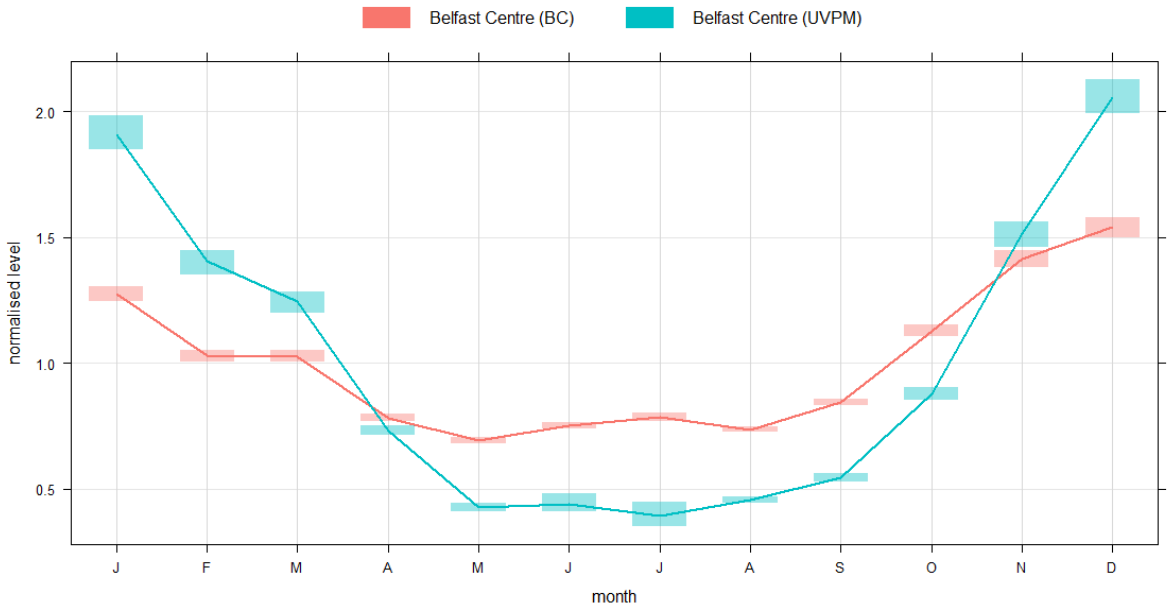

Figure 60 - Normalised monthly variability at Belfast Centre site for the period 2009 - 2021

BC and UVPM concentrations at the Northern Irish sites of Strabane 2, Ballymena Ballykeel and Kilmakee Leisure Centre 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 2, which is not on the natural gas network and where domestic heating mainly comes from oil. Strabane 2 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[17] 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 Ballykeel and Kilmakee Leisure Centre 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 61 gives the normalised monthly variability and Figure 62 gives the hourly variability.

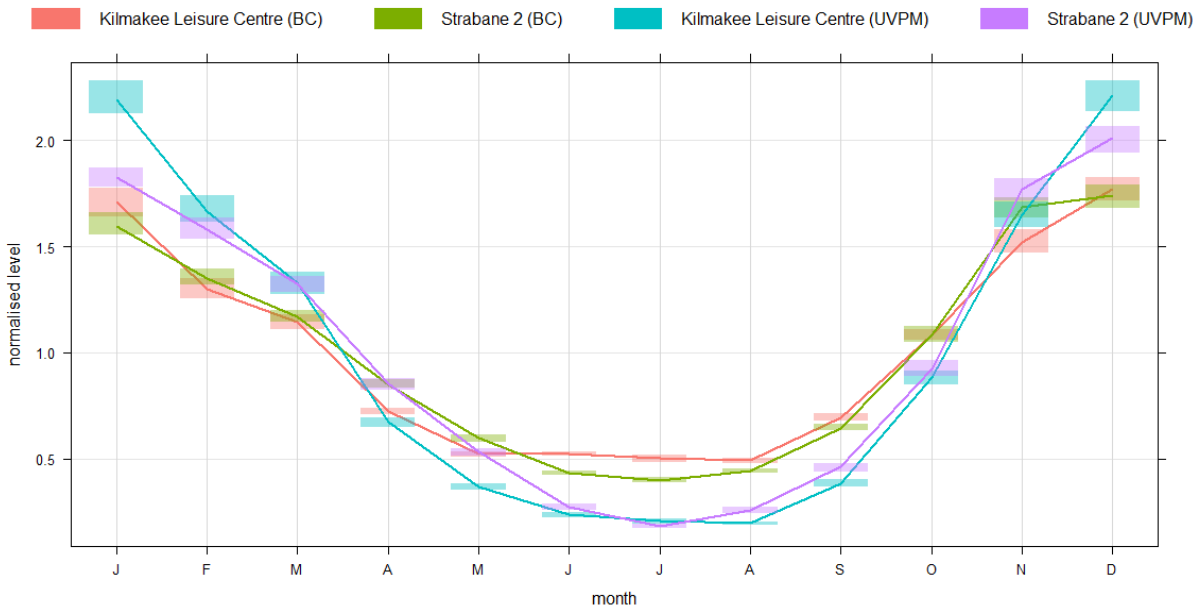

Figure 61 - Normalised monthly variability at Strabane 2 and Kilmakee Leisure Centre for the period 2009 – 2021. The shaded area on the y-axis represents the uncertainty in the mean y-value due to the spread of results, expressed with a level of confidence of 95%.

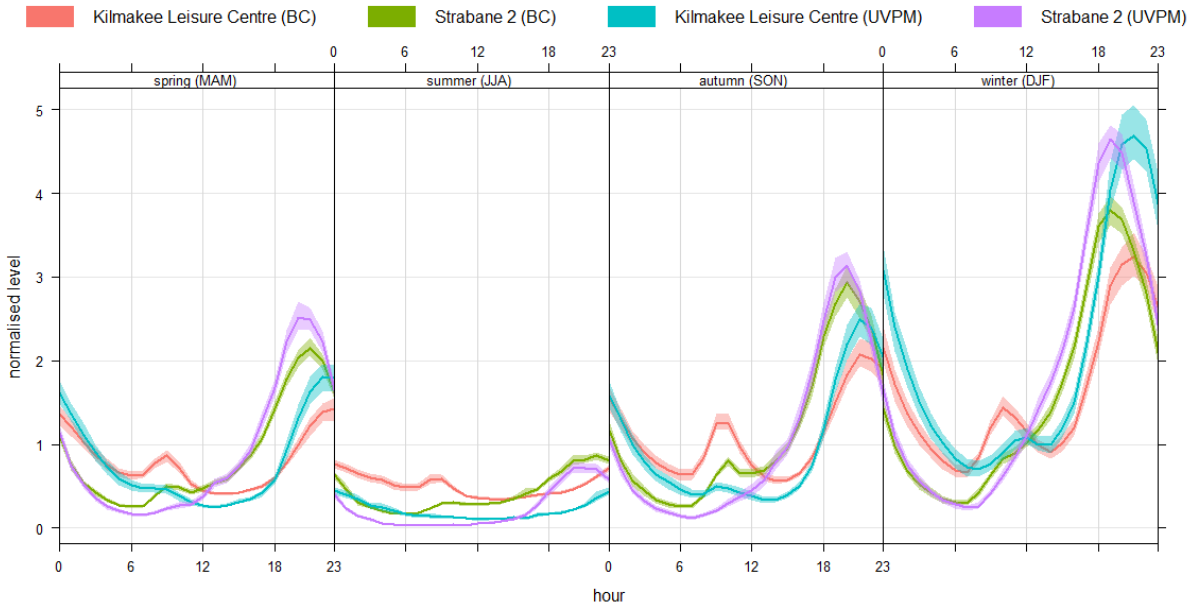

Figure 62 - Seasonal diurnal BC and UVPM concentrations measured at Strabane 2 and Kilmakee Leisure Centre for the period 2009 – 2021. The shaded area on the y-axis represents the uncertainty in the mean y-value due to the spread of results, expressed with a level of confidence of 95%.

The evening concentrations of both BC and UVPM peaked an hour earlier in Strabane 2 than they did in Kilmakee Leisure Centre. Also, there was still a signature of domestic emission during summer in Strabane 2 that was not present at Kilmakee Leisure Centre.

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.

As discussed in 4.5.2, at Detling site two pollution episodes were measured on 21/02/2021 and 24/03/2021. This can be seen in Figure 54.

4.5.7 Long-term trends

Figure 63 and Figure 64 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 2021. The Theil-Sen method in OpenAir[12,13] 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 2.5th and 97.5th percentile slopes are taken from all possible slopes.

Over the period 2009 to 2021 all the long-running sites in the network apart from Strabane 2 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 65 and Figure 66 show the long-term trends in UVPM concentration.

The London Marylebone Road UVPM concentration showed a significant upward trend over the period 2009 to 2021, 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, the trend for London 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 2009-2021 UVPM concentrations at Strabane 2, which were strongly affected by domestic solid fuel use, are plotted in Figure 67, 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 2. 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 68 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.

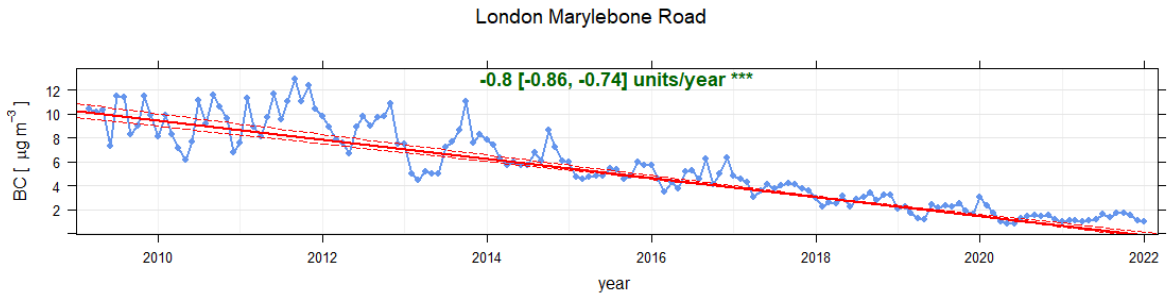

Figure 63 - BC trends measured at the roadside site, 2009 – 2021

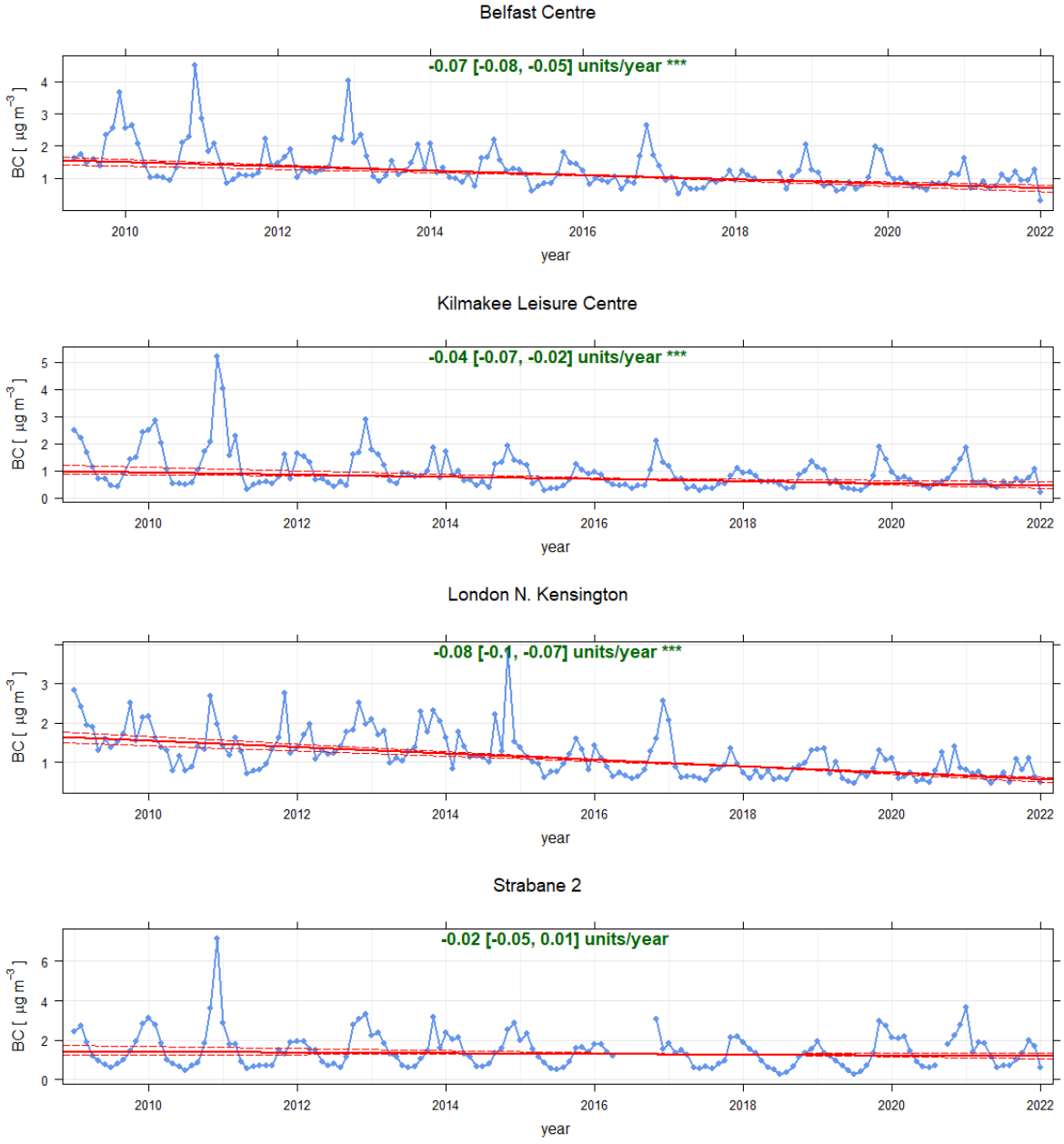

Figure 64 - BC trends measured at urban background sites, 2009 – 2021

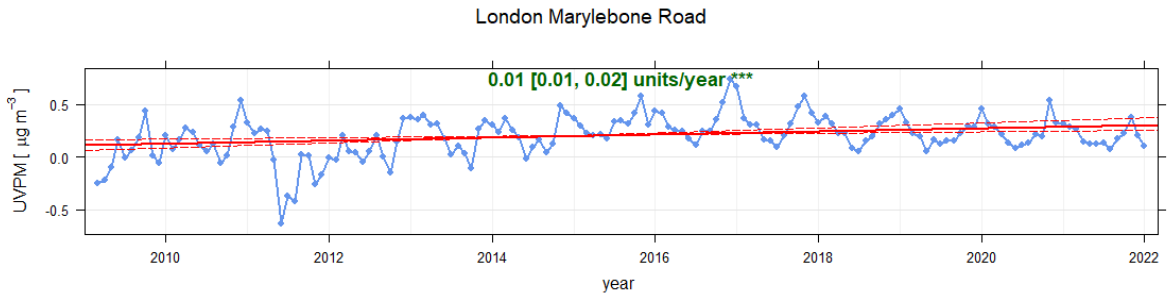

Figure 65 - UVPM concentrations measured at roadside sites, 2009 – 2021

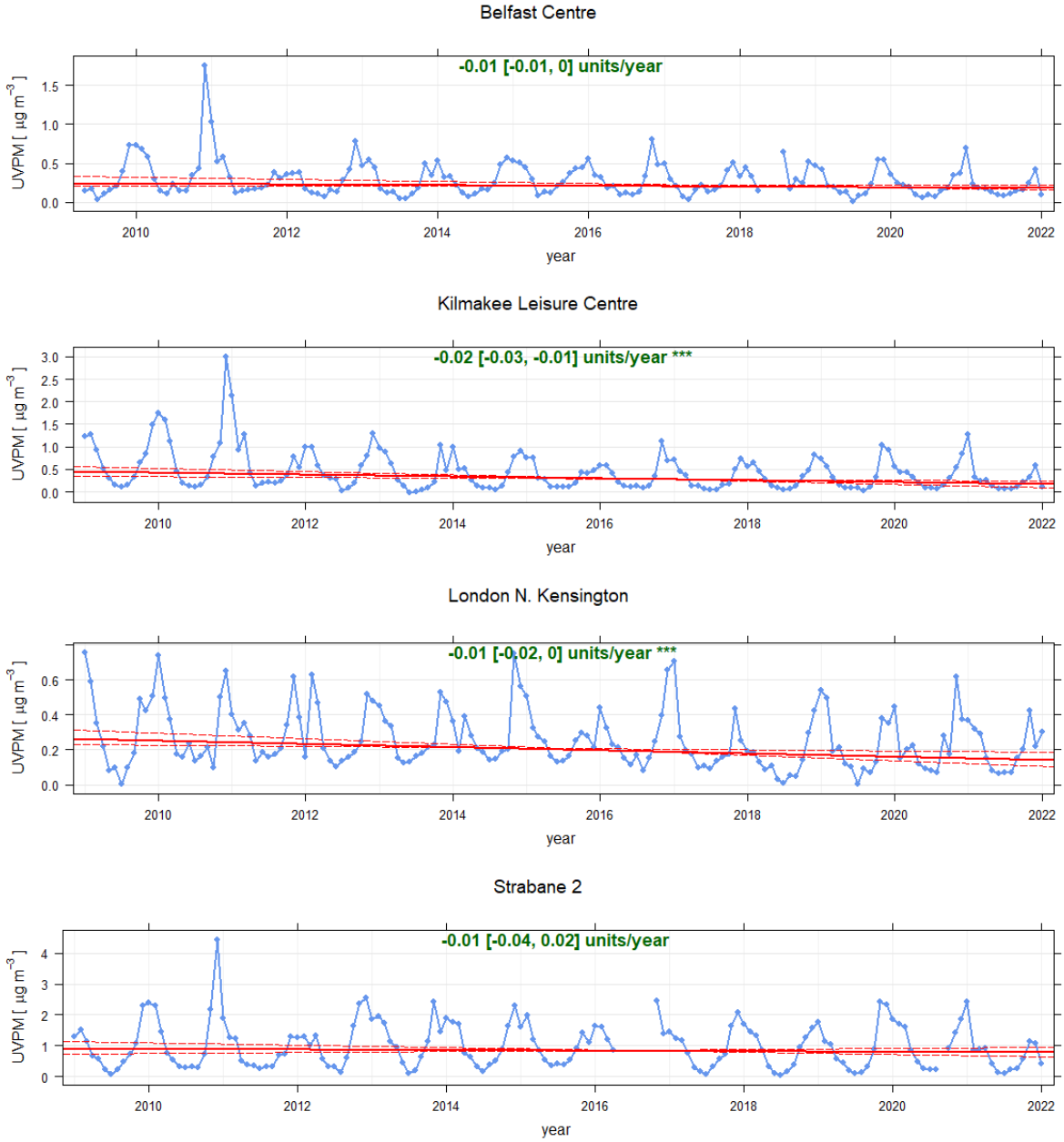

Figure 66 - UVPM concentrations measured at urban background sites, 2009 – 2021

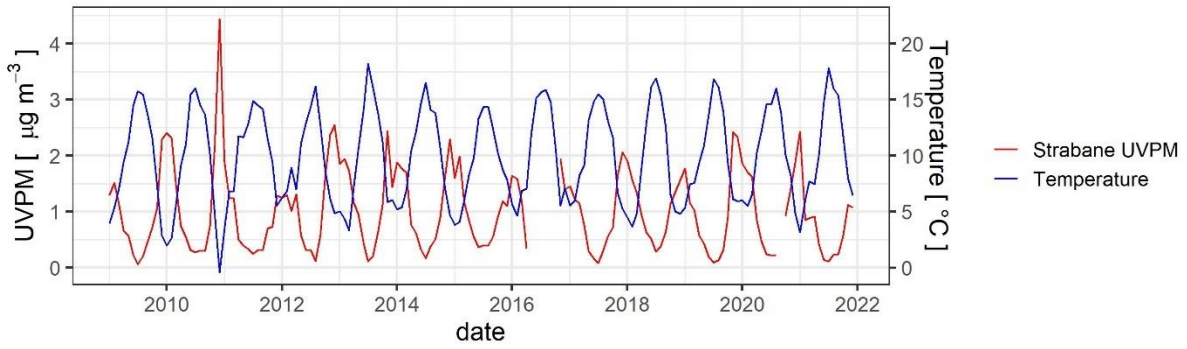

Figure 67 – Strabane 2 monthly UVPM concentration and average ambient temperature for 2009-2021

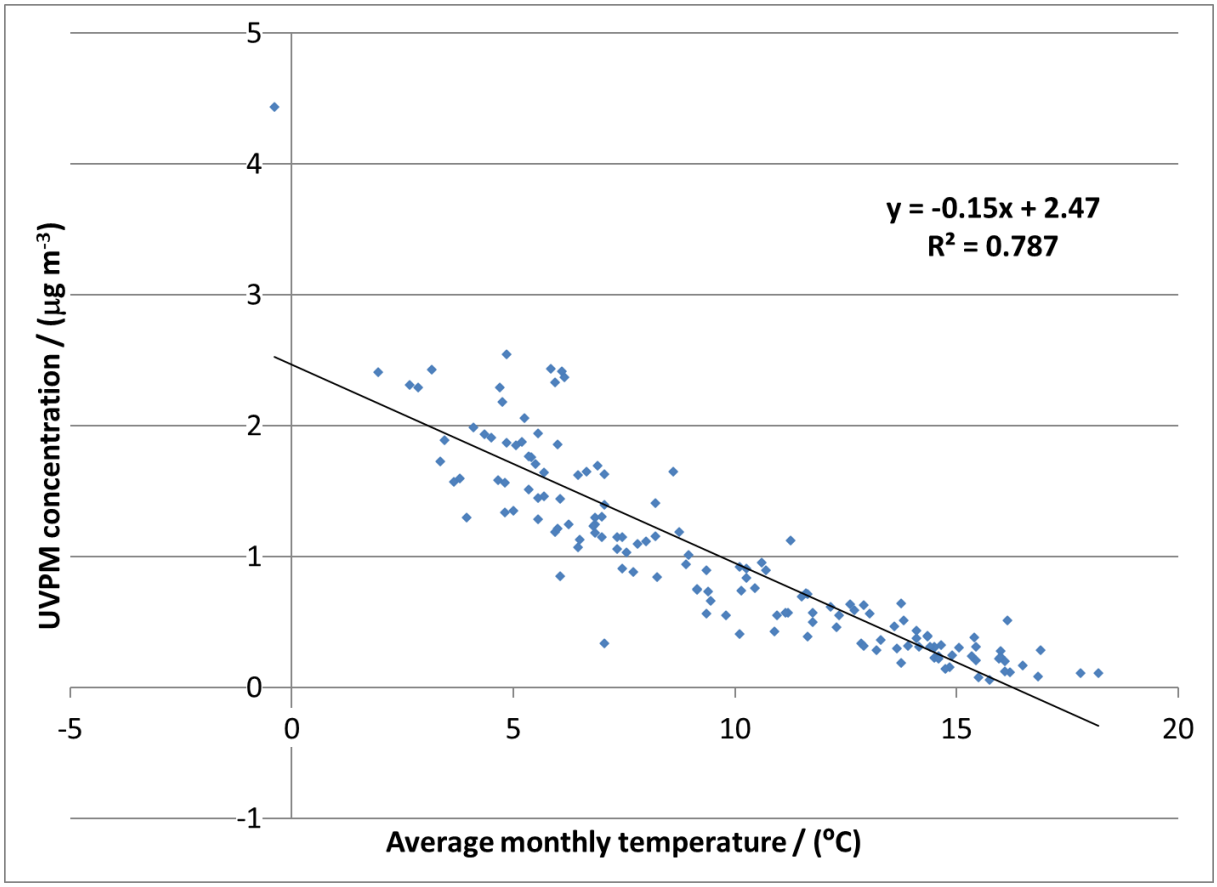

Figure 68 - Scatter plot of monthly UVPM concentration versus ambient temperature at Strabane 2 site over the period 2009 - 2021

4.5.8 Comparisons with other pollutants

Comparisons are possible between elemental carbon and black carbon concentrations at two sites, and with particle mass concentration measurements where these instruments were co-located with the Aethalometer.

4.5.8.1 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 69. The regression is calculated according to the Reduced Major Axis (RMA) method[18], 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.

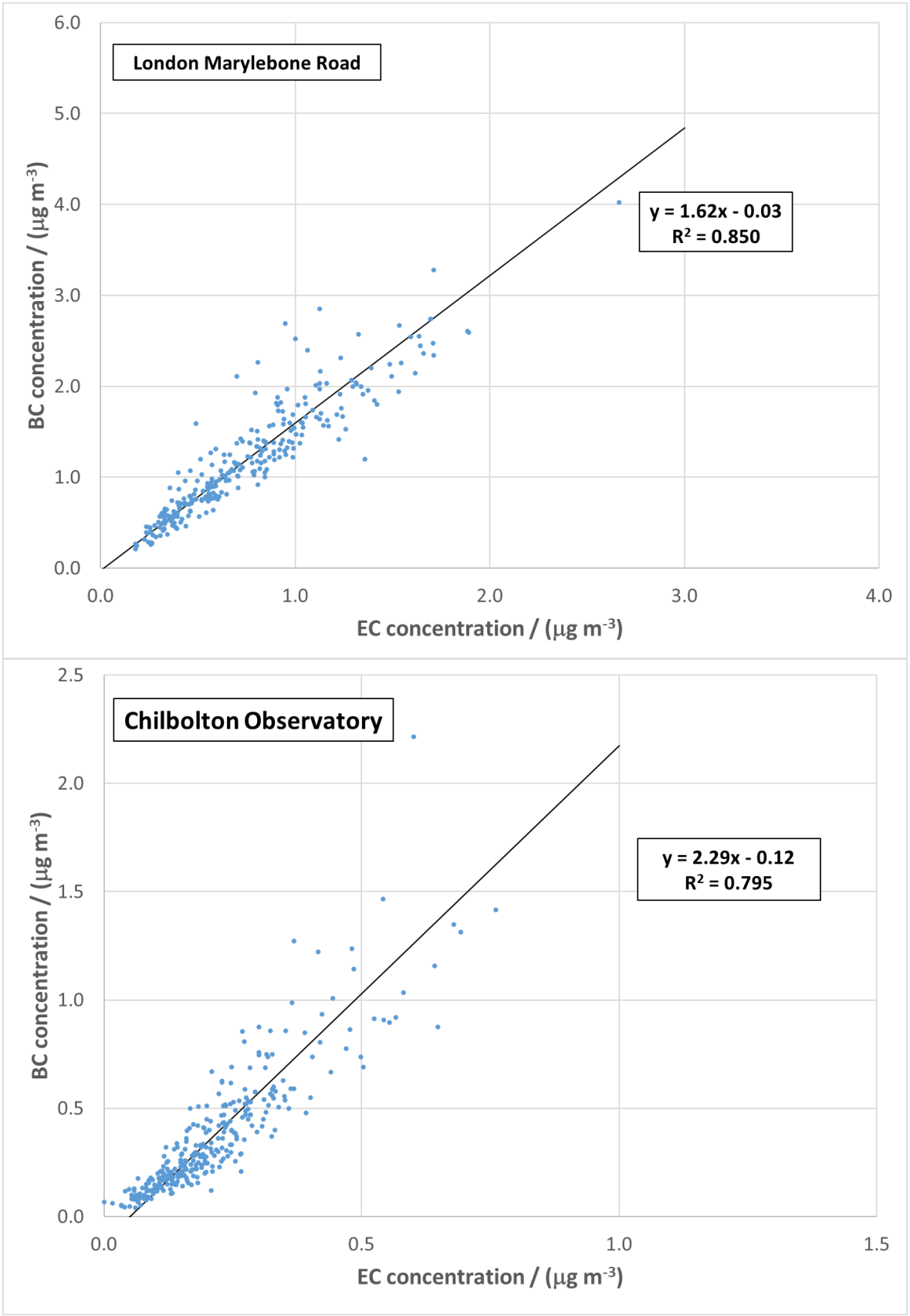

Figure 69 - Comparison between BC and EC at the London Marylebone Road and Chilbolton Observatory sites in 2021

There was a good linear relationship (R^2 ~ 0.8) between the EC and BC concentrations at the Chilbolton Observatory and London Marylebone Road sites in 2021 (see Table 11).

Table 11 - Relationship between black carbon ($PM_{2.5}$) and elemental carbon (PM_{10} & $PM_{2.5}$) and the three Network sites

	Harwell/Chilbolton Observatory*		London North Kensington**		London 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
2021	2.29 x - 0.12	0.795	-	-	1.62 x - 0.03	0.850

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 Observatory 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 and 2021 were similar, however, they were somewhat different between sites, and on a year-to-year basis. 2021 and 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 (the 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.

4.5.8.2 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 12.

Table 12 - 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 (FIDAS)	3	5
Belfast Centre	1.0	13 (FIDAS)	7 (FIDAS)	8	14
Birmingham A4540 Roadside	1.8	15 (FIDAS)	9 FIDAS)	12	20
Birmingham Ladywood	0.8	12 (FIDAS)	7 (FIDAS)	6	11
Cardiff Centre	0.7	13 (BAM)	9 (BAM)	6	8
Chilbolton Observatory	0.4	11 (FIDAS)	7 (FIDAS)	3	5
Detling*	0.5	14 (TEOM FDMS)	-	4	-
Glasgow High Street	1.0	10 (FIDAS)	5 (FIDAS)	10	19
Glasgow Townhead	0.6	9 (FIDAS)	5 (FIDAS)	7	12
London Marylebone Road	1.3	16 (TEOM FIDAS)	11 (TEOM FIDAS)	8	11
London N. Kensington	0.7	14 (FIDAS)	9 (FIDAS)	5	8
Strabane 2	1.5	14 (REF.EQ)	-	11	-

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, Belfast Centre, 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.

5 RELATED RESEARCH PUBLICATIONS

The paper: *Challenges and policy implications of long-term changes in mass absorption cross-section derived from equivalent black carbon and elemental carbon measurements in London and south-east England in 2014–2019*[19] has been published in the Environmental Science: Processes & Impacts journal.

In this paper, we present the long-term changes in the mass absorption cross-section (MAC) in London and south-east England based on equivalent black carbon (eBC) and elemental carbon (EC) measurements between 2014 and 2019. The measurement of eBC is based on light-absorption by atmospheric aerosol particles, with the light absorption coefficient converted to a mass concentration with a fixed mass absorption cross-section (MAC). However, the observed MAC value may vary at different times and locations. Our results indicate significant downward trends in the observed MAC values since 2014 at all sites, whereas the concentrations of eBC and EC changed at different rates and exhibited different long-term trends. This may lead to different conclusions for policy making and determining the effectiveness of the mitigation strategies and intervention actions. We provided possible reasons for the observed change in MAC over time (e.g. real changes in the physical properties of atmospheric aerosols), and the effect of these changes when using optical- and chemical-based instruments. There are a very limited number of studies where eBC and EC are measured in parallel, typically from short-term campaigns were launched to obtain site-specific MAC values used later, e.g. in climate change models. Thus, our long-term measurements are unique, important to air quality studies and add additional value to the delivery of the network.

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