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AIRBORNE PARTICLE CONCENTRATIONS, PARTICLE NUMBERS AND BLACK CARBON IN THE UNITED KINGDOM - ANNUAL REPORT 2022

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Airborne Particle Concentrations, Particle Numbers and Black Carbon in the United Kingdom - Annual report 2022

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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 Particle Concentrations and Numbers (PCN) and Black Carbon (BC) Networks contract. The contract is managed by the Environment Agency (EA) on behalf of the Department for the Environment, Food and Rural Affairs (Defra) and the Devolved Administrations: the Scottish Government, the Welsh Government, and the Department of the Environment in Northern Ireland (DOENI).

This annual report for 2022 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 2022.

And, where applicable:

- Plots of the diurnal, weekly, and monthly trends in ratified Network data in 2022.
- Plots of the long-term trends in ratified Network data.
- Comparisons between pollutants measured by the Network.

In 2022, 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 2022, the Network reported:

- 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 mass concentrations of 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 (ACSM).
- Hourly concentrations of 40 elements in $PM_{2.5}$ and PM_{10} (alternating the size fraction each hour) at London Honor Oak Park and London Marylebone Road using an online X-ray fluorescence (XRF) instrument.
- Weekly mass concentrations of organic carbon and elemental carbon (OC/EC) in $PM_{2.5}$ at Auchencorth Moss; and daily $PM_{2.5}$ mass concentrations of OC/EC at Chilbolton Observatory, London Marylebone Road, and London Honor Oak Park. For all these 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.

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

Some notable features from the Network data in 2022 are:

- The annual average particle number concentrations for 2022 at London Marylebone Road and London Honor Oak Park showed, respectively, a slight increase and slight decrease from the 2021 annual average. The Chilbolton Observatory site recorded the highest annual average particle number concentration since the site moved from Harwell in 2016.

- The annual average chemical mass concentration of secondary particles (nitrate, sulfate and ammonium) and organic mass measured at London Marylebone Road and London Honor Oak Park remained similar to those in 2021. A new ACSM was installed at the rural Chilbolton Observatory site in April 2022.

- Elemental analysis was undertaken on the Network for the first time in 2022. Of the 40 elements measured, the elements that reported the highest annual average concentrations were (in order) iron, chlorine and aluminium at London Marylebone Road, and chlorine, sulfur and iron at London Honor Oak Park.

- The annual average mass concentrations of OC and EC for all sites increased slightly from 2021. As daily (rather than weekly sampling) commenced at Chilbolton Observatory in June 2020, 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 2022 and the concentrations for both components were broadly similar to those measured in 2021. The largest increase of UVPM was observed at the Strabane 2 site from 0.76 µg m^{-3} in 2021 to 0.96 µg m^{-3} in 2022, whereas the largest increase of BC was observed at the Cardiff Centre site from 0.73 µg m^{-3} in 2021 to 1.08 µg m^{-3} in 2022.

- The significant downward trend in measured BC mass concentrations observed at all the long-running sites in the Network, apart from Strabane 2 since 2009, continued into 2022. 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 measured at Birmingham A4540 Roadside.

The annual average data capture across all Network sites was:

- 45 % for particle number concentration measurements
- 62 % for particle size distribution measurements
- 77 % for aerosol mass and chemical composition measurements
- 91 % for elemental measurements
- 93 % for OC and EC measurements
- 88 % for BC measurements

1 INTRODUCTION

The UK Airborne Particle Concentrations and Numbers (PCN) Network, and the UK Black Carbon (BC) 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 of pollution.

These sites provide data on airborne particles by using instruments that measure: particle number concentrations; particle size distributions; organic carbon and elemental carbon (OC/EC); black carbon (BC) and ultraviolet particulate matter (UVPM) concentrations; aerosol mass and chemical compositions and elemental concentrations.

Prior to 2020, these data were reported in two separate annual reports, one for the PCN Network and one for the BC Network.

The PCN 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 (ICL), have operated the Network contract from 2005. It currently comprises four sites (London Marylebone Road, London Honor Oak Park, Chilbolton Observatory and Auchencorth Moss). Multiple instruments are operated at each site, with the purpose of providing data to improve understanding of airborne particulate matter, with a focus on $PM_{2.5}$ (particulate matter with an aerodynamic diameter < 2.5 µm) and monitoring compliance with limits set out in the UK's Air Quality Standards regulations (AQSR 2010)[2,3,4,5], and all associated amendments, which reference the EU Ambient Air Quality Directive 2008[6,7], and support objectives set out in the UK's Clean Air Strategy 2019[8] and Environmental Improvement Plan 2023[9].

The BC Network comprises 14 sites: all the sites shown in Table 1 except for London Honor Oak Park. The purpose of the Network is to continue a historical black smoke dataset (which dates back to the 1920s) and monitor BC concentrations. NPL, supported by ERG, was awarded the contract to restructure and run this Network in September 2006.

As these two Networks are closely linked, they are now reported in one annual report to provide administrative cost-savings to the Environment Agency (EA) and Department for the Environment, Food and Rural Affairs (Defra).

This report presents a summary of the 2022 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 2022)

The Network in 2022 was mostly structured in the same way as the previous year, with the following changes and additions to instrumentation. No new sites were commissioned, and no sites were decommissioned.

- In January 2022, the two Leckel SEQ47/50 ambient air samplers at Auchencorth Moss and Chilbolton Observatory were changed to Digitel DPA14 ambient air samplers.
- In February and March 2022, the Partisol 2025 ambient air samplers at London Honor Oak Park and London Marylebone Road were changed to Digitel DPA14 samplers.
- In February 2022, the Cooper Environmental Xact® 625i X-ray fluorescence (XRF) analyser at London Honor Oak Park was brought within the PCN Network.
- In March 2022, a Cooper Environmental Xact® 625i XRF analyser was installed at London Marylebone Road and was operational from April 2022.
- In April 2022, an Aerodyne Research Inc. (ARI) Q-ACSM Quadrupole Aerosol Chemical Speciation Monitor (ACSM) was installed at Chilbolton Observatory and was operational from May 2022.
- In August 2022, a new TSI 3750200 sampling system was installed at London Marylebone Road for the Scanning Mobility Particle Sizer (SMPS) and stand-alone Condensation Particle Counter (CPC). This replaced the previous sampling system.
- In August 2022, a new TSI 3938W50-CEN SMPS was installed at London Marylebone Road in parallel with the TSI 3936 SMPS as part of the validation campaign described below. The TSI 3936 SMPS was removed in November 2022.

Also of note are that:

- In July and August 2022, a validation campaign took place at NPL Teddington and London Marylebone Road for the new TSI 3938W50-CEN-7 SMPS. The TSI 3938W50-CEN-7 SMPS has a larger size range than the older model, moving from nominally 16 - 600 nm to 10 - 1000 nm. This campaign comprised:
    - Laboratory tests at Teddington using ambient air to confirm that the new SMPS instruments could operate continuously when installed at site.
    - Tests at London Marylebone Road to: (a) co-locate the current and new SMPS models to further challenge the new instruments with roadside air and check for any differences in the data from the new and old instrumentation. (b) validate the relocation of the CPC from a separate inlet to an inlet shared with the SMPS, as a combined drier system would be used with the new SMPS instrumentation.
- The CPC at Birmingham Ladywood continued to not be operational during 2022 due to ongoing discussions about preparing the site for the re-installation of the equipment. This CPC was also used at the London Marylebone Road validation campaign.
- The operation of the Network was affected by Covid-19 in early 2022, but for the latter part of the year there was little to no impact.
    - The main effect of Covid-19 was minor delays for Equipment Support Units (ESUs) responding to equipment breakdowns and carrying out the routine service visits in the first half of 2022.
    - On a few occasions local site operators (LSOs) had Covid-19 and could not attend sites as planned. Most notably, some LSO *ad hoc* visits to diagnose and fix breakdowns or change Aethalometer tapes were delayed in first quarter of 2022.

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 ERG. 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 during 2022 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 PCN Network (Auchencorth Moss, Chilbolton Observatory, London Marylebone Road, and London Honor Oak Park) are located to provide $PM_{2.5}$ OC/EC mass concentration data to assist in requirements of AQSR 2010[2,3,4,5] (and all associated amendments). 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 London Honor Oak Park) constitute the BC Network. These are located to target the measurement of traffic emissions of BC 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.

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 CMCU and QA/QC unit. 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 ESUs; collection and storage of data; reporting; and providing technical advice to the EA. QA/QC activities include ensuring adherence to the appropriate technical standards; training and auditing LSOs; managing equipment services and calibrations; and data ratification and submission to the data dissemination unit (DDU).

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

ERG have continued to undertake the CMCU and QAQC activities for the ACSM equipment with support from NPL. With the addition of the two XRFs to the Network, ERG have taken on the CMCU and QA/QC roles for XRF as well. As the CMCU for the ACSMs and XRFs, ERG manage the equipment; perform LSO and ESU activities, including health and safety; collection and storage of data; providing 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.

Table 1 - Network structure in 2022.
The colour key indicates the emissions sources representative of each site:
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	Hourly $PM_{2.5}$ or PM_{10} elements [4]	Daily $PM_{2.5}$ OC/EC	Weekly $PM_{2.5}$ OC/EC	Hourly particle number concentration	15 min 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 [7]			X	3
Birmingham A4540 Roadside	Urban roadside							X	4
Birmingham Ladywood	Urban background							X	5
Chilbolton Observatory	Rural background	X [1][2]		X [7]		X	X	X	6
London North Kensington	Urban background							X	7
London Marylebone Road	Urban roadside	X [3]	X [5]	X [7]		X	X [8]	X	8
London Honor Oak Park	Urban background	X [2]	X [6]	X [7]		X	X		9
Detling	Rural background							X	10
Belfast Centre	Urban background							X	11
Kilmakee Leisure Centre	Urban background							X	12
Strabane 2	Urban background							X	13
Ballymena Ballykeel	Urban background							X	14
Cardiff Centre	Urban background							X	15

<u>Notes</u>
[1] The Chilbolton Observatory ACSM was operational from May 2022.
[2] The Chilbolton Observatory and London Honor Oak Park ACSMs sample $PM_{2.5}$.
[3] The London Marylebone Road ACSM samples PM_1.
[4] The XRFs have a size fraction sampling switching inlet, measuring $PM_{2.5}$ and PM_{10} on alternate hours.
[5] The London Marylebone Road XRF was operational from April 2022.
[6] The London Honor Oak Park XRF was affiliated to the PCN Network in February 2022.
[7] Samplers changed from Leckel/Partisol to Digitel in Q1 2022.
[8] The TSI 3936 SMPS was replaced with a TSI 3938W50-CEN SMPS in November 2022.

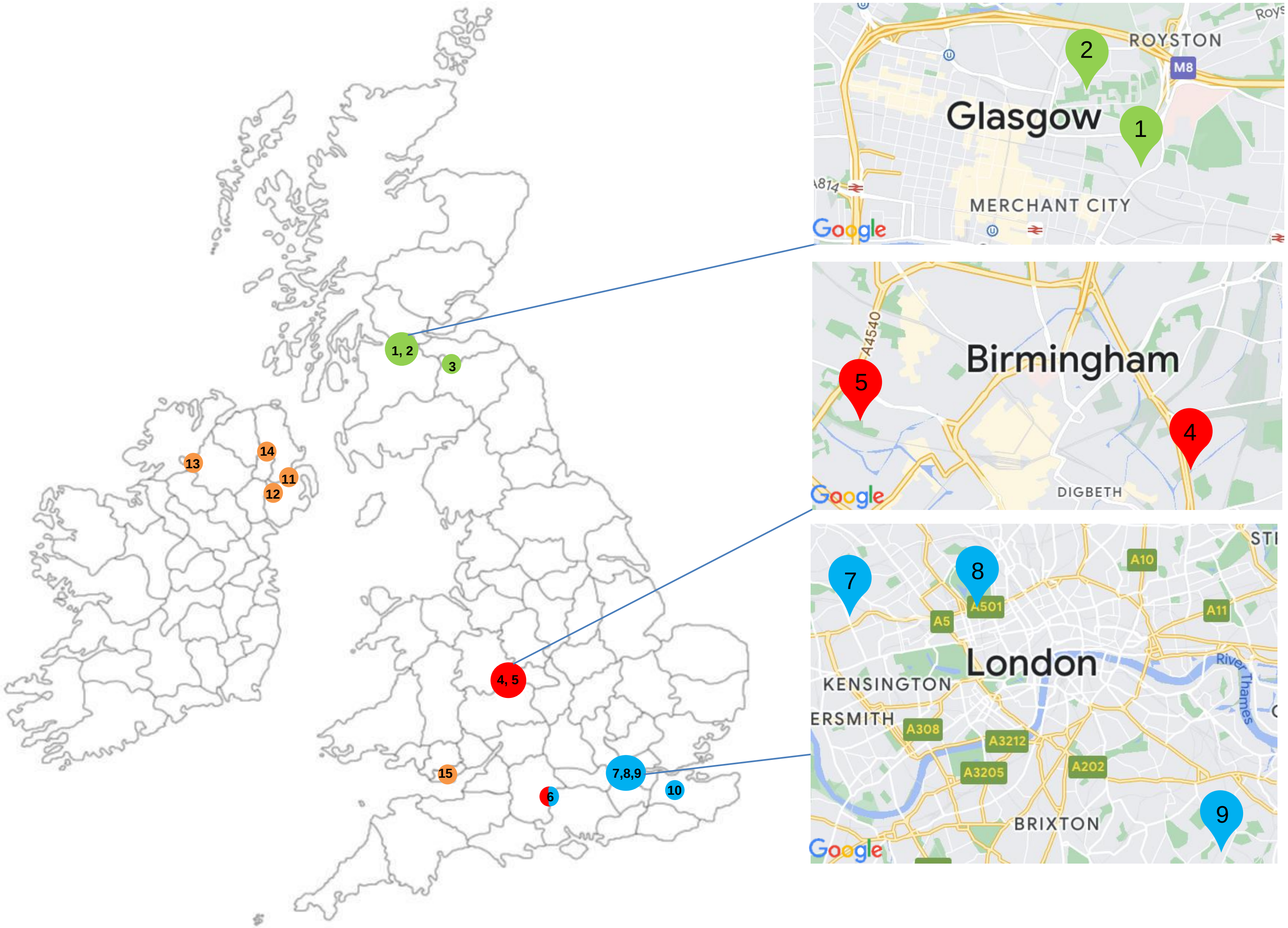

Figure 1 - Network sites in 2022. The colour key indicates the emissions sources representative of each site: Green = Glasgow Urban; Red = Birmingham Urban; Blue = London Urban; Orange = solid fuel use / domestic emissions.

2.3 DATA CAPTURE

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

The tables below show the annual data capture for 2022 for each instrument at each site. In the cases where an instrument measures more than one analyte, an average has been calculated for each site. All values are stated to the nearest whole percentage.

2.3.1 Particle number concentration

Extensive data loss occurred across the Network because of CPC faults (e.g. non-linearity and butanol leaks), and delays with instrument calibrations, diluter testing and equipment maintenance, repair and return to site. Mitigation measures have been put in place to significantly reduce the time taken to deal with such events from 2023 onwards.

Table 2 - Data capture for particle number concentration measurements

Site Name	Data capture [%]
Chilbolton Observatory	33
London Marylebone Road	35
London Honor Oak Park	65
Average	**45**

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 at the beginning of the year. This was sent to the instrument manufacturer for repair. Once returned to site there were further flooding issues and a reinstallation delay until successful reinstallation in October 2022.

Other extensive data loss occurred in March and April 2022 at both Chilbolton Observatory and London Marylebone Road due to delays in instrument calibration, routine maintenance and repair. Mitigation measures have been put in place to significantly reduce the time taken to deal with such events from 2023 onwards.

Further data loss occurred at London Honor Oak Park in September 2022 due to a delay in returning the instrument to site after a scheduled comparison with the new SMPS instrument.

Table 3 - Data capture for particle size distribution measurements

Site Name	Data capture [%]
Chilbolton Observatory	35
London Marylebone Road	73
London Honor Oak Park	78
Average	**62**

2.3.3 Aerosol mass and chemical composition

The Chilbolton Observatory ACSM was installed on site at the end of April 2022 and ran with only minor issues (e.g. computer reboots required) until the end of the year. The ACSM at London Marylebone Road was returned to the manufacturer for diagnosis and repair of a faulty temperature control module in December 2021. It was sent back to the UK and reinstalled on site at the end of May 2022 and ran without issue until the end of 2022. The ACSM at London Honor Oak Park was operational for the whole year. The main cause of data loss occurred due to the failure of the cooling fan in the Prisma head in May 2022 and a switching servo failure at the end of November.

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

Site Name	Data capture [%]
Chilbolton Observatory	94
London Marylebone Road	57
London Honor Oak Park	80
Average	**77**

2.3.4 Elemental analysis

There were data losses due to scheduled maintenance such as services, calibration checks, leak checks and flow checks. Minor, non-scheduled data losses occurred due to the tape running out outside of scheduled tape changes and unexpected errors, such as tape wheel loosening and power cuts.

Table 5 - Data capture for elemental measurements

Site Name	Data capture [%]
London Marylebone Road	91
London Honor Oak Park	91
Average	**91**

2.3.5 OC/EC

The common cause of data loss at each site was due to filter ripping which prevented laboratory analysis.

Table 6 - Data capture for OC/EC measurements

Site Name	Data capture [%]
Auchencorth Moss	94
Chilbolton Observatory	91
London Marylebone Road	93
London Honor Oak Park	95
Average	**93**

2.3.6 BC

The main causes of data loss were electric fuse failure and problems with the inner memory of the Aethalometers. At the Cardiff Centre site there was no data in February and March 2022 due to instrument failure and delays in servicing due to the Covid-19 situation.

Table 7 - Data capture for BC measurements

Site Name	Data capture [%]
Auchencorth Moss	85
Ballymena Ballykeel	96
Belfast Centre	89
Birmingham A4540 Roadside	82
Birmingham Ladywood	88
Cardiff Centre	75
Chilbolton Observatory	98
Detling	88
Glasgow High Street	91
Glasgow Townhead	93
Kilmakee Leisure Centre	90
London Marylebone Road	99
London North Kensington	91
Strabane 2	67
Average	**88**

2.4 INSTRUMENTATION

2.4.1 Particle number concentration

Particle number concentrations are measured using TSI 3772-CEN-7 CPCs.

The CPC instruments operate 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 micrometres in size and have a concentration measurement range from zero to 50,000 cm^{-3}. The TSI 3772-CEN-7 CPC has been developed to comply with the requirements of CEN/TS 16976:2016[10]. At all concentrations each particle is counted individually. CEN/TS 16976:2016[10] outlines the measurement criteria for the control of humidity in the sampled aerosol.

When the TSI 3772-CEN-7 CPCs were installed in 2017, drier systems manufactured by TSI were installed with them. After some initial teething problems, a solution of a TSI 3772200 Nafion drier sampling system for the stand-alone CPC and a separate NPL-designed Nafion drier sampling system for the SMPS were employed. Figure 2 shows the TSI 3772-CEN-7 CPC and TSI 3772200 drying unit equipment at a typical site.

Figure 2 - TSI 3772200 drying unit and TSI 3772-CEN-7 CPC (left); TSI 3750200 sampling system (right), photographs courtesy of TSI Incorporated.

As part of the installation of new Network SMPS systems planned for 2023, a new TSI 3750200 sampling system, shared between the SMPS and stand-alone CPC, will replace the older separate drier systems (Figure 2). This system was installed at London Marylebone Road in August 2022 for use with the CPC. The main difference between the old and new drier systems is that the new system does not dilute the particle number concentration of the ambient air sampled.

2.4.2 Particle size distribution

Particle size distributions were measured using a TSI 3936 SMPS at all sites, except for the last two months of the year at London Marylebone Road (see below).

The TSI 3936 SMPS consists of a TSI 3775 CPC combined with an TSI 3080 electrostatic classifier, consisting of a charge neutraliser (incorporating an ^{85}Kr radioactive source) and a TSI 3081 Differential Mobility Analyser (DMA). 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 changed and a size distribution obtained. The SMPS instruments generate particle number size spectra between 16 nm and 605 nm. A stand-alone NPL drier system has been used with the SMPS since January 2018; prior to this, a combined NPL drier was used for CPC and SMPS. Figure 3 shows the TSI 3936 SMPS and NPL drying unit equipment at a typical site.

A new TSI 3938W50-CEN-7 SMPS system was purchased and trialled in 2022 for use across the Network in 2023. This new version has a larger size range (nominally 10 - 800 nm) than the older model (nominally 16 - 600 nm). London Marylebone Road was used as a test site for this system, and network data for November and December 2022 were produced by this new SMPS, which consists of a TSI 3750-CEN-7 CPC combined with an TSI 3082 electrostatic classifier and a new Vienna-type TSI 3083 DMA. This new 3083 DMA is designed to cover from 10 - 800 nm in a single scan. This SMPS is compliant with CEN Technical Specification CEN TS 17434:2020[11].

In addition to the new SMPS system, a new TSI 3750200 sampling system will be used across all Network sites from 2023, shared between both the SMPS and CPC. One of these systems was installed at the London Marylebone Road from August 2022 for the old SMPS and stand-alone CPC. Figure 4 shows the new configuration of the TSI 3938W50-CEN SMPS, TSI 3772-CEN-7 CPC, and TSI 3750200 sampling system. NB: TSI 3750-CEN-7 CPC is shown in image.

In July and August 2022, a validation campaign took place at NPL. Teddington and London Marylebone Road for the new TSI 3938W50-CEN-7 SMPS.

- Laboratory tests at Teddington using ambient air to confirm that the new SMPS instruments could operate continuously when installed at site.
- Tests at London Marylebone Road to: (a) co-locate the current and new SMPS models to further challenge the new instruments with roadside air and check for any differences in the data from the new and old instrumentation. (b) validate the movement of the CPC from a separate inlet to an inlet shared with the SMPS, as a combined drier system would be used with the new SMPS instrumentation.

In January 2023, further tests took place to compare the old and new drier sampling systems. The results from the comparison and validation campaign for the new TSI 3938W50-CEN SMPS system will be included in a separate report.

Figure 3 - NPL drying unit, (left); TSI 3936 SMPS, consisting of: TSI 3080 electrostatic classifier and TSI 3081 DMA, top-right; and TSI 3775 CPC, bottom-right. Photographs courtesy of NPL, Envco, and TSI Incorporated respectively.

Figure 4 – (left to right) TSI 3750-CEN-7 CPC; TSI 3750200 sampling system; and TSI 3938W50-CEN-7 SMPS, consisting of: TSI 3082 electrostatic classifier, TSI 3083 DMA, and TSI 3750-CEN-7 CPC, photograph courtesy of TSI Incorporated.

2.4.3 Aerosol mass and chemical composition

The ARI Q-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 (many weeks) unattended operation.

The instrument operates by sampling air into a high vacuum system through a size-selective particle aerodynamic lens at either PM_1 or $PM_{2.5}$. The particle lens focuses particles into a narrow beam which is directed to a resistively heated particle vaporiser, typically operated at 600°C, mounted inside the ionisation chamber of a mass spectrometer where non-refractory components in/on the particle flash vaporise on impact. The vaporised constituents are ionised by electron impact then analysed with a quadrupole mass spectrometer which reports aerosol mass spectra (< 200 amu). These spectra are used to extract the chemically speciated aerosol mass loadings. Figure 5 shows a schematic diagram of the set up.

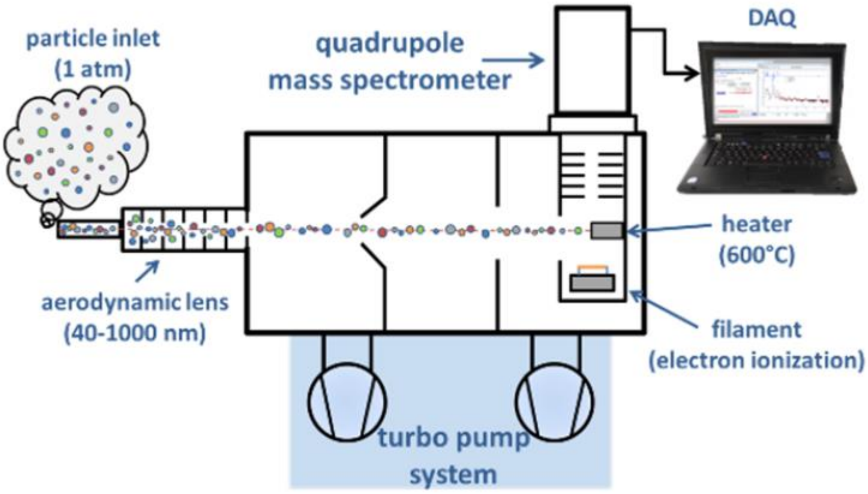

Figure 5 - ARI Q-ACSM schematic diagram (DAQ = Data acquisition (control)). Image copyright of Deutscher Wetterdienst (DWD).

The Q-ACSM instrument was installed at London North Kensington in 2013 with a standard vaporiser and PM_1 aerodynamic lens. It was moved to London Honor Oak Park in November 2018 and the standard vaporiser was changed to a capture vaporiser and the aerodynamic lens changed to $PM_{2.5}$. The Q-ACSM instrument installed at London Marylebone Road in July 2020 has a capture vaporiser and PM_1 aerodynamic lens. At Chilbolton Observatory a Q-ACSM with a capture vaporiser and $PM_{2.5}$ aerodynamic lens was installed in April 2022. Table 8 summarises the current configuration of the three Network ACSMs.

Table 8 - Configuration of Network ACSM instruments

Site	Installation year	Vaporiser	Lens size fraction
London Honor Oak Park	2018	Capture	$PM_{2.5}$
London Marylebone Road	2020	Capture	PM_1
Chilbolton Observatory	2022	Capture	$PM_{2.5}$

2.4.4 Elemental analysis

The Cooper Environmental Xact® 625i XRF analyser continuously and simultaneously measures the ambient concentration of 40 elements. The instrument collects PM on filter tape and the PM is analysed by non-destructive XRF. The reel-to-reel filter tape sampling and subsequent analysis is engineered in a way that enables near real time and continuous monitoring of the elemental composition of PM.

The instrument uses a flow rate of 16.7 L min^{-1} and draws air through a size selective inlet and across a filter tape. The sample that collects on the filter tape is automatically moved into the analysis area and analysed while the next sample is being collected. Measurements of one hour time resolution are achieved by conducting continuous sampling and analysis simultaneously. The sampling is only interrupted during tape advances and during internal QA/QC checks at midnight daily.

The XRF instrument installed at London Honor Oak Park was incorporated into the PCN Network in February 2022. At London Marylebone Road the instrument was installed in March 2022 and was fully operational from April 2023. Both instruments use a switching valve, which alternates between sampling PM_{10} and $PM_{2.5}$ on an hourly basis.

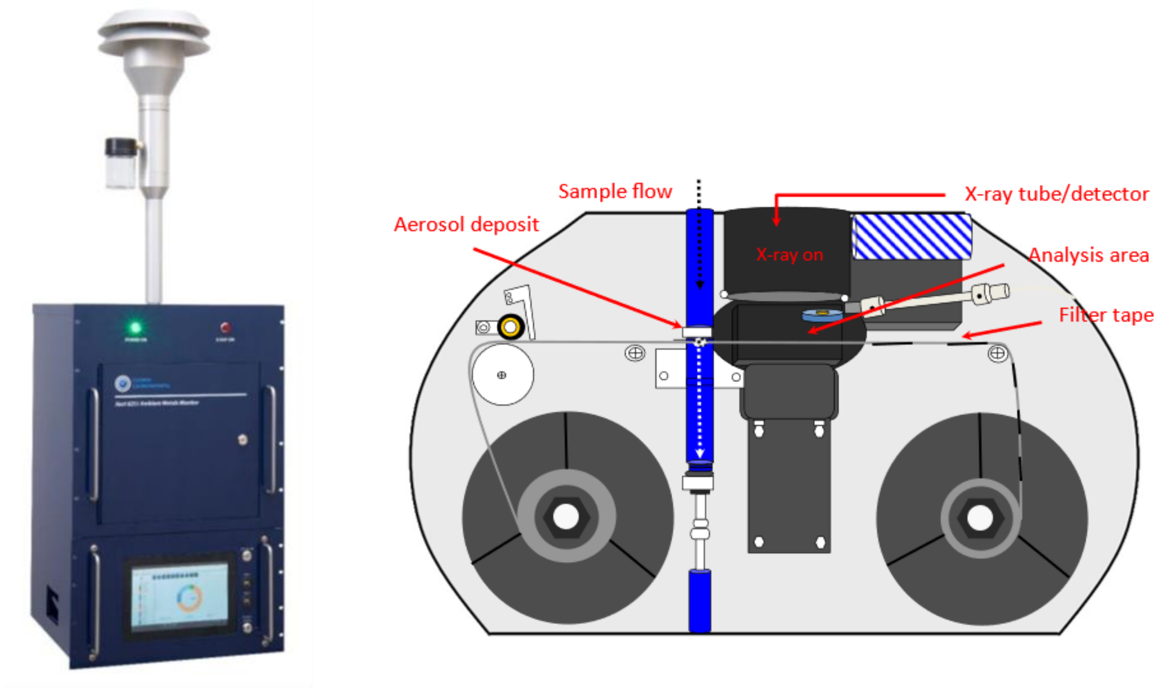

Figure 6 - Xact 625i instrument (left) and sampling schematic (right), images courtesy of Cooper Environmental Services.

2.4.5 OC/EC

OC and EC 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) were used for sampling.

In 2022, sampling of $PM_{2.5}$ continued at Auchencorth Moss (weekly) and Chilbolton Observatory (daily), initially using Leckel SEQ47/50 sequential samplers (Figure 7(a)). These samplers were replaced by Digitel DPA14 samplers (Figure 7(c)) in January 2022. At London Honor Oak Park and London Marylebone Road, daily $PM_{2.5}$ sampling initially took place using a Thermo Partisol 2025 sequential air sampler (Figure 7(b)). These samplers were replaced by Digitel DPA14 samplers in February and March 2022 respectively.

Although sampling at Auchencorth Moss was weekly throughout the majority of 2022, between 9 July and 20 July 2022, daily samples were taken for the EMEP/ACTRIS (European Monitoring and Evaluation Programme / Aerosol, Clouds and Trace Gases Research Infrastructure) intensive summer campaign.

OC/EC analysis was carried out using the Sunset Laboratory Inc. L5 thermal/optical carbon analyser (Figure 8). 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 EC. Measuring the transmission of a laser beam through the filter continuously monitors this pyrolytic conversion and allows a correction to be made for it. EC 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[12]. The protocol also specifies that the transmittance correction must be used to determine concentrations for OC and EC. Data are reported as the mass of carbon per volume of air.

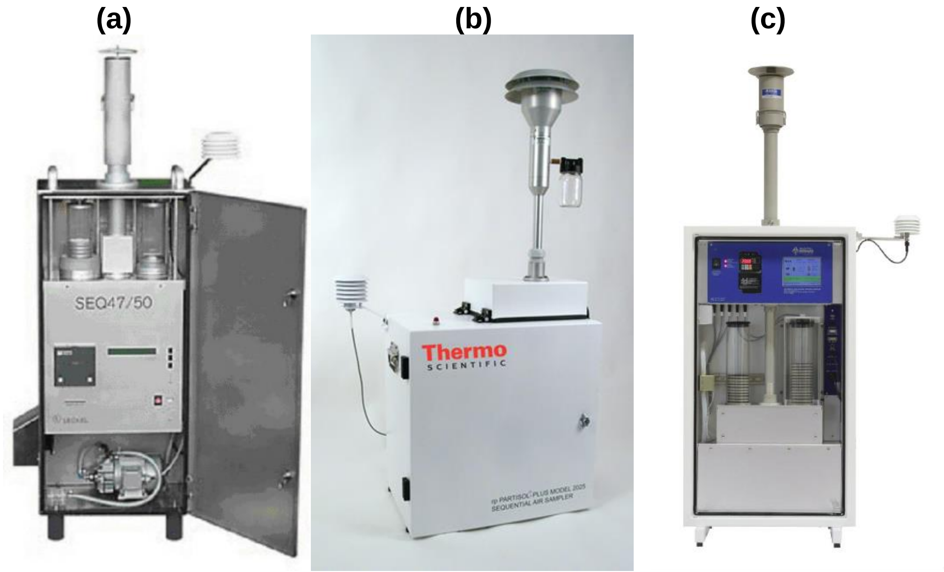

Figure 7 - (a) Leckel SEQ47/50 sampler (b) Partisol 2025 sampler (c) Digitel DPA14 sampler, photographs courtesy of Sven Leckel, Thermo Scientific and Digitel AG respectively.

Figure 8 - Sunset Laboratory Inc. L5 thermal/optical carbon analyser, photograph courtesy of Sunset Laboratory Inc.

2.4.6 BC and UVPM

Aethalometers measure BC on filter samples based on the transmission of light through a sample.

This 7-wavelength Aerosol Magee Scientific AE33 instrument (Figure 9) operates at 950 nm, 880 nm, 660 nm, 590 nm, 520 nm, 470 nm, and 370 nm and samples $PM_{2.5}$ using an inlet flow of 5 L min^{-1}. 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 (approximately 1.5 and 3.5 L min^{-1}) 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 BC 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*.[13]. 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 UVPM is calculated as the difference between UV and BC channels.

At all sites, ambient air was drawn into the sampling system through a standard rain cap mounted on the end of a vertical 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.

The Aethalometers were upgraded in November 2019 from model AE22 to model AE33. Although the methodology, in principle, is the same, both models use different algorithms and factors to calculate the final BC mass concentration. These are: 1) the multiple scattering factor, *C*, used in both models as a fixed value, and 2) the Mean Ratio factor used only in early-model aethalometers (including the AE22) to correct surface area of the filter spot where particles are collected. Results from comparison campaigns run by NPL in 2020 and 2022 show that concentrations measured by the AE33 model are approximately 40 % higher than from the AE22 model. Thus, all results provided in this report should be treated with caution when comparing data from the AE33 model with earlier years when the AE22 model was used. A note to this effect has been added to the BC Network page of the UK AIR website[14].

Figure 9 - Aerosol Magee Scientific AE33 Aethalometer, photograph courtesy of NPL.

3 DATA QUALITY

3.1 QA/QC PROCEDURES

NPL operates under a Quality Management System certified for scientific research and development and the provision of internal services by Lloyd's Register Quality Assurance (LRQA) according to ISO 9001:2015[15]. NPL is accredited to International Standard ISO/IEC 17025:2017[16] for the general requirements for the competence of testing and calibration laboratories for OC/EC measurements and CPC calibration.

A summary of the general QA/QC procedures used during the measurement and ratification process is given below:

- A Technical Lead (supported by expert consultants) is appointed for each instrument type to manage data collection and ratification.
- 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 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.
- Calibrations and checks are carried out at regular intervals throughout the year.
- Data collection is performed manually for Digitel samplers (formally the Leckel and Partisol samplers) by NPL and automated by the MONNET data handling system at ERG for all other instruments. All data are stored securely and backed up.
- The quarterly Network reports include data capture values from the verified data of the previous quarter.
- Automatic and manual data validation is followed by rigorous ratification procedures.
- Data quality circle meetings are held at least annually to review and validate the data. Other measurements made in this monitoring programme and in other EA monitoring programmes are also used to check the validity of the measurements.

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

3.1.1 Particle number concentration

- The manufacturer's software is set up to automatically repeat measurements every 15 minutes, providing verified data.
- NPL is accredited by UKAS to ISO 17025 to perform the primary calibration of CPCs and is the only institute in the 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

- The LSO attends the instruments bi-monthly to perform checks on the instrument and software. These 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 DMA of the SMPS. 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 Elemental analysis

- During daily data checking, the results from the internal standards and automated overnight standards are checked for deviations.
- The LSO attends the instruments bi-monthly to perform checks on the instrument and software. These include flow rate checks, inlet cleaning and tape changes (as required).
- Calibration checks are performed every quarter by trained technical users. Five thin film standards covering different analysis conditions of the instrument are used to verify the instrument operates within its parameters.
- Yearly services are carried out by trained engineers from the ESU.
- A full calibration of the instrument is performed after any change of the X-ray tube.
- Ratification is performed using ERG owned software. Data are scaled and corrected for flow. Sensibility checks are performed by comparison to co-located PM and chemical speciation instrument measurements.

3.1.5 OC/EC

- The Digitel DPA14 sampler is compliant with EN 12341:2014[17]. The four flow calibrations and flow checks carried out during the year are used to calculate and apply a flow correction for the data.
- 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 OC and EC. As part of this procedure, field blank filters are analysed to evaluate the contamination due to the transport of the filters to the sites and back to the laboratory.

3.1.6 BC and UVPM

- Measurements of BC, 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 are 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 min measurements are averaged to 15 min means in line with measurements made using gaseous and particulate monitors in the AURN. A valid 15 min measurement is only calculated where at least ten 1 min measurements exist in that 15 min period. Hourly averages are calculated if there are at least three valid 15 min averages in that period.

3.2 MEASUREMENT UNCERTAINTY

3.2.1 Particle number concentration

The expanded (k = 2) uncertainty of these measurements is 5 %, in accordance with NPL's Calibration and Measurement Capabilities, which were 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"[18].

3.2.2 Particle size distribution

The expanded uncertainty of these size measurements is 4.1 %. The main component of uncertainty, which has been determined by NPL, 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 is taken into account in this process.

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[19]. Uncertainties for individual species are 15 % for nitrate, 19 % for organics, 28 % for sulfate and 36 % for chloride.

3.2.4 Elemental analysis

The XRF calculates and reports an uncertainty with each hourly concentration measurement. These calculated uncertainties vary depending on the concentration and element being measured, with the relative uncertainty of each hourly measurement typically being larger at lower concentrations. The uncertainties reported by the XRF should currently only be taken as estimates as the manufacturer of the XRF is in the process of modifying the uncertainty calculations implemented in the software of the instruments.

The dominant uncertainty contribution is typically from the spectral deconvolution process applied by the instrument (i.e. the process of resolving the signal from the detector into individual peaks that can be quantified); smaller uncertainty contributions are associated with the sample volume and the deposited area.

As examples of the magnitude of the estimated uncertainties reported by the XRF, the average relative uncertainties from an hourly measurement of iron (one of the elements of highest abundance) in 2022 were 1.2 % in $PM_{2.5}$ and 0.72 % in PM_{10} at London Marylebone Road, and 3.2 % in $PM_{2.5}$ and 2.6 % in PM_{10} at London Honor Oak Park. For zinc (an element of lower abundance, but still with almost all measurements above the limit of detection), the average relative uncertainties were 4.1 % in $PM_{2.5}$ and 2.7 % in PM_{10} at London Marylebone Road, and 6.7 % in $PM_{2.5}$ and 5.7 % in PM_{10} at London Honor Oak Park.

3.2.5 OC/EC

As the methods for assessing the accuracy of the OC/EC split of 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[17] requires the consistency of the average volumetric flow for $PM_{2.5}$ and PM_{10} samplers to be ≤ 2 % over the sampling period. The uncertainty of the measurement of OC and EC is therefore dominated by the analytical uncertainty.

3.2.6 BC and UVPM

The expanded uncertainty for the annual concentration of BC measured using the AE33 Aethalometer is estimated to be 9 %, with the dominant uncertainty contribution being the measurement of the flow rate. It should be noted that a method for the determination of the uncertainty of BC mass concentration is not yet standardised.

The Aethalometer measurement of BC does not depend on the absolute calibrated response of the detectors, but instead relies upon their ability to determine very small relative changes in optical transmission. The repeatability of the Aethalometer when sampling zero air has been assessed to be less than 0.2 % relative to typical network concentrations over a period of a year, and so is a negligible uncertainty contribution.

The uncertainty in the annual concentration of UVPM will be of the same order as the uncertainty in the annual concentration of BC as both are dominated by the uncertainty in the flow rate.

3.3 SCHEDULED INSTRUMENT SERVICE AND CALIBRATION

3.3.1 CPCs

NPL obtained ISO 17025[16] 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 SMPS

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 ACSM

The ACSMs are managed 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 XRF

The XRF instruments are managed by ERG and ACOEM UK Ltd. ERG carry out tape changes and *ad hoc* checks, as well as routine flow checks and three-monthly calibration checks. Annual services are carried out by ACOEM UK Ltd. These services can include a full instrument calibration if the x-ray tube has been changed. ACOEM UK Ltd also carries out *ad hoc* call-outs and repairs.

3.3.5 Digitel air samplers and OC/EC analyser

The Digitel DPA14 samplers at Chilbolton Observatory, London Honor Oak Park and London Marylebone Road were serviced by the EA Ambient Air Monitoring (AAM) Team, during 2022. The Digitel DPA14 sampler at Auchencorth Moss was serviced by Enviro Technology Services. These 6-monthly services include replacing old or worn parts, cleaning, sensor and flow checks and calibrations, leak tests, and time and date checks. The Partisol and Leckel samplers taken out of service in early 2022 had no routine checks or services performed in 2022.

The Sunset Laboratory Inc. L5 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 Aethalometers

The AE33 Aethalometer instruments were serviced by ACOEM UK Ltd. 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 2022 time series

Time series of hourly particle number concentrations (between approximately 7 nm and 2.5 µm in diameter) measured at Network sites during 2022 are shown in Figure 10.

4.1.2 2022 diurnal, weekly, and monthly profiles

The diurnal, weekly, and monthly profiles for particle number concentrations in 2022 are shown for the London Honor Oak Park, London Marylebone Road, and Chilbolton Observatory sites in Figure 11, Figure 12 and Figure 13 respectively (plots generated using the OpenAir Tools run on the R software platform[20,21]). At all three sites there are higher concentrations during the working week and lower concentrations on a Sunday. The concentrations remain high on a Saturday at Marylebone Road which is a change from previous years (although the 2022 trend comes from a limited dataset taken over the winter months). There is also a clear increase in particle number concentration at all three sites during the evening.

4.1.3 Long-term trends

Figure 14 and Figure 15 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 14 (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)[22].

UK-wide legislation[23] 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)[24] 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 effect on annual particle concentrations for 2020 and 2021 was difficult to determine, predominately due to the potential influence of the Covid-19 lockdown in those years. The 2022 data at London Marylebone Road suggests that the annual particle concentrations are not returning to pre-lockdown levels, which may represent the changing emissions profile of the vehicle fleet. This could be driven by the completion of the upgrade of old diesel buses to meet EURO VI legislation in 2021.

Annual particle number concentrations at Chilbolton Observatory have increased in recent years and are now at the same level seen at Harwell in 2010.

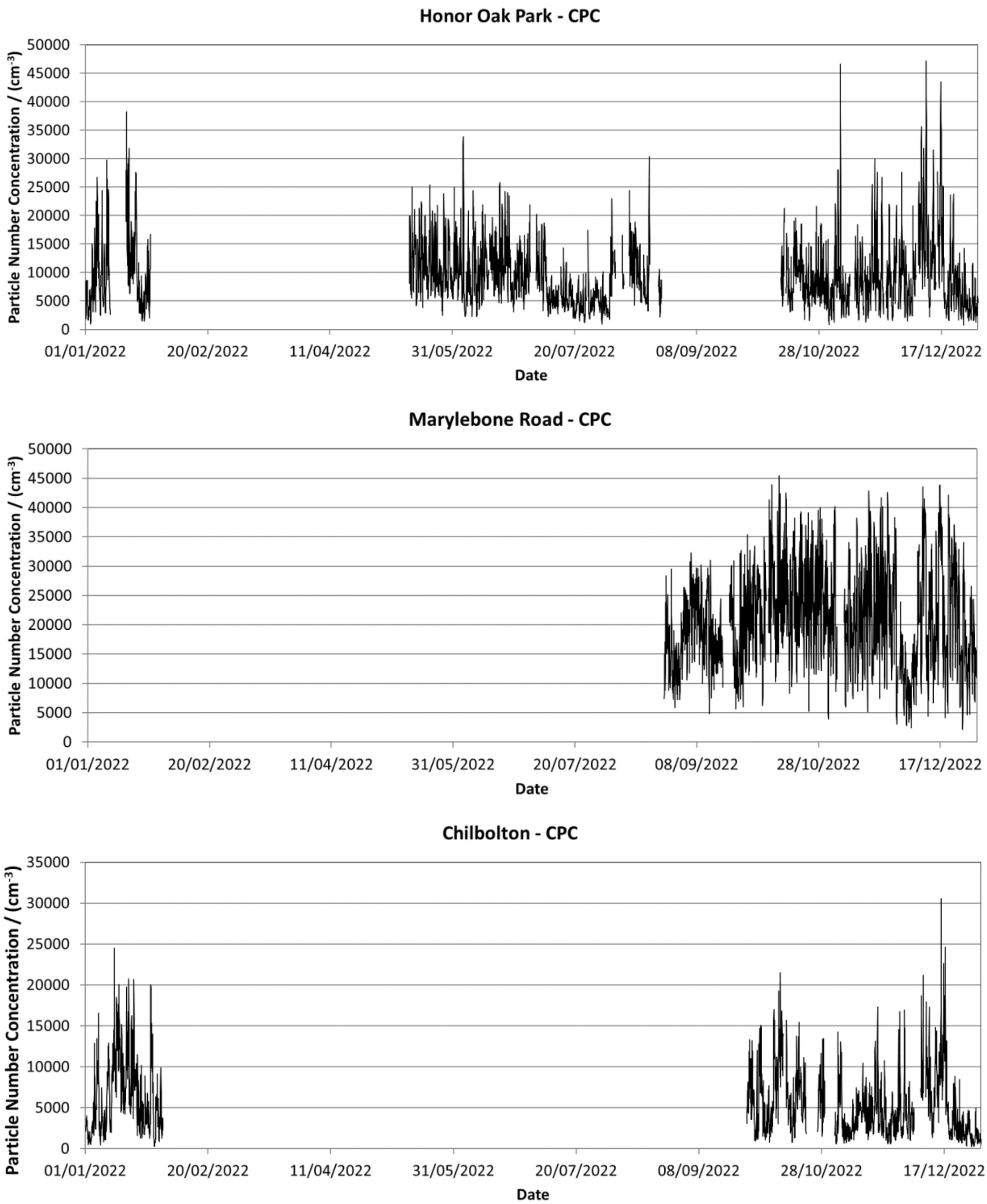

Figure 10 - Hourly particle number concentrations at London Honor Oak Park, London Marylebone Road and Chilbolton Observatory in 2022

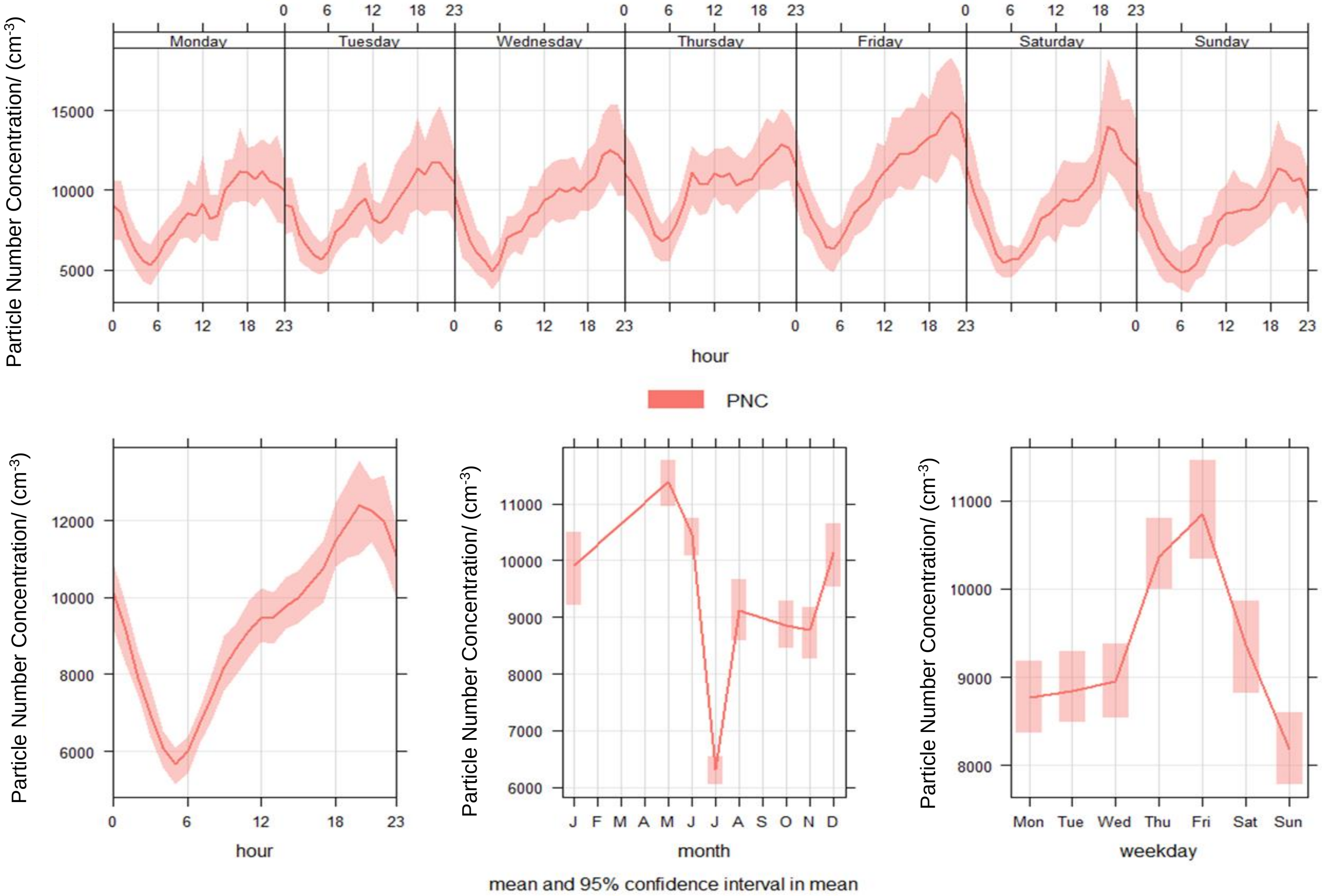

Figure 11 - Temporal variations of particle number concentrations in 2022 at London Honor Oak Park. Note that any line joining non-consecutive months in the monthly plot is automatically produced by the software used to generate the plot and is not intended to represent the particle number concentration of the 'missing' month(s).

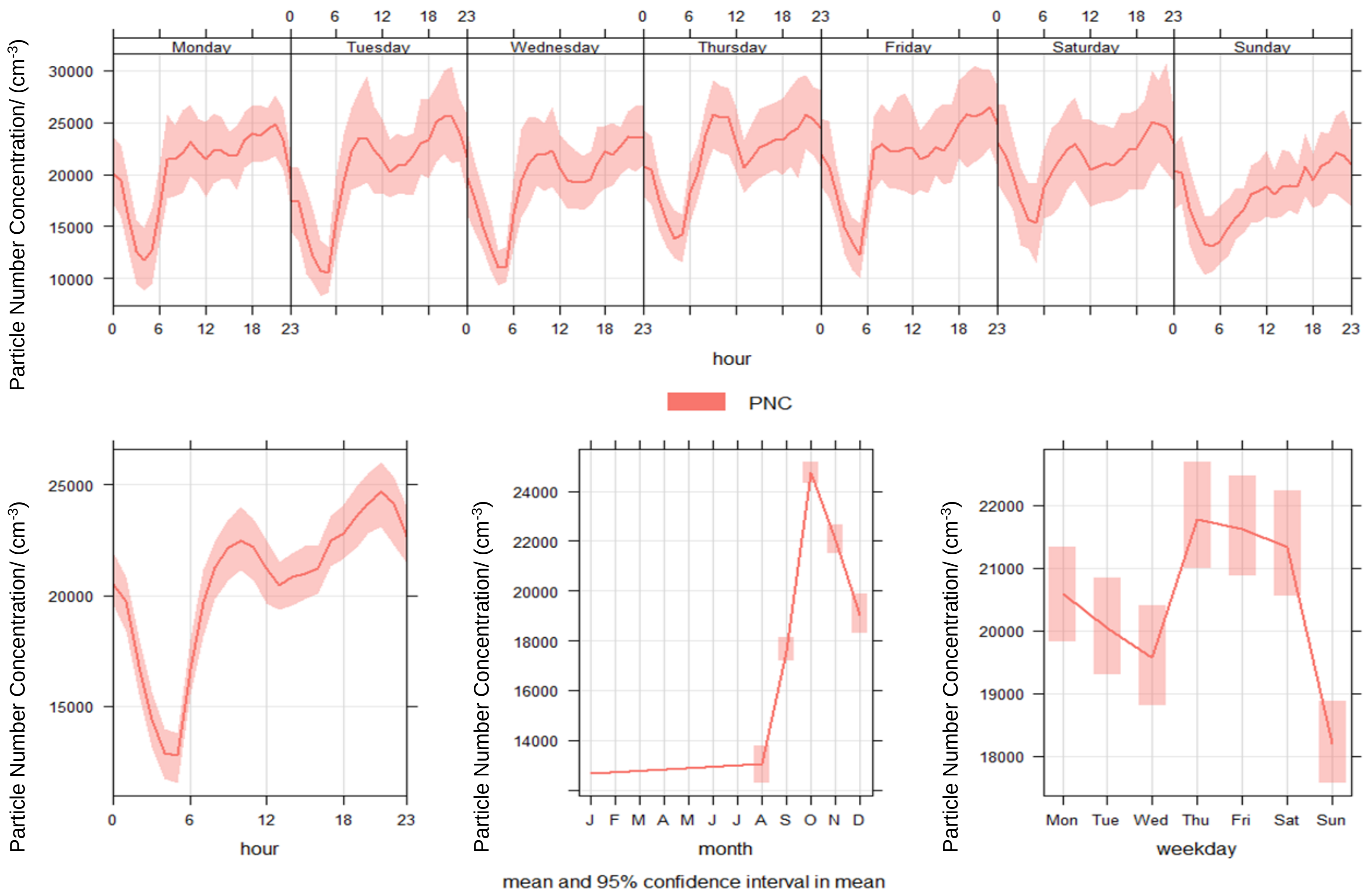

Figure 12 - Temporal variations of particle number concentrations in 2022 at London Marylebone Road. Note that any line joining non-consecutive months in the monthly plot is automatically produced by the software used to generate the plot and is not intended to represent the particle number concentration of the 'missing' month(s).

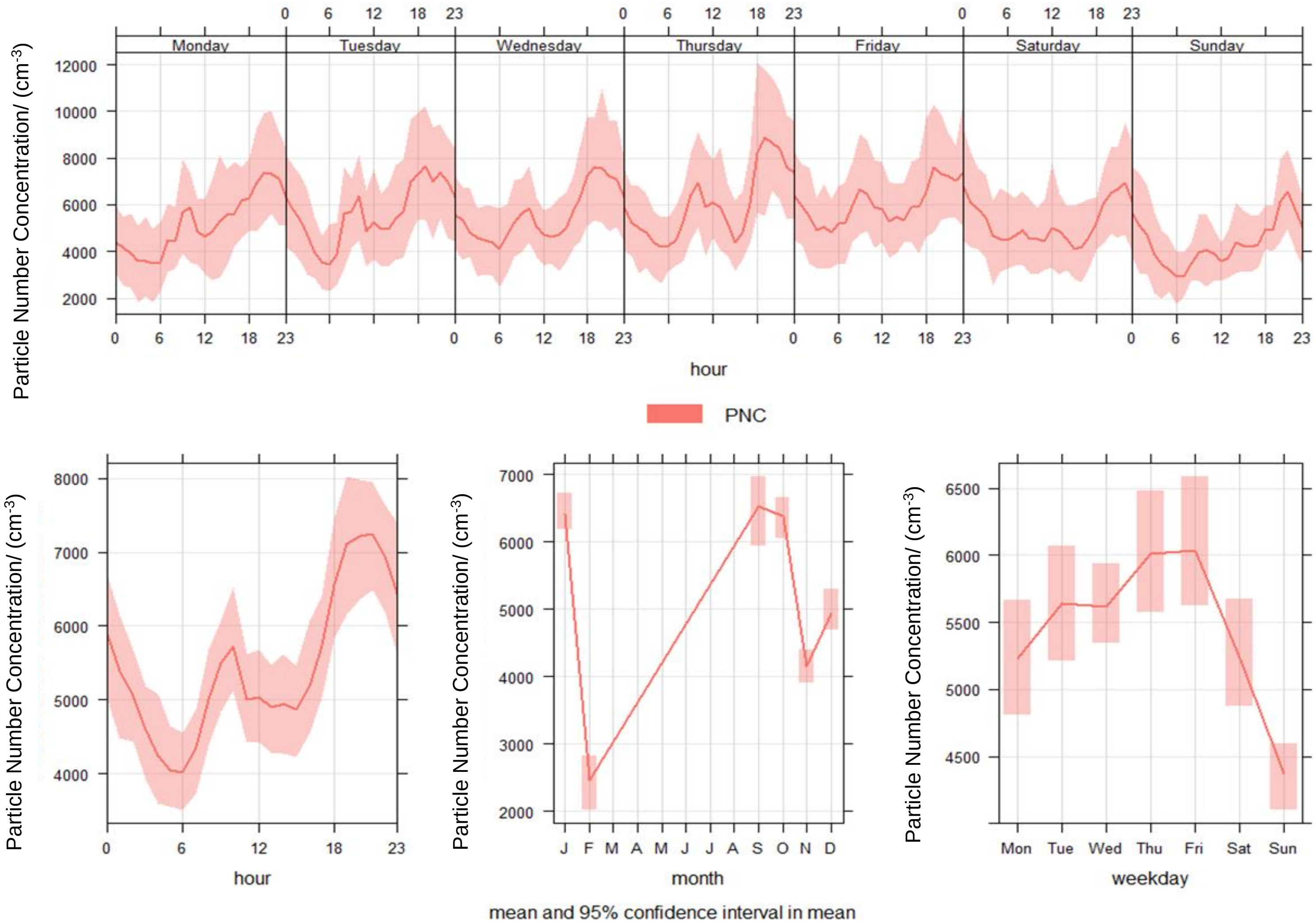

Figure 13 - Temporal variations of particle number concentrations in 2022 at Chilbolton Observatory. Note that any line joining non-consecutive months in the monthly plot is automatically produced by the software used to generate the plot and is not intended to represent the particle number concentration of the 'missing' month(s).

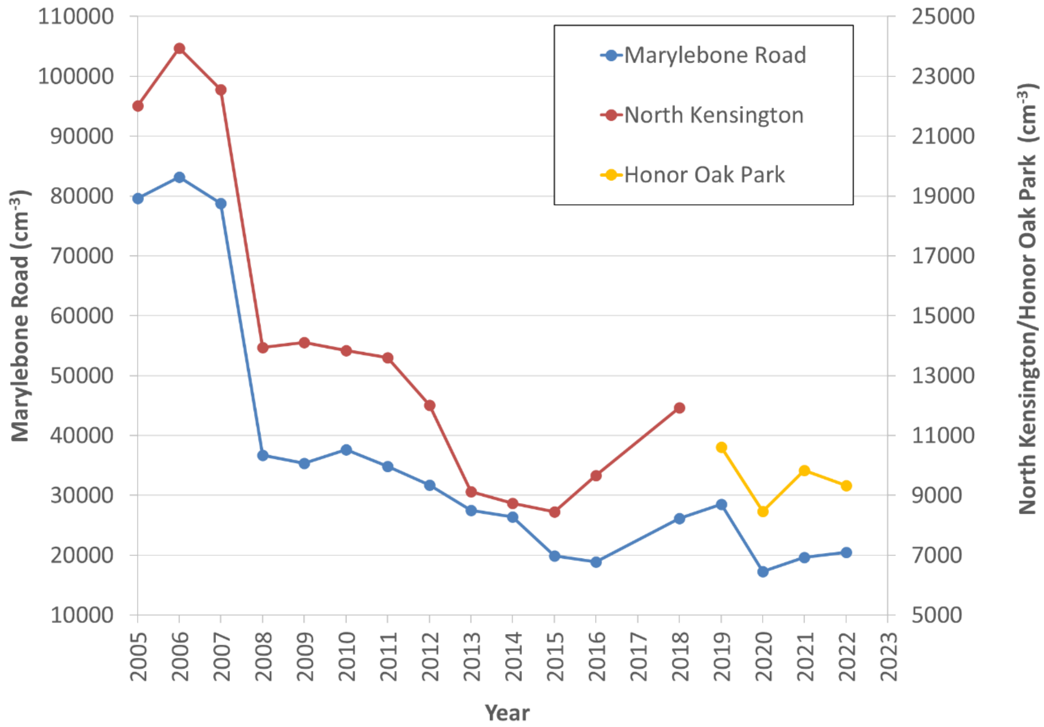

Figure 14 - Historical long-term particle number concentrations annual trends at all London sites. The London North Kensington site moved to London Honor Oak Park in mid-November 2018.

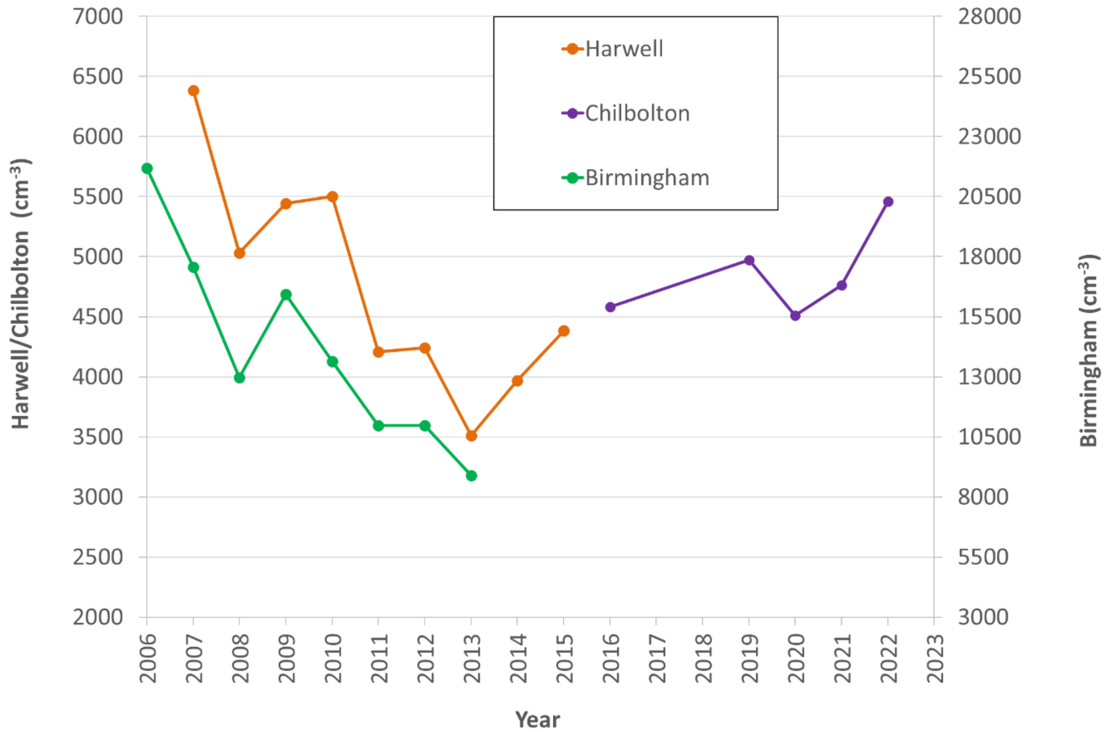

Figure 15 - Historical long-term particle number concentrations annual trends at all non-London sites. The Harwell site moved to Chilbolton Observatory in 2016. The 2016 data uses an adjusted SMPS total number concentration due to low time coverage. Insufficient data was available from Chilbolton Observatory for reliable averages in 2017 and 2018.

4.2 PARTICLE SIZE DISTRIBUTIONS

4.2.1 2022 time series

Time series of monthly particle size distributions measured at Network sites during 2022 are shown in Figure 16. The plots show both the variation in particle number concentration and the shape of the particle size distribution across 2022 at each site.

4.2.2 Long-term trends

Time series of annual particle size distributions measured at Network sites from 2013 to 2022 are shown in Figure 17. The plots show both the variation in particle number concentration and particle size distribution.

4.2.3 2022 diurnal, weekly, and monthly profiles

The diurnal, weekly, and monthly profiles for particle number concentrations as a sum over the collected SMPS particle sizes in 2022 are shown for the London Honor Oak Park, London Marylebone Road, and Chilbolton Observatory sites in Figure 18, Figure 19, and Figure 20 respectively (plots generated using the Open Air Tools run on the R software platform[20,21]). At all three sites there are higher concentrations during the working week and less on the weekend. The higher concentrations seen from the CPC data on a Saturday at London Marylebone Road are not reflected here. This could demonstrate that the elevated particles levels measured by the CPC are due to particles outside of the SMPS size range, such as in the $PM_{2.5}$ size range. There is also a clear increase in particle number concentration at all three sites during the evening.

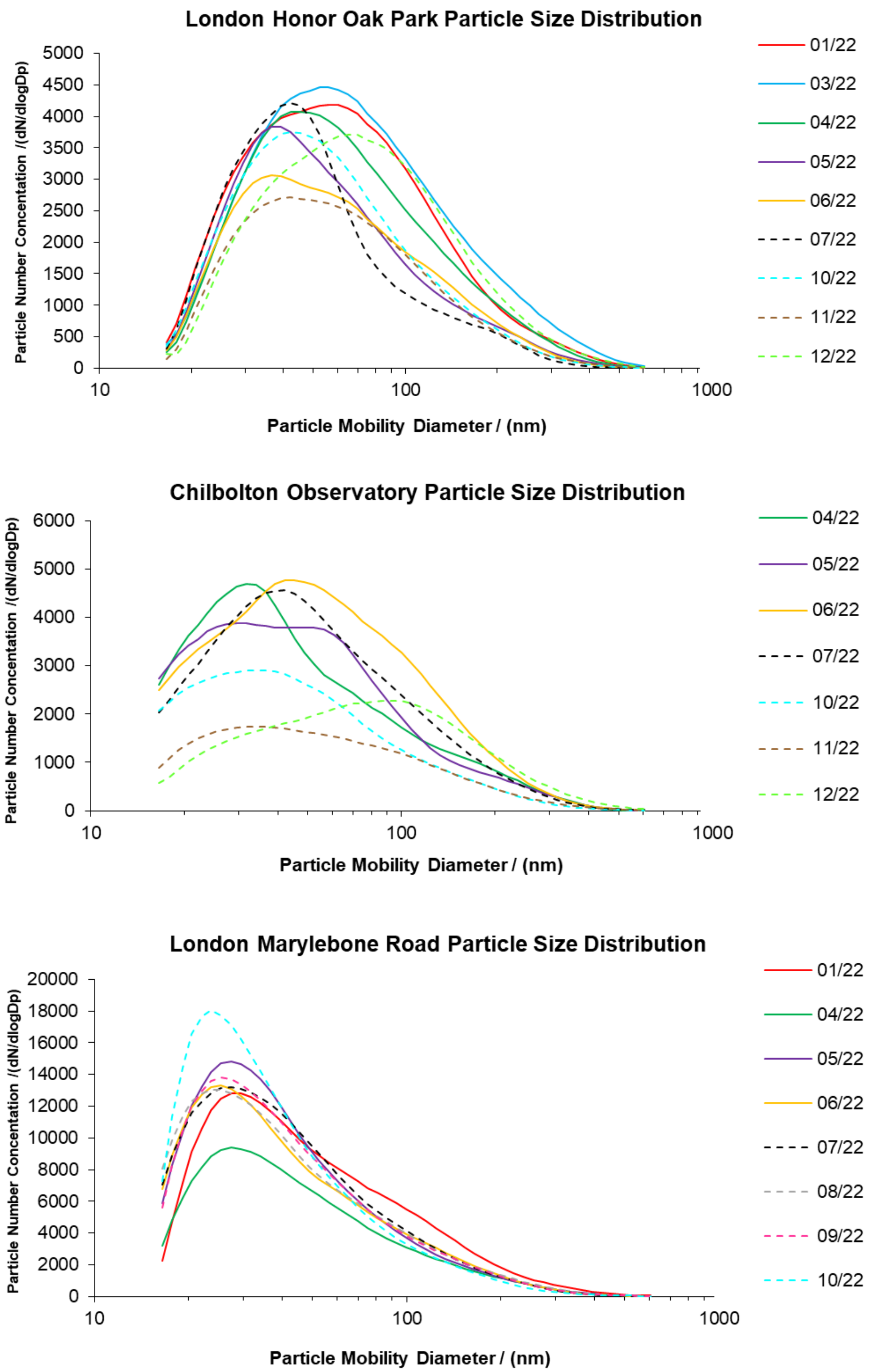

Figure 16 - Monthly averaged particle size distributions at the Network sites for each month during 2022. Data for November and December 2022 from the new 3938W50-CEN-7 SMPS at the London Marylebone Road site are not included here as the data have yet to be fully ratified.

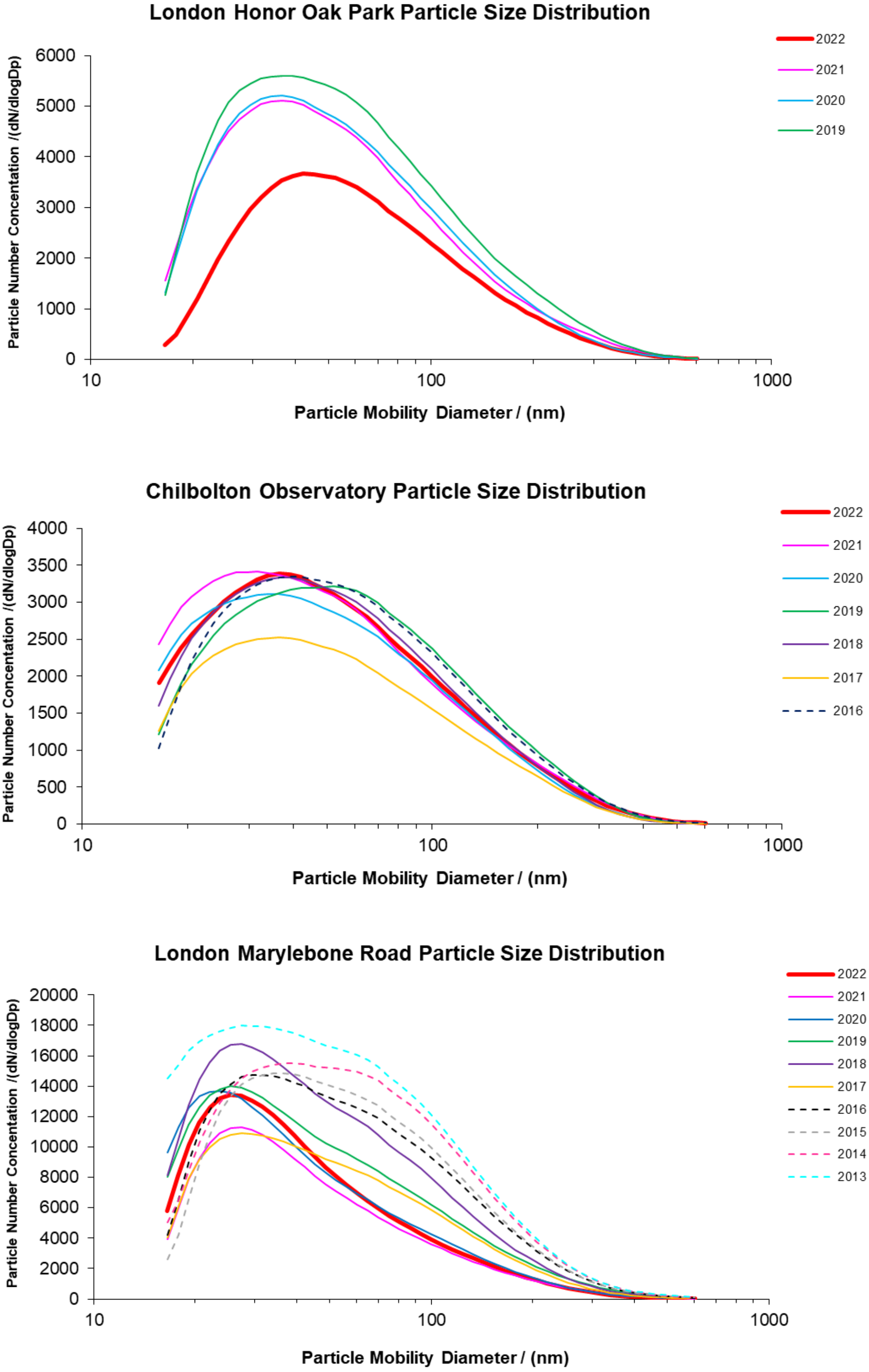

Figure 17 - Comparison of the 2013 to 2022 annual average size distribution. Note that measurements have only taken place at London Honor Oak Park since 2019 and at Chilbolton since 2016. The data for November and December 2022 from the new 3938W50-CEN-7 SMPS at the London Marylebone Road site are not included here as the data have yet to be fully ratified.

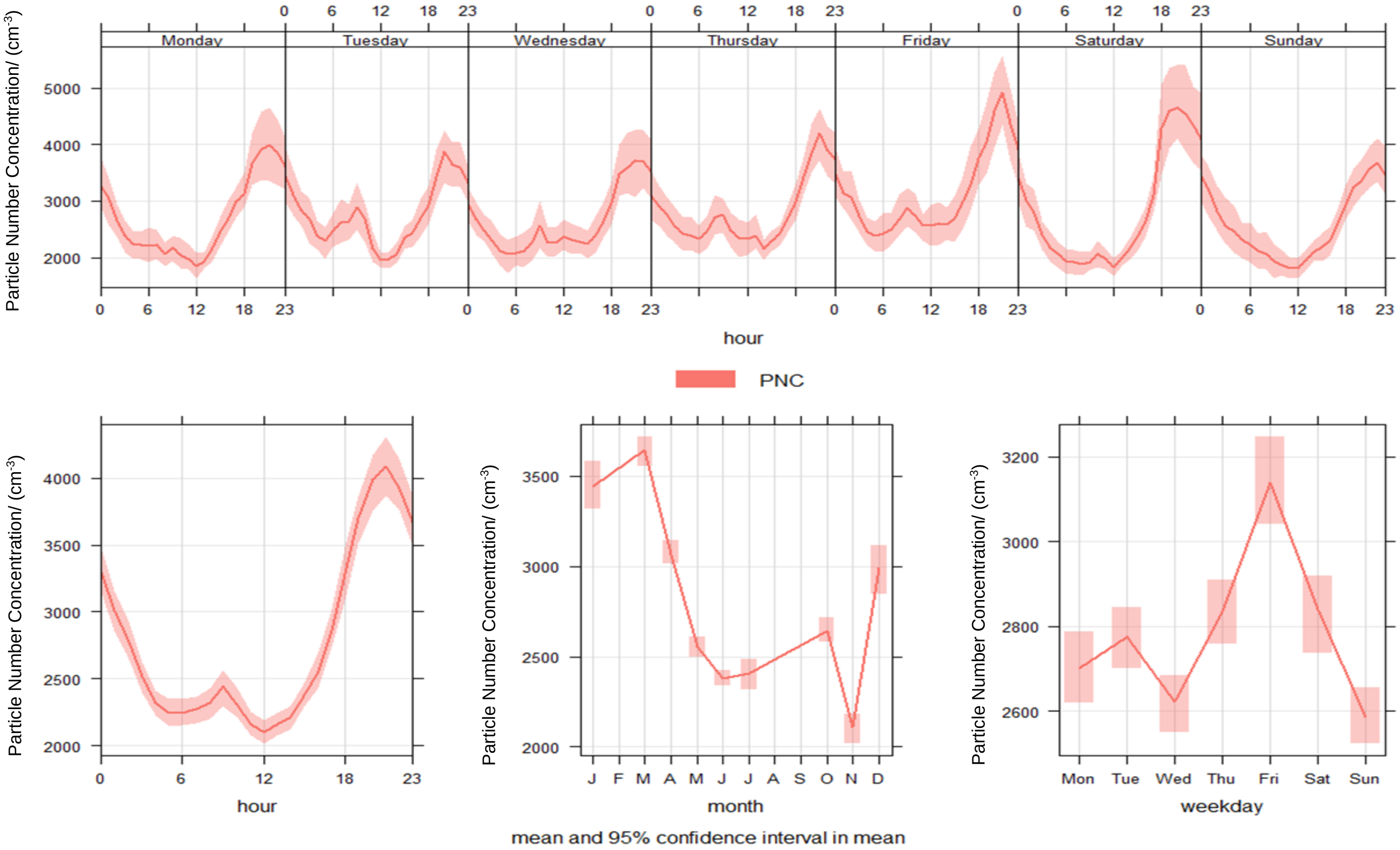

Figure 18 - Temporal variations of particle number concentrations from SMPS averages in 2022 at London Honor Oak Park. Note that any line joining non-consecutive months in the monthly plot is automatically produced by the software used to generate the plot and is not intended to represent the particle number concentration of the 'missing' month(s).

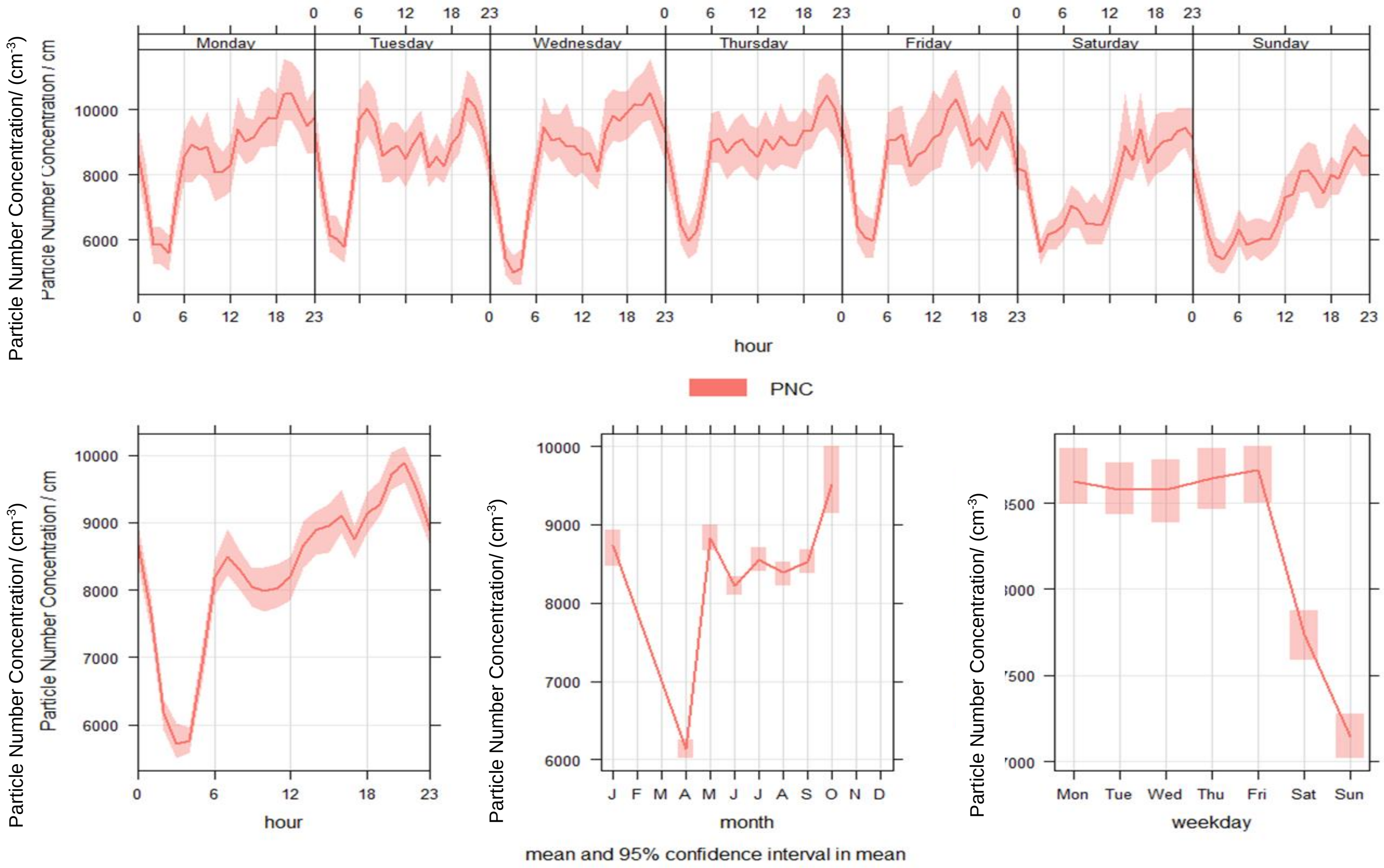

Figure 19 - Temporal variations of particle number concentrations from SMPS averages in 2022 at London Marylebone Road. Note that any line joining non-consecutive months in the monthly plot is automatically produced by the software used to generate the plot and is not intended to represent the particle number concentration of the 'missing' month(s). The data for November and December 2022 from the new 3938W50-CEN-7 SMPS are not included here as the data have yet to be fully ratified.

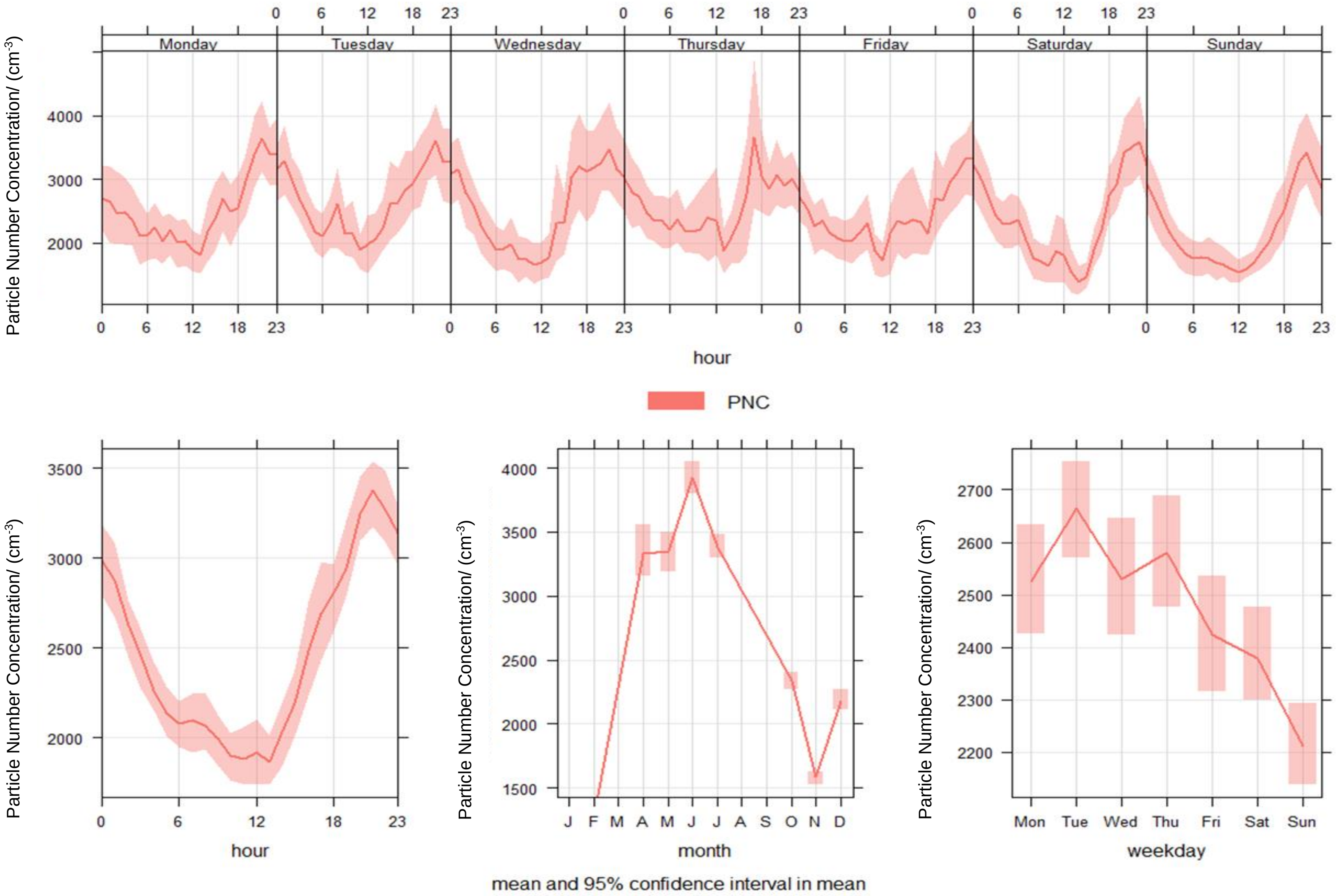

Figure 20 - Temporal variations of Particle number concentrations from SMPS averages in 2022 at Chilbolton Observatory. Note that any line joining non-consecutive months in the monthly plot is automatically produced by the software used to generate the plot and is not intended to represent the particle number concentration of the 'missing' month(s)

4.3 AEROSOL MASS AND CHEMICAL COMPOSITION

4.3.1 2022 time series

Figure 21 to Figure 23 (plots generated using the OpenAir Tools run on the R software platform[20,21]) show the time series of monthly average mass concentrations of organics, nitrate, sulfate and ammonium at London Honor Oak Park, London Marylebone Road, and Chilbolton Observatory during 2022.

It should be noted that although the intended measurands of the ACSM analysis are ions (e.g. Cl^- and NO^{3-}) in particulate matter, the ACSM actually measures elements, or combinations of elements, e.g. Cl or NO_3. For simplicity, all the results in this report are presented as if these are equivalent to ions.

4.3.2 Long-term trends

An ACSM instrument was installed at London North Kensington in 2013 measuring PM_1. 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 ammonium in $PM_{2.5}$.

An ACSM instrument measuring the PM_1 size fraction was installed at London Marylebone Road in mid-July 2020. In April 2022 a new ACSM measuring $PM_{2.5}$ was installed at Chilbolton.

Figure 24 to Figure 27 (plots generated using the Open-Air Tools run on the R software platform[20,21]) 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, London Marylebone Road, and Chilbolton Observatory.

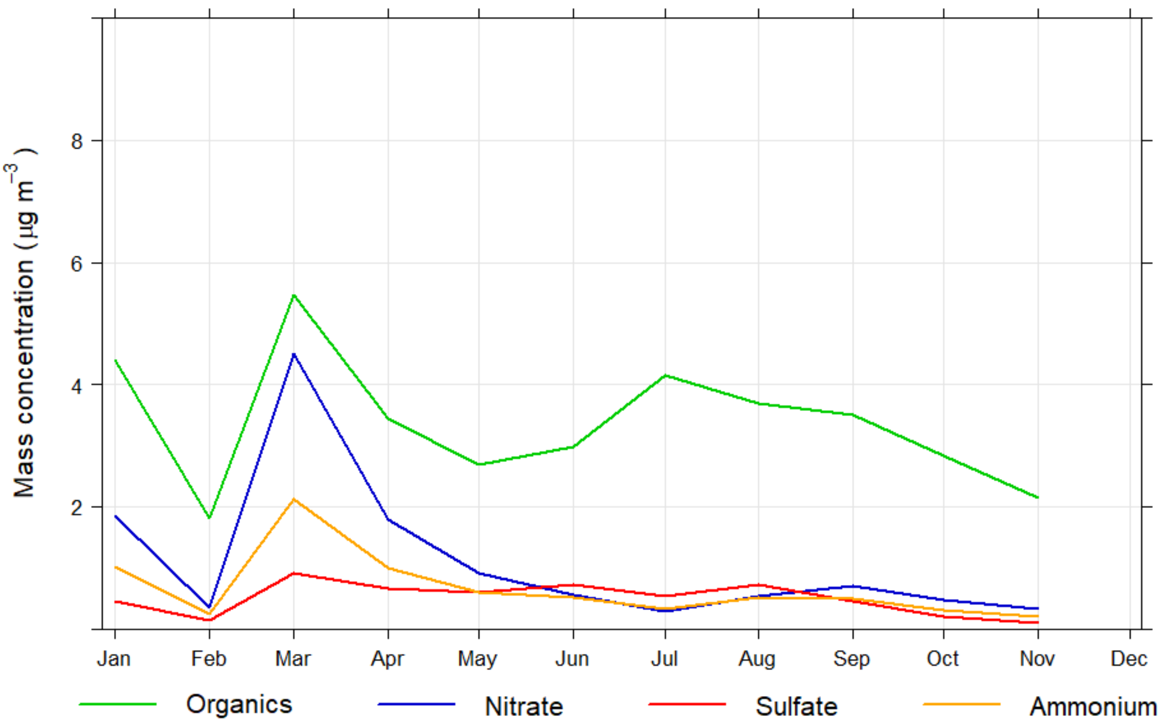

Figure 21 - Monthly average mass concentrations of organics, nitrate, sulfate and ammonium in $PM_{2.5}$ measured by ACSM in 2022 at London Honor Oak Park

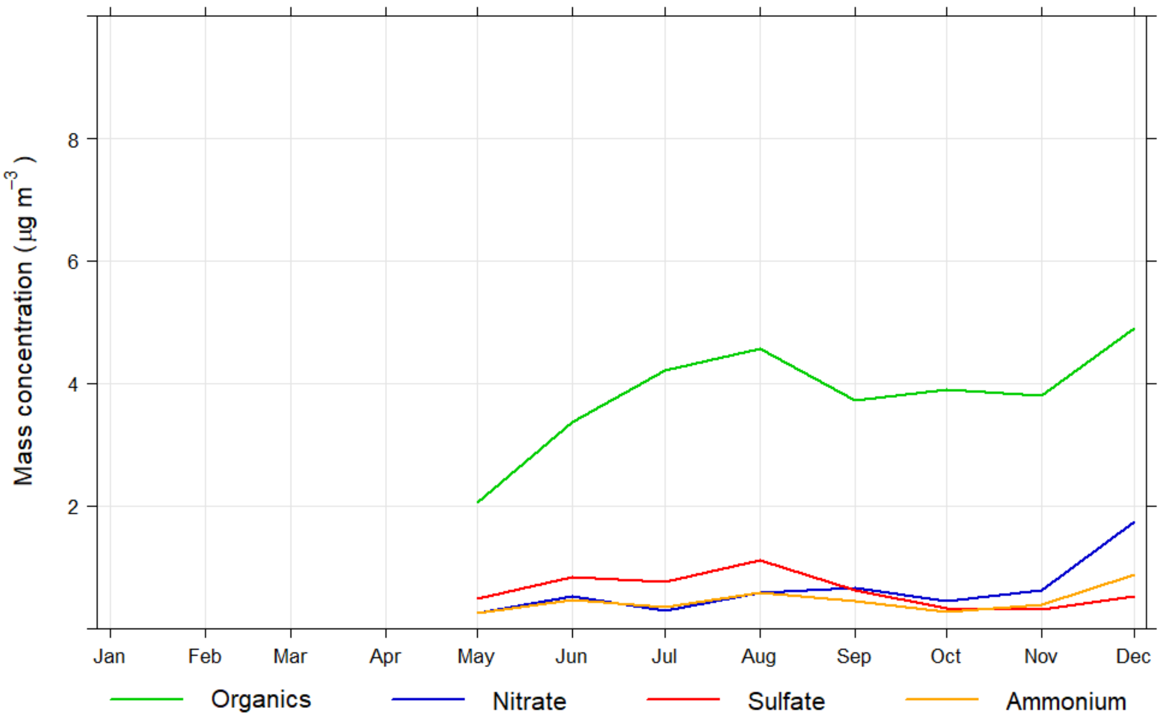

Figure 22 - Monthly average mass concentrations of organics, nitrate, sulfate and ammonium in PM_1 measured by ACSM in 2022 at London Marylebone Road

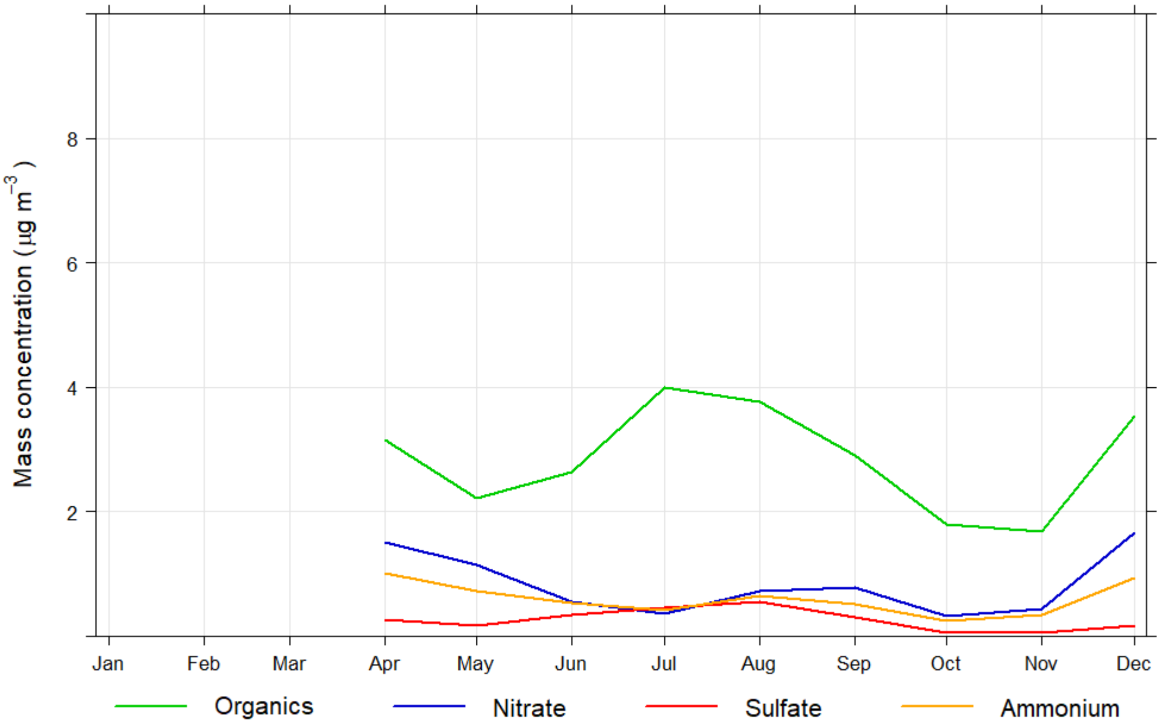

Figure 23 - Monthly average mass concentrations of organics, nitrate, sulfate and ammonium in $PM_{2.5}$ measured by ACSM in 2022 at Chilbolton Observatory

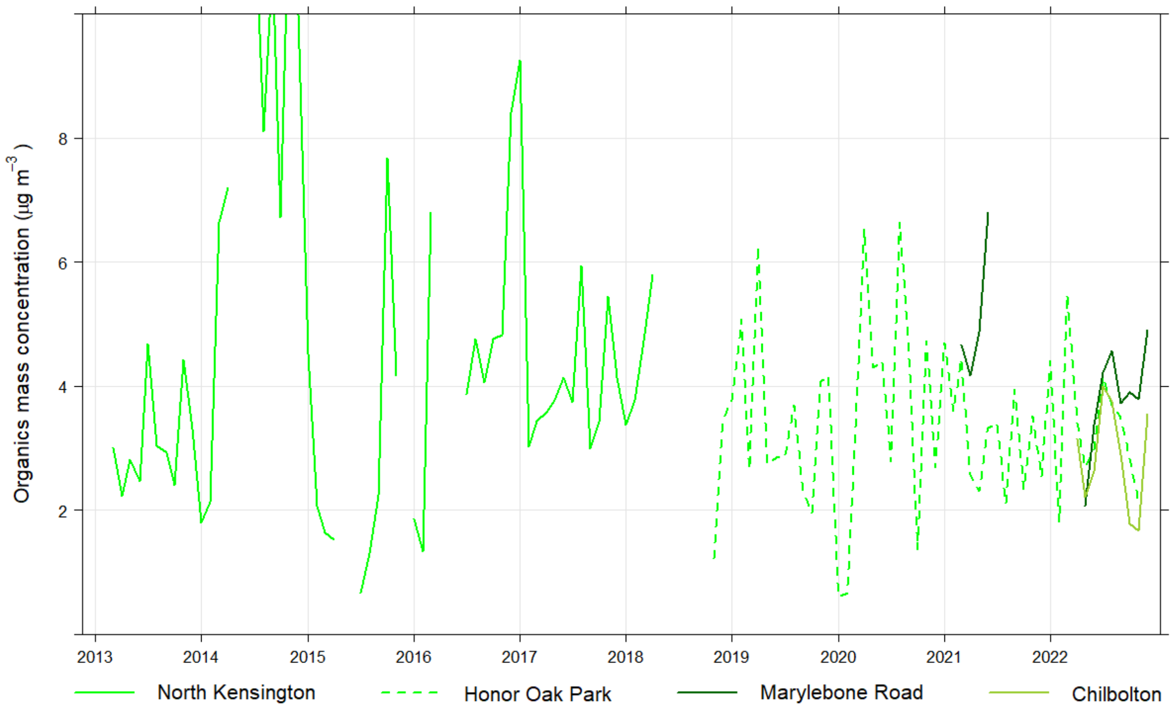

Figure 24 - Long-term mass concentration trends of organics at the rural background site Chilbolton Observatory, urban background site London Honor Oak Park (London North Kensington before 2019) and roadside site London Marylebone Road. The tick marks on the x-axis indicate the start of each year.

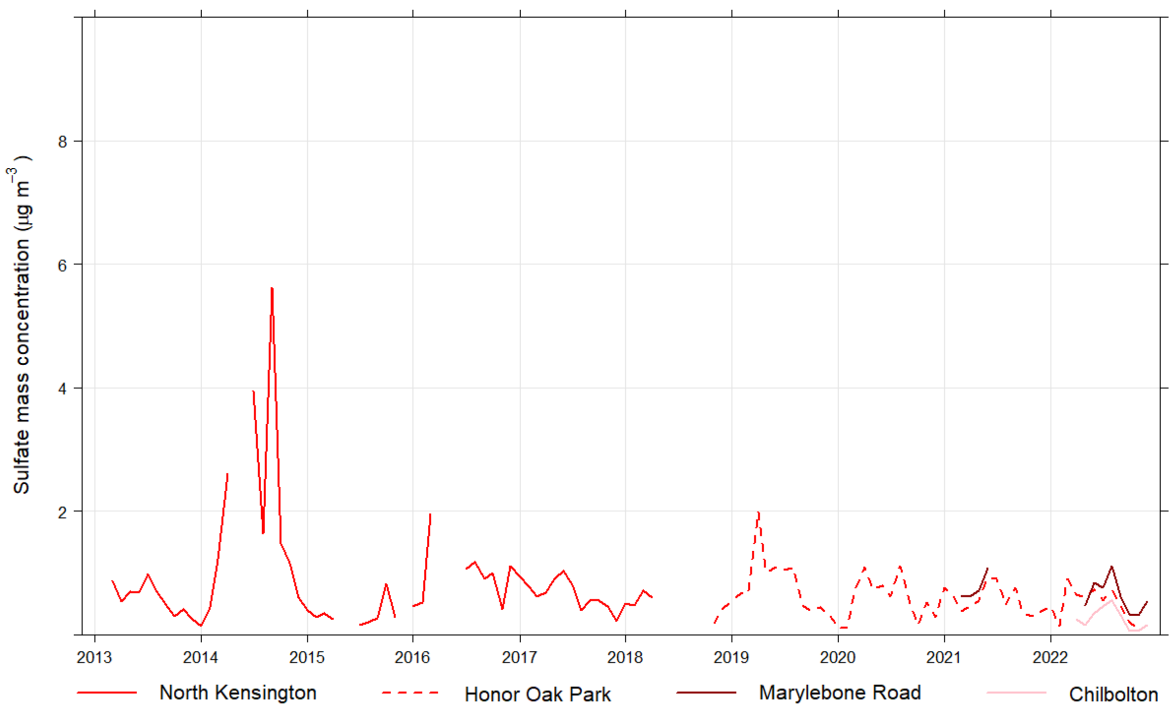

Figure 25 - Long-term mass concentration trends of sulfate at the rural background site Chilbolton Observatory, urban background site London Honor Oak Park (London North Kensington before 2019) and roadside site London Marylebone Road. The tick marks on the x-axis indicate the start of each year.

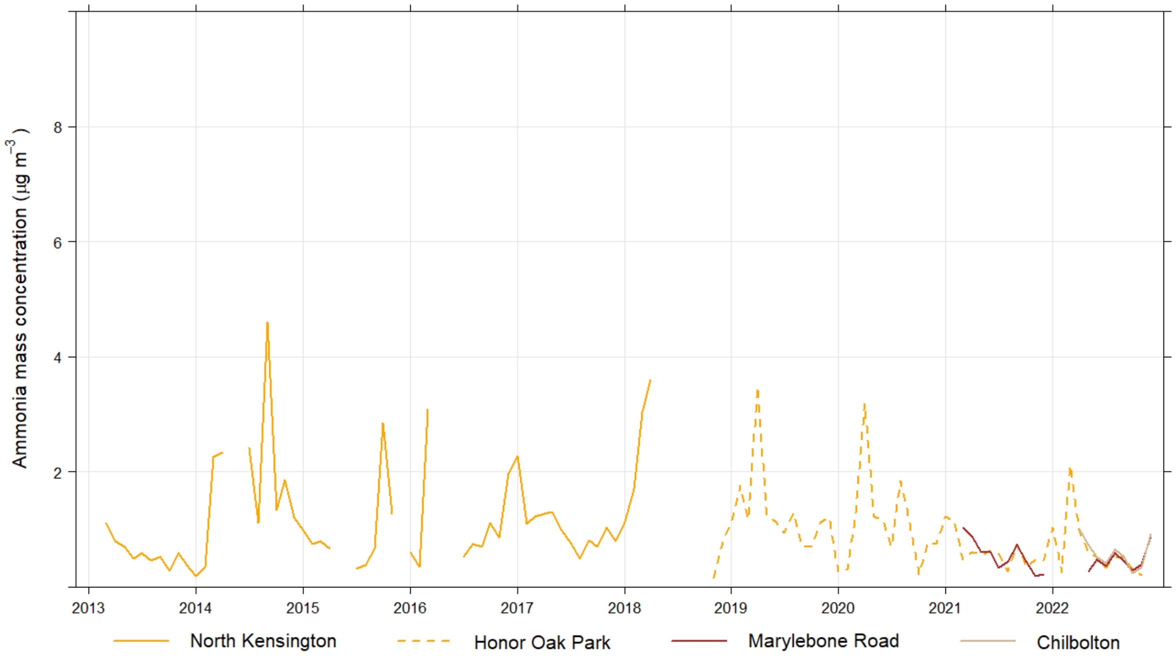

Figure 26 - Long-term mass concentration trends of ammonium and nitrate at the rural background site Chilbolton Observatory, urban background site London Honor Oak Park (London North Kensington before 2019) and roadside site London Marylebone Road. The tick marks on the x-axis indicate the start of each year.

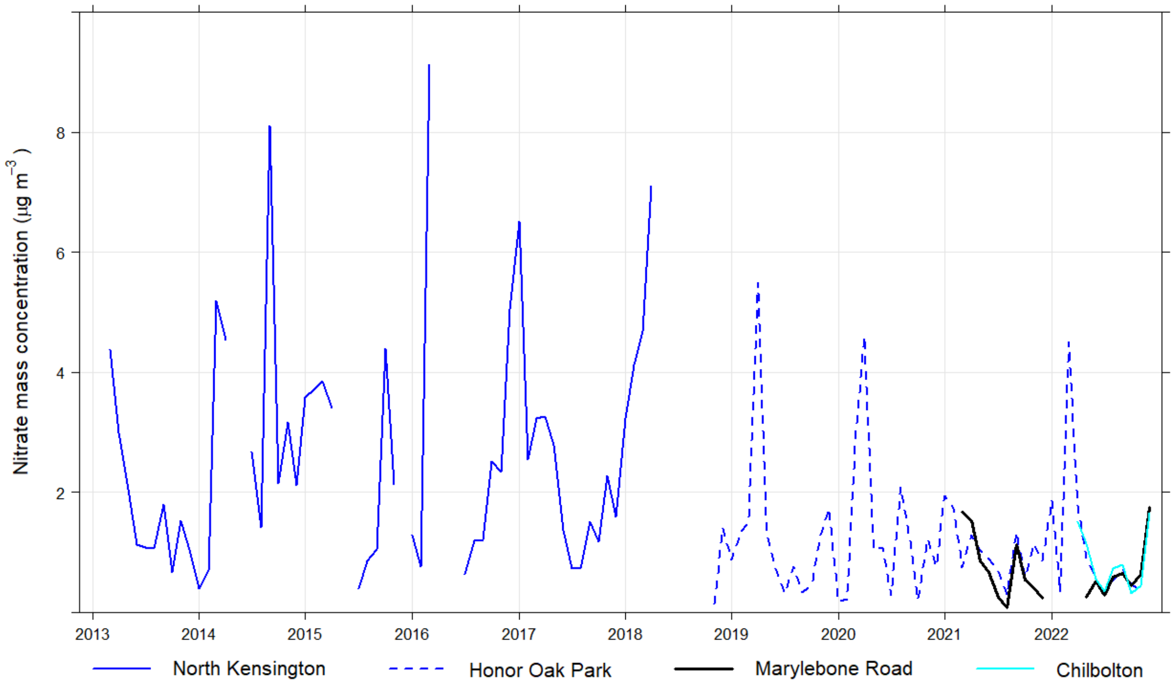

Figure 27 - Long-term mass concentration trends of ammonium and nitrate at the rural background site Chilbolton Observatory, urban background site London Honor Oak Park (London North Kensington before 2019) and roadside site London Marylebone Road. The tick marks on the x-axis indicate the start of each year.

4.4 ELEMENTAL ANALYSIS

4.4.1 2022 time series

Data for the XRF at London Honor Oak Park has been available since February 2022, when the instrument was incorporated into the Network. At London Marylebone Road the XRF was installed at the end of March, with the $PM_{2.5}$ / PM_{10} switching valve being operational from the 5 April 2022; thus, the initial data are PM_{10} data only, and only the data obtained from this date are reported in this section

Figure 28 to Figure 30 shows the time series of the daily concentrations of six elements (Ca, Cl, K, S, Cu and Zn) at London Honor Oak Park and London Marylebone Road during 2022 for both $PM_{2.5}$ and PM_{10}. These elements were chosen as examples as a significant proportion (more than 70 %) of the data are above the detection limit for both size fractions at both sites. In these figures, note that as the sampled size fraction changed every hour, the graphs include extrapolated data to have a full time series

Table 9 gives an overview of the hourly mean concentration of each element at London Honor Oak Park and London Marylebone Road in 2022. It also shows the limit of detection (LOD) of the measurement, which is the same at both sites, and the percentage of data below the LOD for measurements of $PM_{2.5}$ and PM_{10} measurements. Note that the data is based on bi-hourly data, which is accounted for in the data capture calculation.

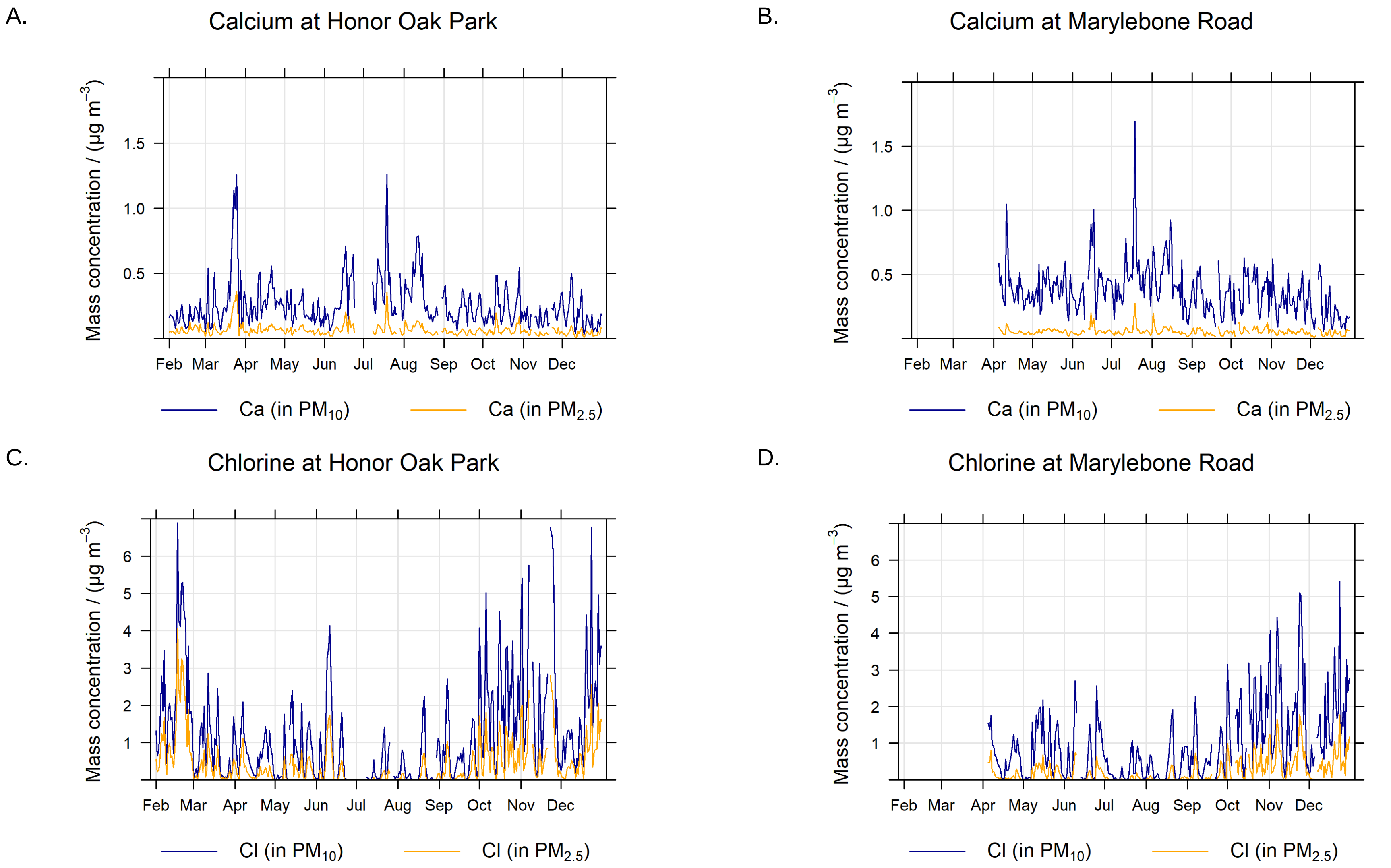

Figure 28 - Daily calcium (A, B) and chlorine (C, D) concentrations in 2022 at London Honor Oak Park (A, C) and London Marylebone Road (B, D) based on interpolated bihourly data. The tick marks on the x-axes indicate the start of each month.

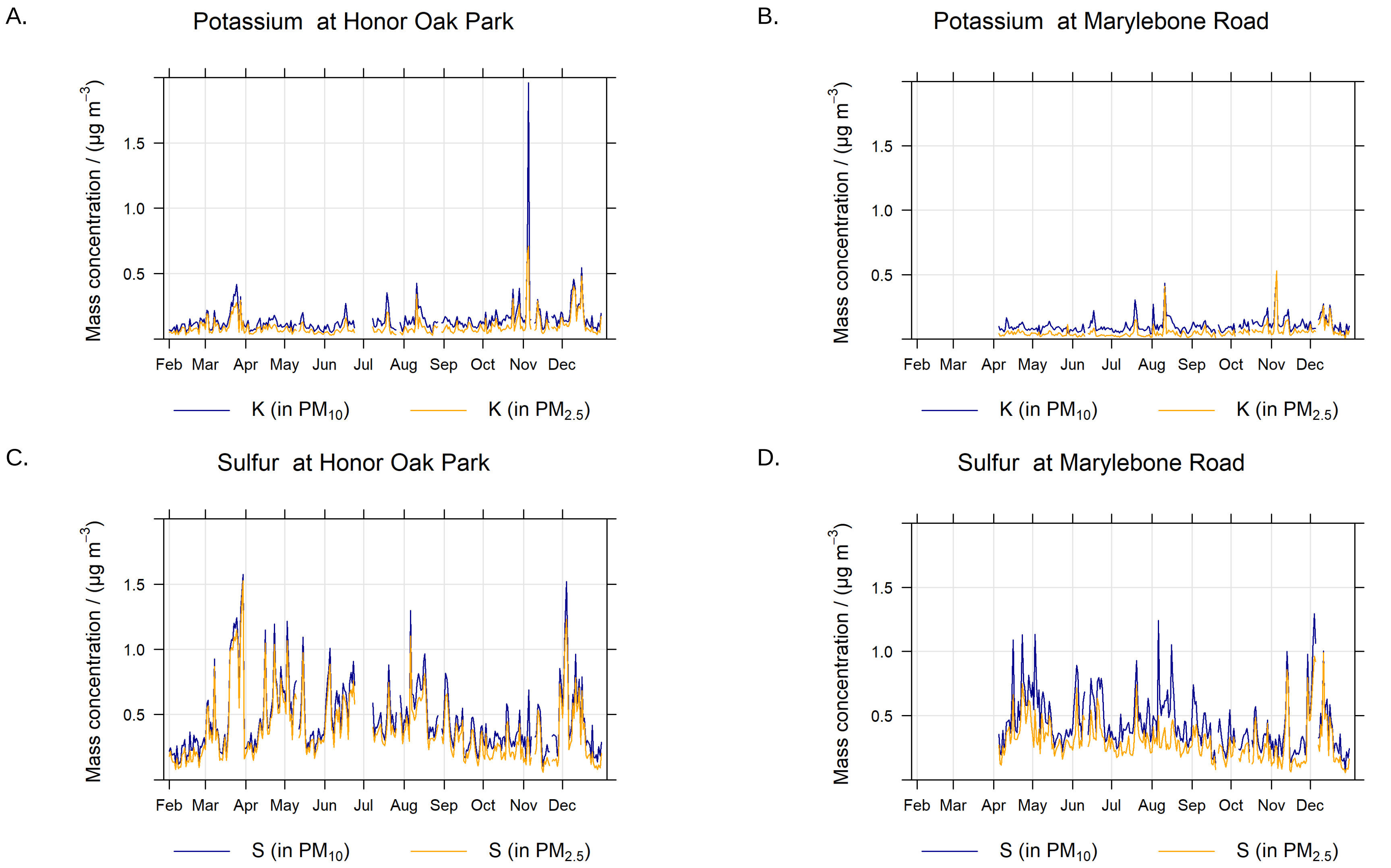

Figure 29 - Daily potassium (A, B) and sulfur (C, D) concentrations in 2022 at London Honor Oak Park (A, C) and London Marylebone Road (B, D) based on interpolated bihourly data. The tick marks on the x-axes indicate the start of each month.

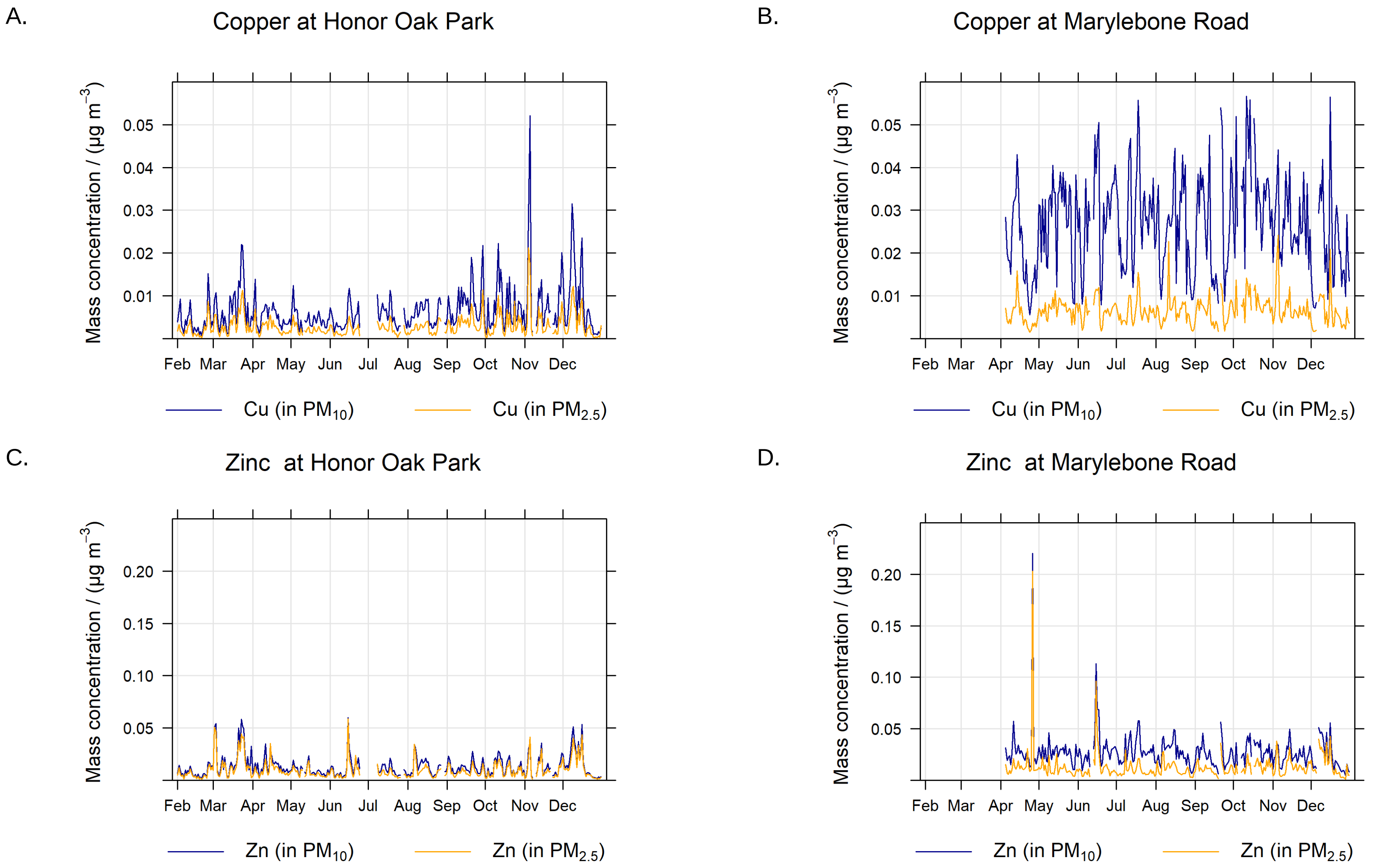

Figure 30 - Daily copper (A, B) and zinc (C, D) concentrations in 2022 at London Honor Oak Park (A, C) and London Marylebone Road (B, D), based on interpolated bihourly data. The tick marks on the x-axes indicate the start of each month.

Table 9 - Mean mass concentration, limit of detection (LOD), and percentage of data below LOD in $PM_{2.5}$ and PM_{10} from XRF measurements at London Honor Oak Park and London Marylebone Road in 2022. The data are based on bihourly sampling, which is taken into account for the data capture calculation.

Element	LoD for metals in PM / (µg m^{-3})	London Honor Oak Park				London Marylebone Road			
		Mean $PM_{2.5}$ mass concentration / (µg m^{-3})	% of $PM_{2.5}$ data <LoD	Mean PM_{10} mass concentration / (µg m^{-3})	% of PM_{10} data <LoD	Mean $PM_{2.5}$ mass concentration / (µg m^{-3})	% of $PM_{2.5}$ data <LoD	Mean PM_{10} mass concentration / (µg m^{-3})	% of PM_{10} data <LoD
Ag	0.0033	0.0015	81	0.0015	80	0.0013	86	0.0012	89
Al	0.17	0.11	77	0.14	73	0.55	5.2	0.54	9.8
As	0.00011	0.0018	14	0.0020	10	0.0013	13	0.0017	4.5
Ba	0.00067	0.00066	84	0.0015	74	0.0021	32	0.012	3.8
Bi	0.00023	0.00012	97	0.00017	97	0.00011	97	0.00015	93
Br	0.00018	0.0036	1.2	0.0050	0.5	0.0032	0.7	0.0045	0.1
Ca	0.00052	0.066	0.1	0.26	0	0.054	0.2	0.37	0
Cd	0.0044	0.011	47	0.012	47	0.0018	89	0.0019	89
Ce	0.00052	0.000015	99	0.000015	99	0.0000011	100	0.0000002	100
Cl	0.003	0.45	33	1.2	17	0.24	44	0.94	19
Co	0.00024	0.0000003	100	0.0000003	100	0.0000029	100	0.0000036	100
Cr	0.0002	0.00038	43	0.00098	17	0.00090	25	0.0057	1.4
Cu	0.00014	0.0029	6.7	0.0065	2.7	0.0065	0.2	0.026	0
Fe	0.0003	0.10	0	0.27	0	0.26	0	1.0	0
Ga	0.0001	0.000039	85	0.000034	87	0.0000004	100	0.0000001	100
Ge	0.0001	0.0000052	99	0.0000041	99	0.0000006	100	0.0000003	100
Hg	0.00021	0.0000038	100	0.0000024	100	0	100	0.0000001	100
In	0.0054	0.00088	96	0.00092	95	0.00029	100	0.00034	100
K	0.002	0.094	0	0.14	0	0.054	0.6	0.10	0
La	0.00063	0.000014	100	0.000011	100	0.0000002	100	0	100
Mn	0.00025	0.00083	51	0.0027	18	0.0010	35	0.0065	2.1
Mo	0.00084	0.000061	99	0.000064	98	0.0000048	100	0.00017	95
Ni	0.00017	0.00022	73	0.00028	66	0.00040	32	0.00068	14
P	0.009	0.00037	99	0.00025	99	0.000027	100	0.0000029	100
Pb	0.00022	0.0024	71	0.0025	68	0.0015	66	0.0022	50
Pd	0.0038	0.0031	70	0.0031	71	0.0045	51	0.0043	53
Pt	0.0002	0.0000004	100	0	100	0.0000001	100	0.0000001	100
S	0.0055	0.38	0	0.46	0	0.30	0.1	0.44	0
Sb	0.009	0.0020	92	0.0020	93	0.00031	100	0.00049	99
Se	0.00014	0.00012	74	0.00014	69	0.00015	72	0.00016	69
Si	0.031	0.032	92	0.22	55	0.0096	98	0.23	39
Sn	0.0071	0.00099	96	0.00097	96	0.0013	97	0.0026	89
Sr	0.00038	0.00056	58	0.0014	25	0.00027	87	0.0014	24
Te	0.001	0.011	8.3	0.012	8.3	0.0025	57	0.0025	57
Ti	0.00028	0.0027	13	0.0090	3.7	0.0030	3.9	0.017	0
Tl	0.0002	0.0000025	100	0.0000029	100	0	100	0	100
V	0.00021	0.00077	51	0.00095	43	0.00038	71	0.00038	71
Y	0.00048	0.0018	0.1	0.0019	0.1	0.000017	99	0.000020	99
Zn	0.00012	0.0097	0.2	0.013	0.1	0.013	0.2	0.027	0
Zr	0.00057	0.00014	92	0.00038	77	0.000047	98	0.0022	35

4.5 OC and EC

OC 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. EC, 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 UK's AQSR 2010[2,3,4,5] (and all associated amendments), 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.

4.5.1 2022 time series

The time series of OC, EC and TC (the sum of OC and EC) are displayed in Figure 31 to Figure 34 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. Note that for a period of two weeks in July 2022, daily (rather than weekly) samples were taken Auchencorth Moss for an EMEP/ACTRIS measurement campaign. For consistency, these data are plotted in Figure 34 as calculated weekly averages.

4.5.2 Long-term trends

Figure 35 and Figure 36 show the long-term time series for the measurements since the installation of the samplers at Harwell / Chilbolton Observatory and Auchencorth Moss. The data from Chilbolton Observatory (February 2016 - December 2022) is plotted continuously with the data from the former Harwell site and its daily data is plotted continuously with the former weekly data.

Figure 37 shows the long-term trends in annual average mass concentrations for OC, EC, and TC measurements for the daily sampling at the two London sites (London Marylebone Road and London Honor Oak Park).

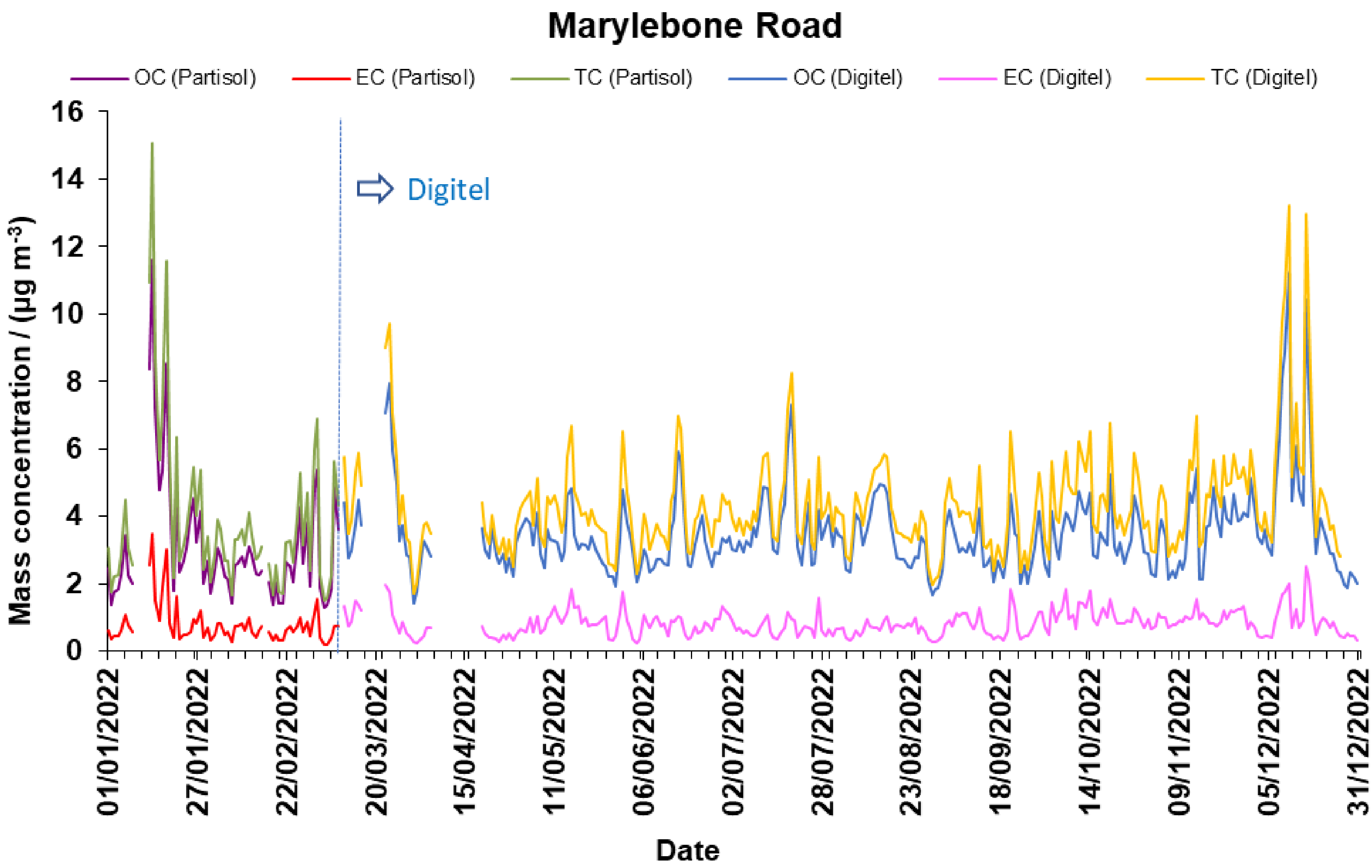

Figure 31 - Daily $PM_{2.5}$ OC, EC, and TC mass concentrations measured at London Marylebone Road during 2022

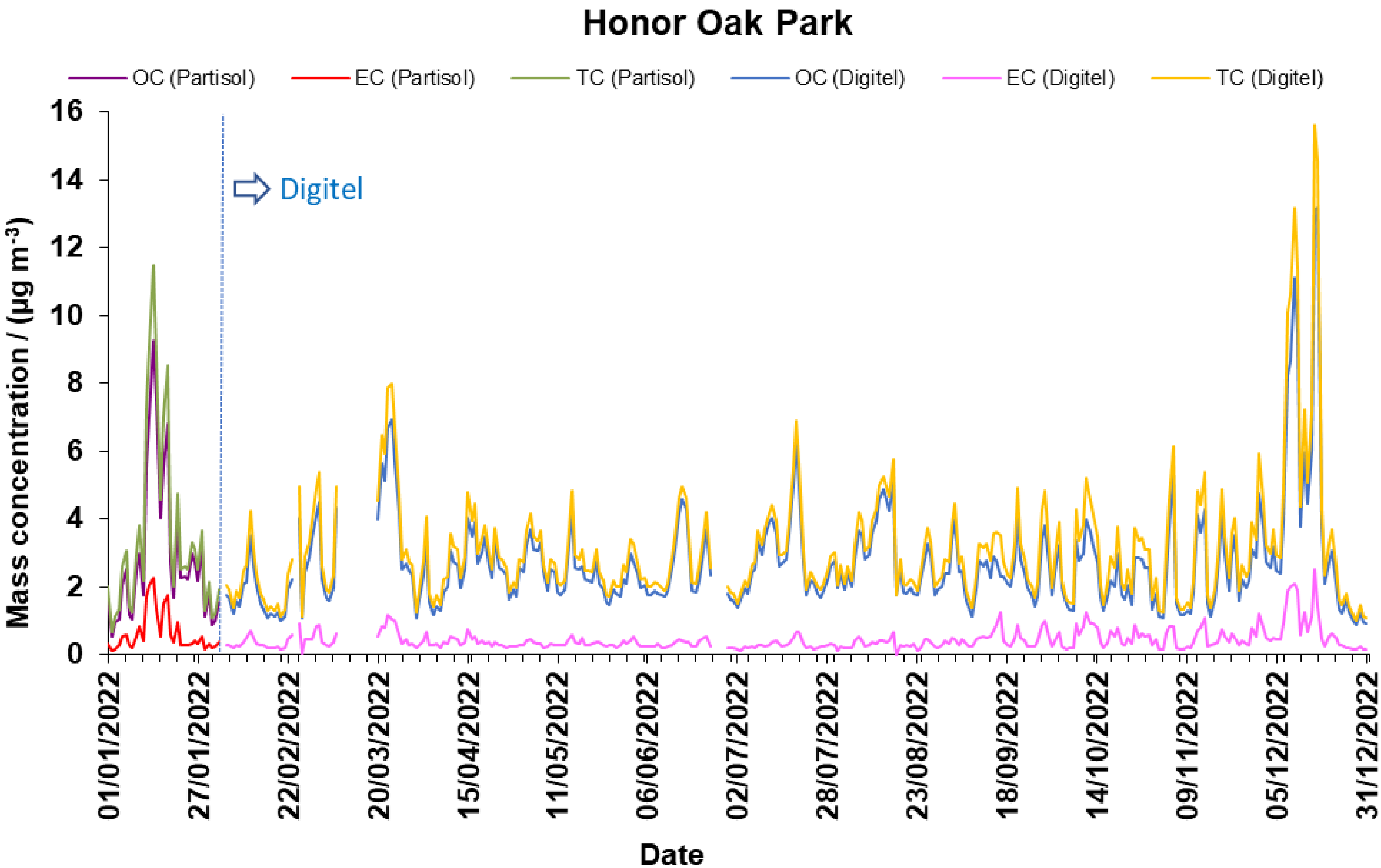

Figure 32 - Daily $PM_{2.5}$ OC, EC, and TC mass concentrations measured at London Honor Oak Park during 2022

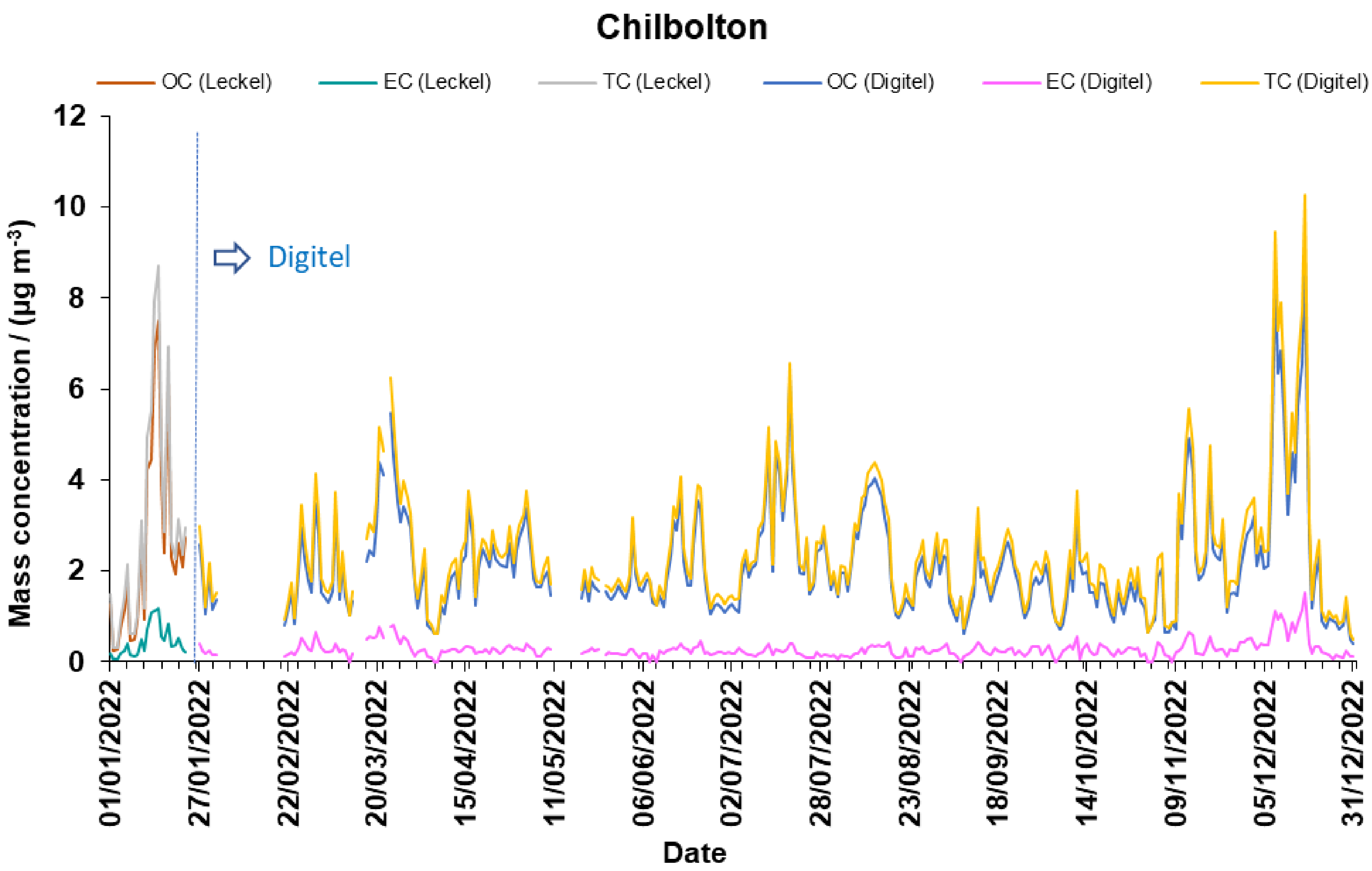

Figure 33 - Daily $PM_{2.5}$ OC, EC, and TC mass concentrations measured at Chilbolton Observatory during 2022

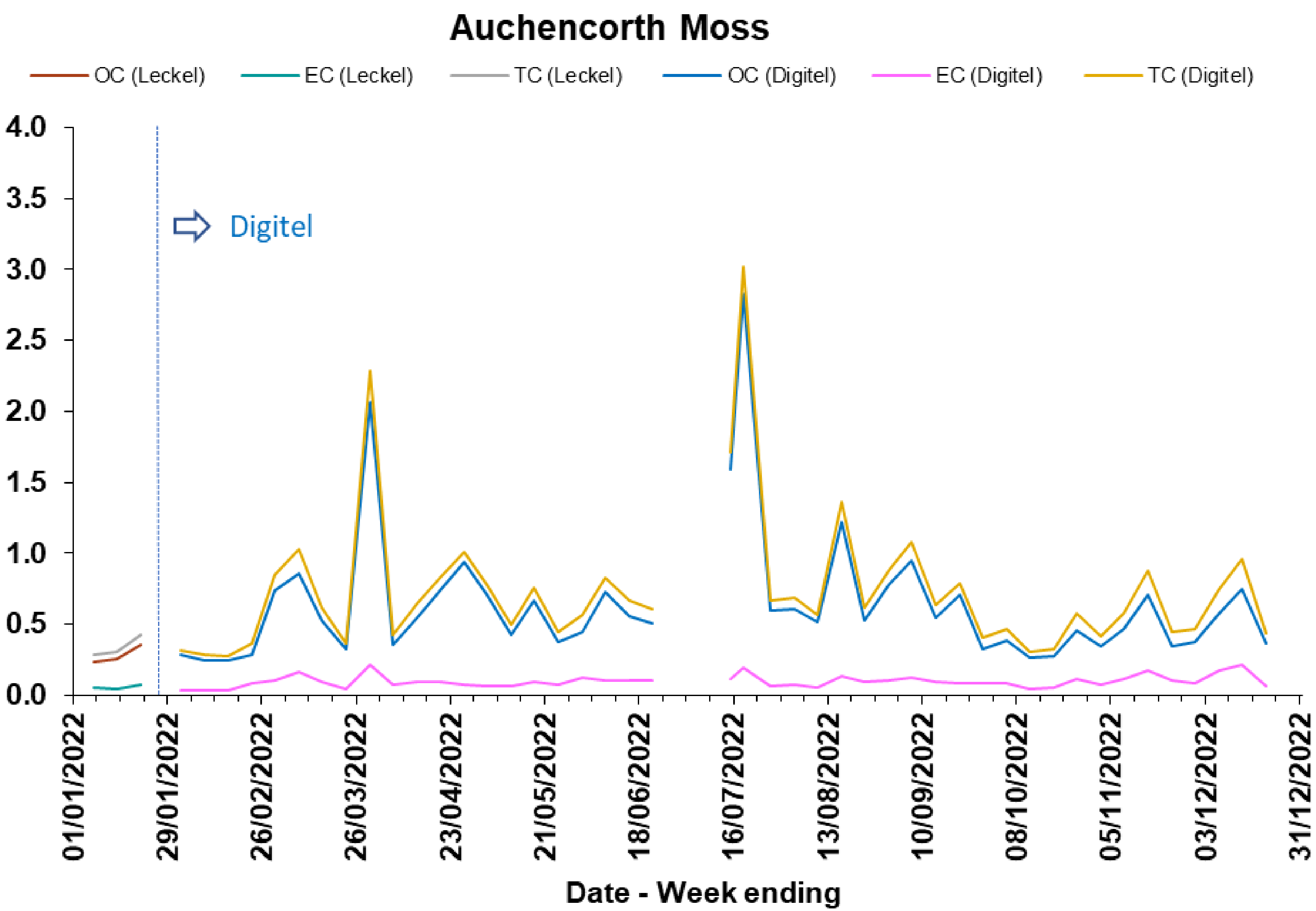

Figure 34 - Weekly $PM_{2.5}$ OC, EC, and TC mass concentrations measured at Auchencorth Moss during 2022. Note that the data from 9-20 July are plotted as weekly averages calculated from daily samples. All other data are from weekly samples

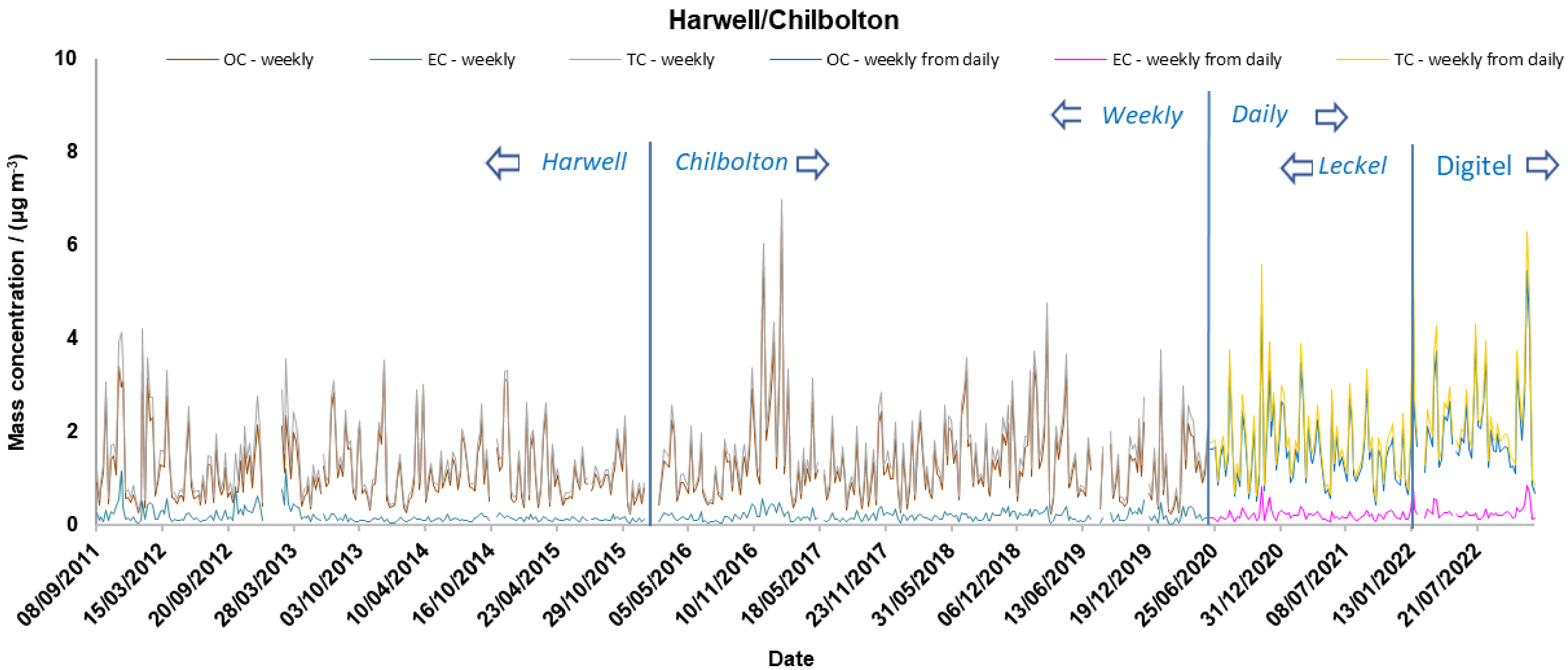

Figure 35 - Time series of the weekly OC, EC, and TC mass concentrations in the $PM_{2.5}$ fraction at Harwell/Chilbolton Observatory since the installation of the sampler up to June 2020 and daily mass concentrations from 11 June 2020. The sampler was replaced by a Digitel sampler in January 2022. The daily mass concentrations measured since June 2020 have been plotted as calculated weekly average for consistency.

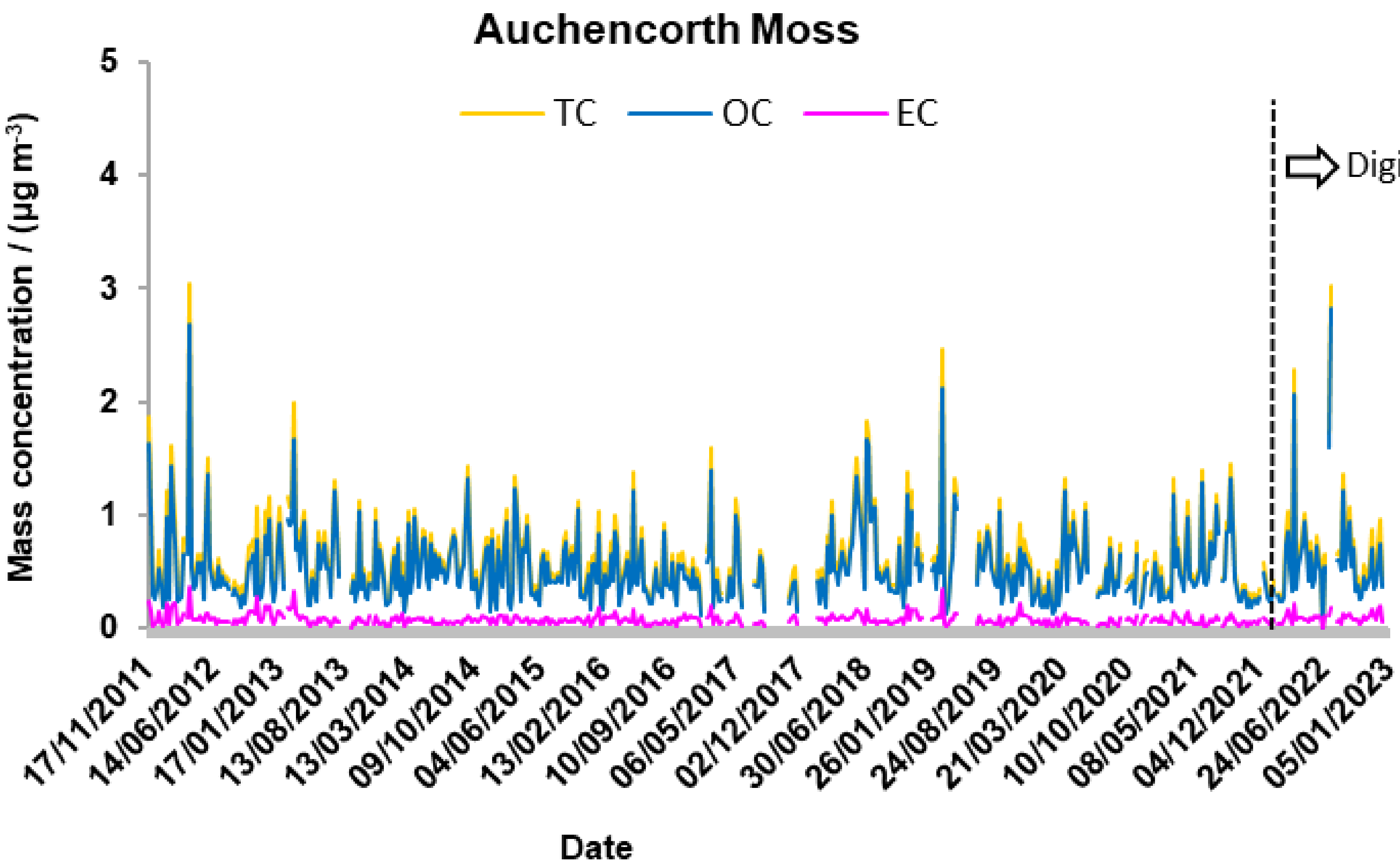

Figure 36 - Time series of weekly OC, EC, and TC in the $PM_{2.5}$ fraction at Auchencorth Moss to the end of 2022

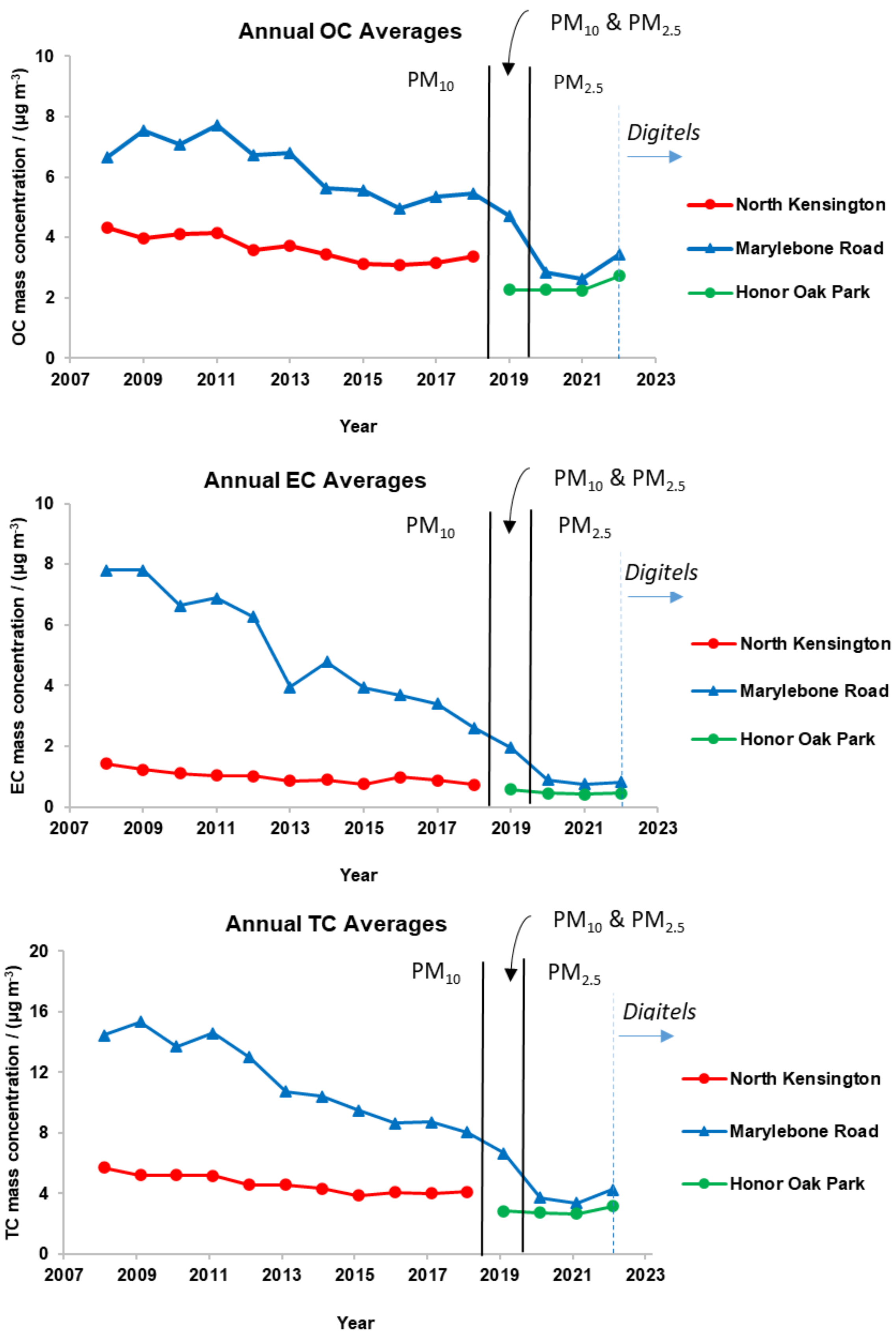

Figure 37 - Annual trends for OC, EC, and TC measurements. PM10 sampling heads were changed to $PM_{2.5}$ heads at London Honor Oak Park and London Marylebone Road in February 2019 and October 2019, respectively. Samplers were replaced with Digitels at London Honor Oak Park and London Marylebone Road.

4.6 BC and UVPM

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 EC, a measure of soot-like carbon determined by thermo-optical (chemical) techniques, although in practice the EC fraction of TC depends strongly on the method chosen. The term “equivalent black carbon” is formally recommended for data which simply converts an aerosol absorption coefficient to a mass concentration as described in section 2.4.6. The AE33 Aethalometer 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 term BC concentration refers to the mass concentration of particulate matter measured at 880 nm. Annual mean data from all channels, are shown in Table 10. Aethalometer measurements can be used in source apportionment studies and to determine the particle absorption wavelength dependence.

Table 10 - Annual mean of particulate matter concentrations measured at specific wavelength (indicated in nm in brackets) by AE33 Aethalometers in 2022. UVPM is calculated by subtracting the BC mass concentration from the UV mass concentration.

	PM mass concentration (μg m^{-3})							
Site	**UV** (370)	**Blue** (470)	**Green** (520)	**Yellow** (590)	**Red** (660)	**BC** (880)	**IR-2** (950)	**UVPM**
Auchencorth Moss	0.19	0.18	0.17	0.17	0.16	0.15	0.16	0.04
Ballymena Ballykeel	1.11	0.96	0.87	0.83	0.78	0.73	0.73	0.37
Belfast Centre	1.14	1.06	0.99	0.97	0.92	0.88	0.88	0.25
Birmingham A4540 Roadside	2.03	2.06	1.95	1.91	1.84	1.81	1.82	0.22
Birmingham Ladywood	0.96	0.94	0.89	0.86	0.82	0.80	0.83	0.16
Cardiff Centre	1.27	1.17	1.14	1.14	1.10	1.08	1.10	0.19
Chilbolton Observatory	0.60	0.52	0.47	0.44	0.42	0.39	0.38	0.21
Detling	0.66	0.61	0.57	0.55	0.53	0.51	0.50	0.15
Glasgow High Street	1.02	1.04	0.99	0.97	0.92	0.92	0.91	0.10
Glasgow Townhead	0.64	0.63	0.59	0.59	0.56	0.55	0.55	0.08
Kilmakee Leisure Centre	1.14	1.00	0.91	0.87	0.81	0.77	0.80	0.37
London Marylebone Road	1.31	1.27	1.23	1.17	1.13	1.10	1.10	0.21
London North Kensington	0.95	0.88	0.81	0.78	0.74	0.70	0.70	0.25
Strabane 2	2.32	1.89	1.67	1.57	1.46	1.36	1.24	0.96
Average	**1.10**	**1.01**	**0.95**	**0.92**	**0.87**	**0.84**	**0.84**	**0.25**

BC and UVPM concentration data for 2022 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 earlier years when the AE22 model was used (see details in section 2.4.6).

4.6.1 2022 time series - BC

Figure 38 to Figure 42 show the BC concentrations measured in 2022. The time resolution of the measurements is hourly, and the data have been split into figures covering areas of the UK for presentation purposes. 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.

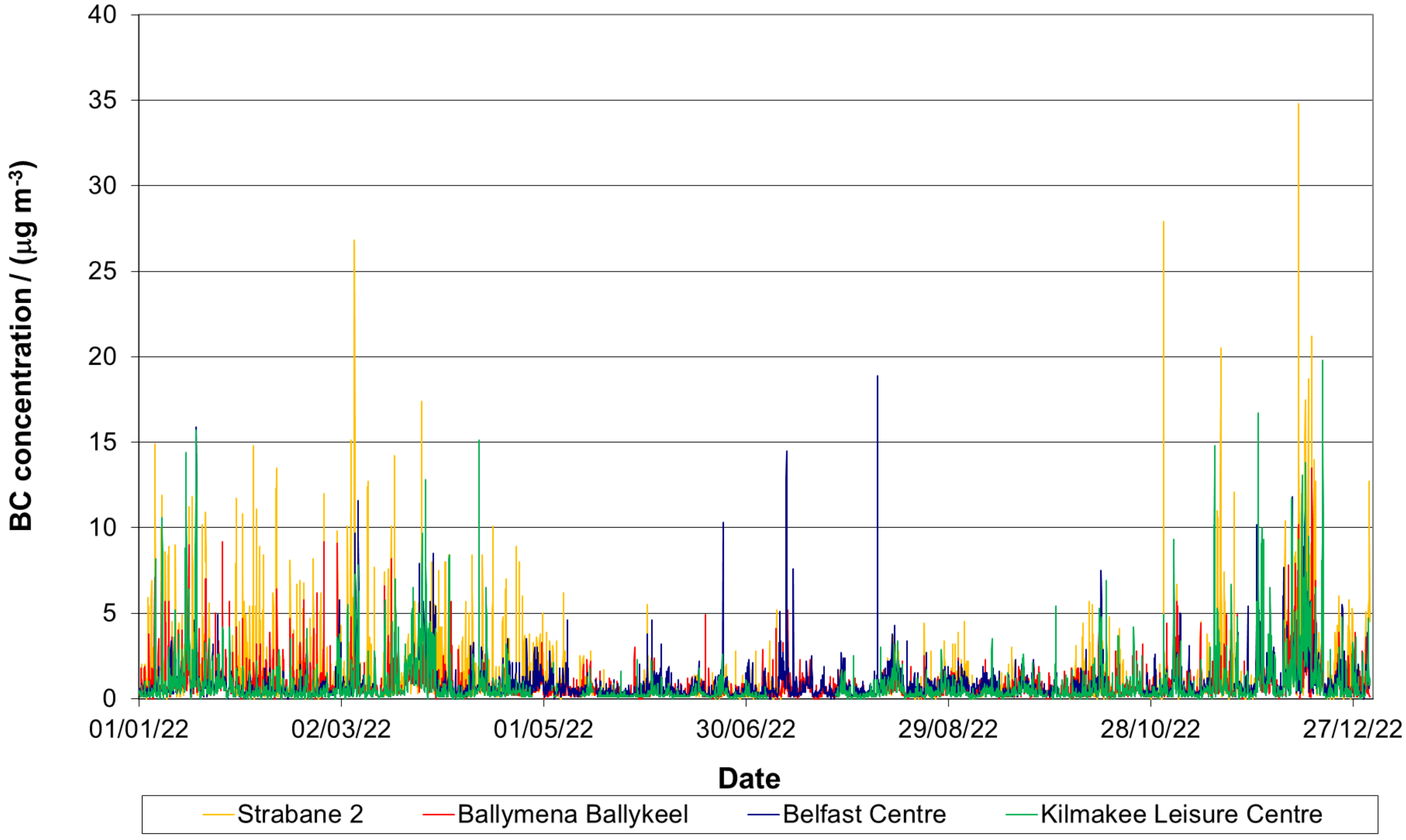

Figure 38 - BC concentrations during 2022 in Northern Ireland

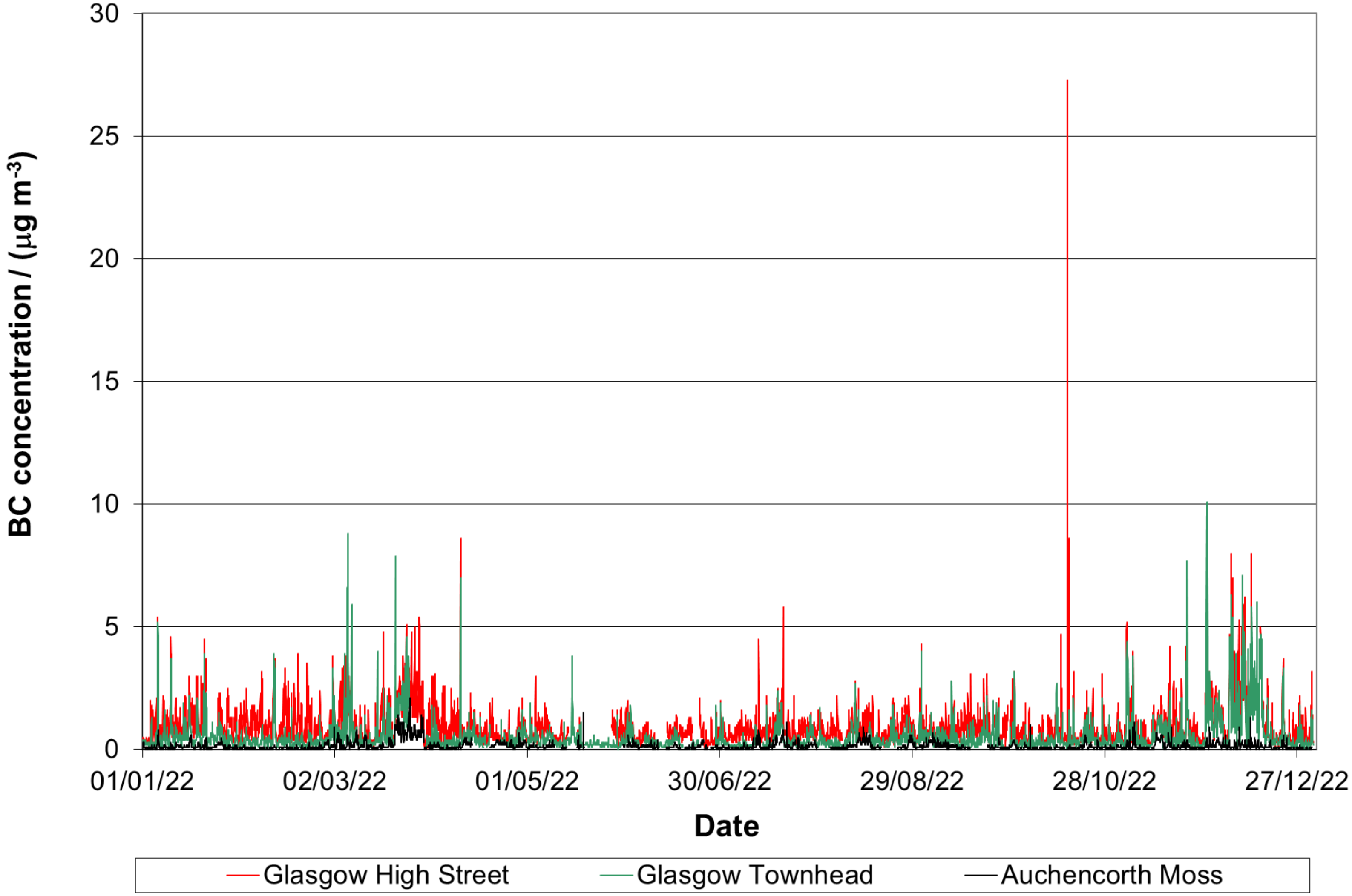

Figure 39 - BC concentrations during 2022 in Scotland

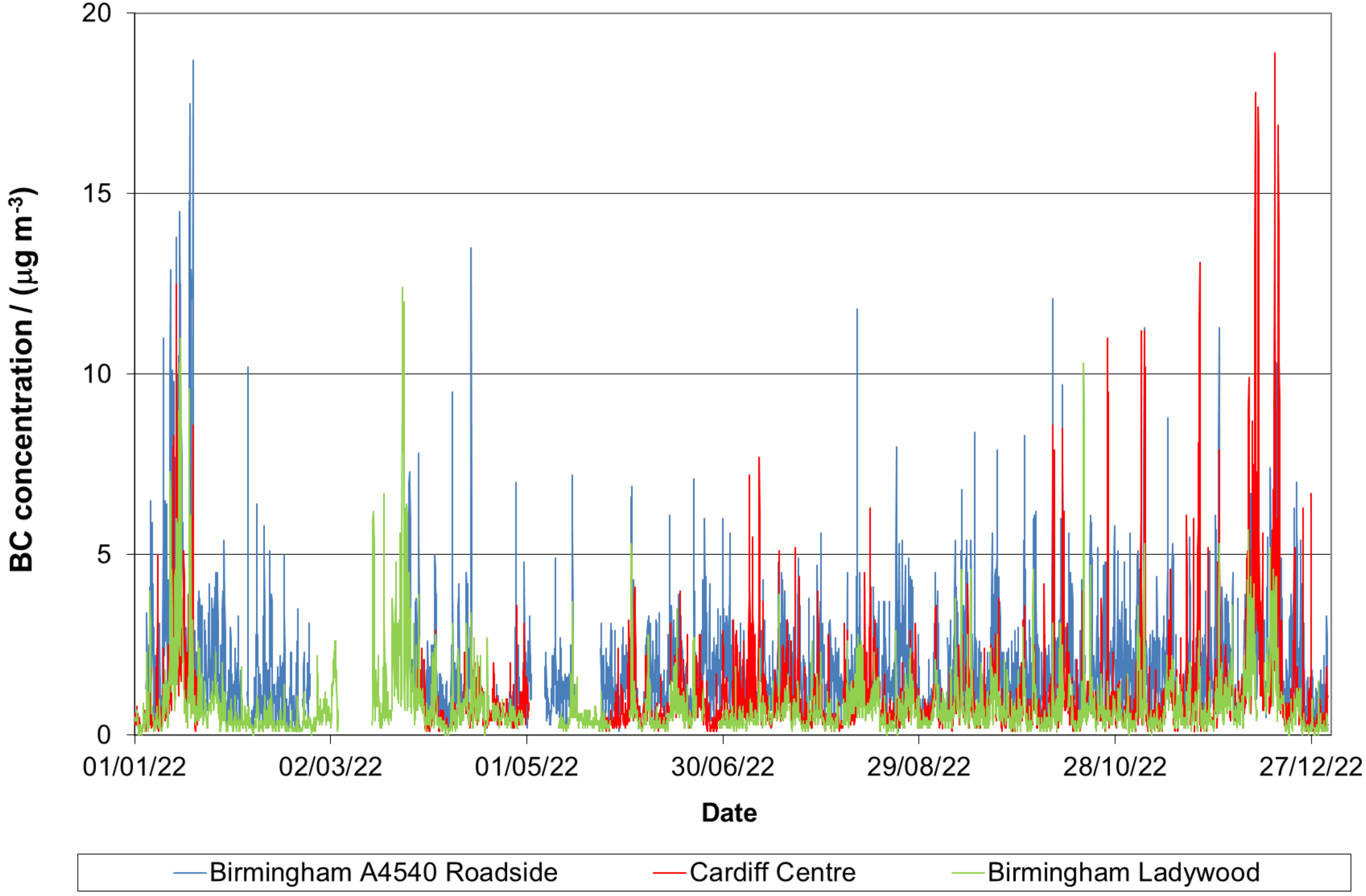

Figure 40 - BC concentrations during 2022 in Wales and the Midlands of England

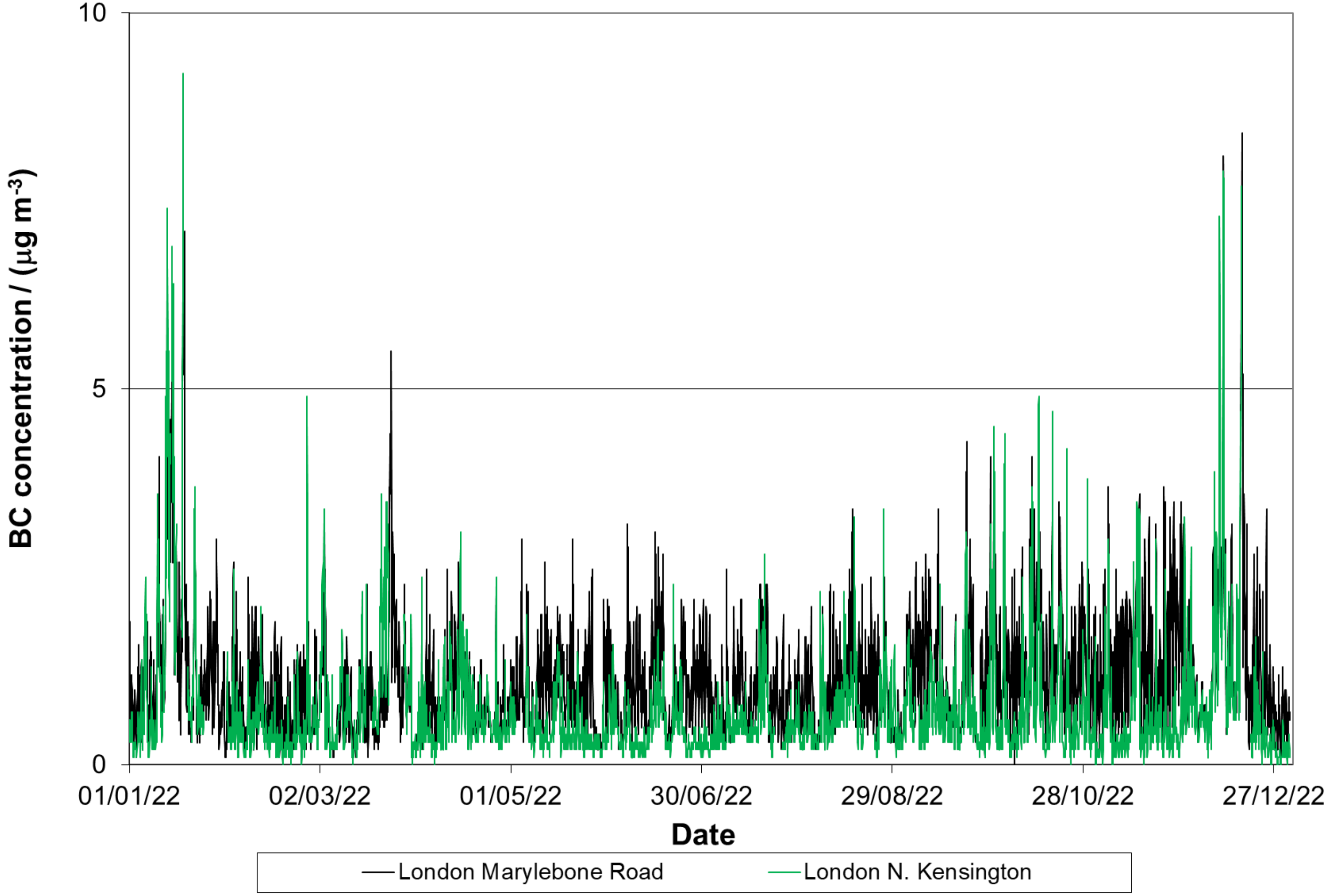

Figure 41 - BC concentrations during 2022 in London

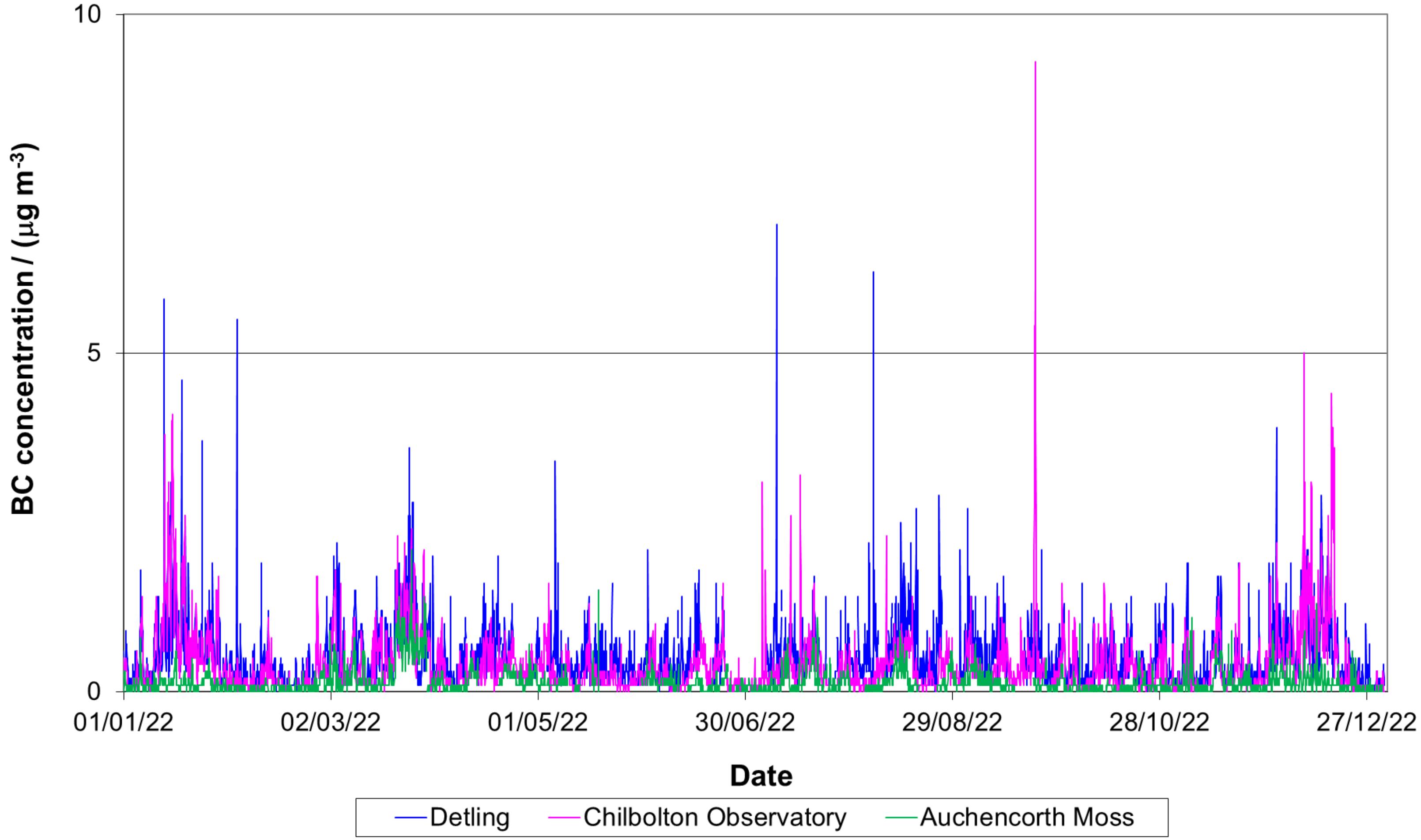

Figure 42 - BC concentrations during 2022 at rural locations

4.6.2 2022 annual averages - BC

The annual mean concentrations are presented as a bar graph (Figure 43) to aid the comparison of sites:

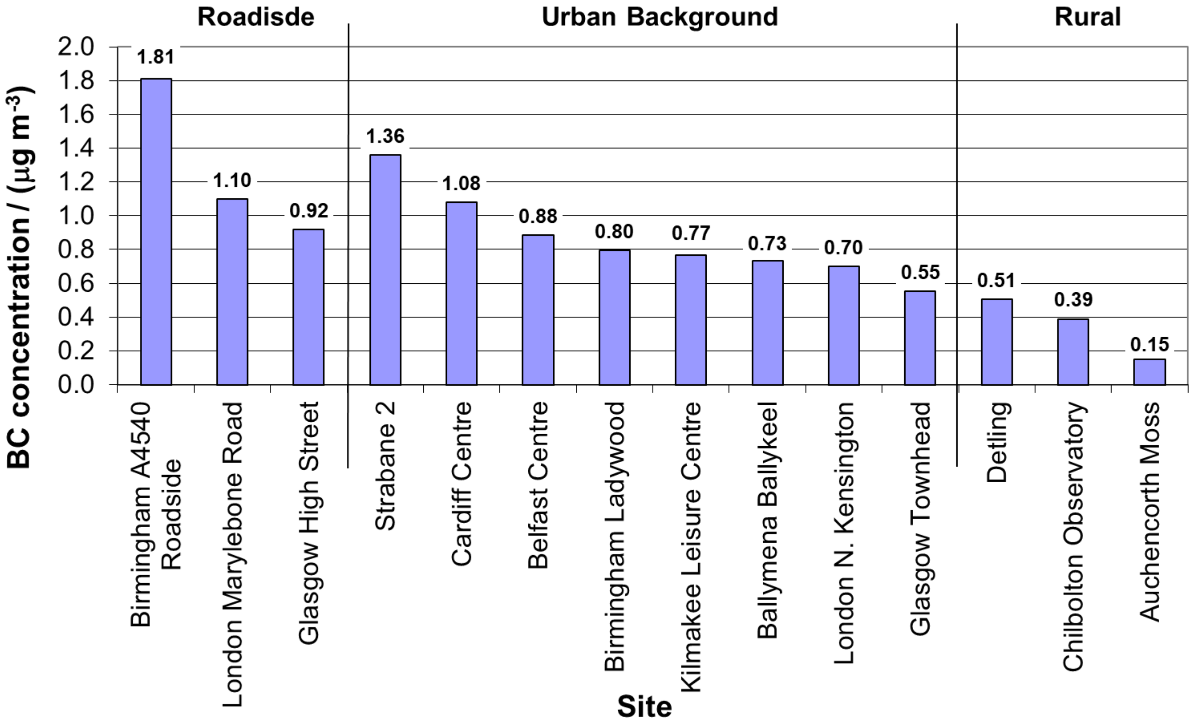

Figure 43 - Annual mean BC concentrations for 2022

BC urban and roadside increments for London, Birmingham and Glasgow have been calculated by subtracting rural background measurements. Table 11 shows these calculated results.

The urban increments for London, Birmingham and Glasgow were all similar in 2022. The roadside increment for Birmingham was larger than that for London, where it has dropped from 0.47 µg m^{-3} in 2021.

Table 11 - Urban and roadside increments in BC concentrations in 2022

	BC increment / (µg m^{-3})	
Conurbation	**Urban**	**Roadside**
London	0.30	0.36
Birmingham	0.39	1.07
Glasgow	0.43	0.37

Figure 44 shows how the urban and roadside increments in London have changed over the period 2012 to 2022. 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 44.

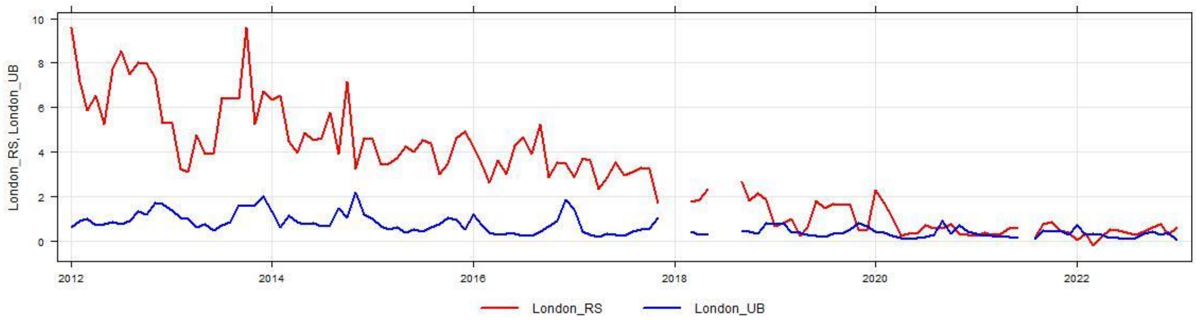

Figure 44 - Urban (UB) and roadside (RS) increments in London for the period 2012 to 2022. The tick marks on the x-axis indicate the start of each year.

4.6.3 2022 annual averages - UVPM

The annual mean concentrations are presented as a bar graph (Figure 45) to aid the comparison of sites:

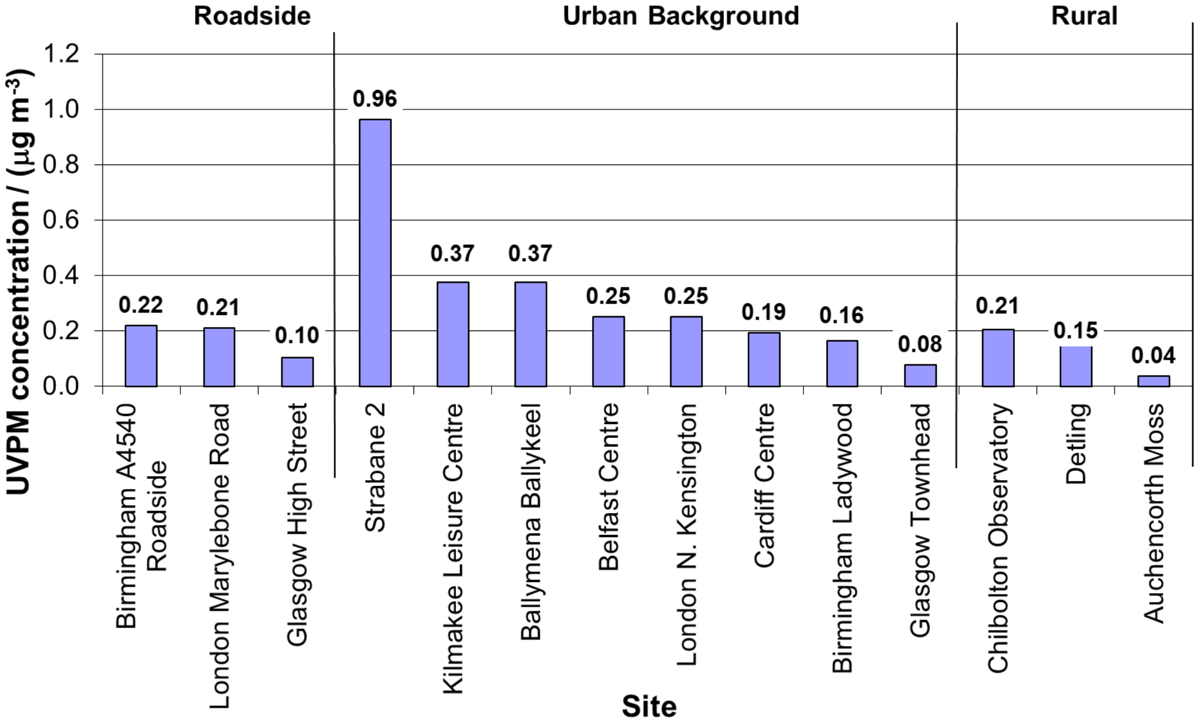

Figure 45 - Annual Mean UVPM concentrations for 2022

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

Table 12 - Urban and roadside increments in UVPM concentrations in 2022

	UVPM increment / (µg m^{-3})	
Conurbation	**Urban**	**Roadside**
London	0.10	-0.06
Birmingham	-0.06	0.07
Glasgow	0.05	0.03

The urban and roadside increments at all sites were small (or slightly negative), indicating that domestic emissions in the three conurbations were negligible, and that road traffic was not a significant source for the UVPM. There was no significant difference in increments between 2021 and 2022, however, the urban increment for London increased from 0.04 µg m^{-3} and the roadside increment dropped from 0.01 µg m^{-3} in 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 13.

Table 13 - Increment in UVPM concentration in Northern Ireland

	Increment compared to Belfast Centre (µg m^{-3})	Increment compared to Belfast Centre (%)
Kilmakee Leisure Centre	0.10	39
Ballymena Ballykeel	0.13	51
Strabane 2	0.66	261

The increments at Kilmakee Leisure Centre, Ballymena Ballykeel and Strabane 2 are in line with a history of solid fuel usage for secondary heating in the area of Kilmakee Leisure Centre site, 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 46.

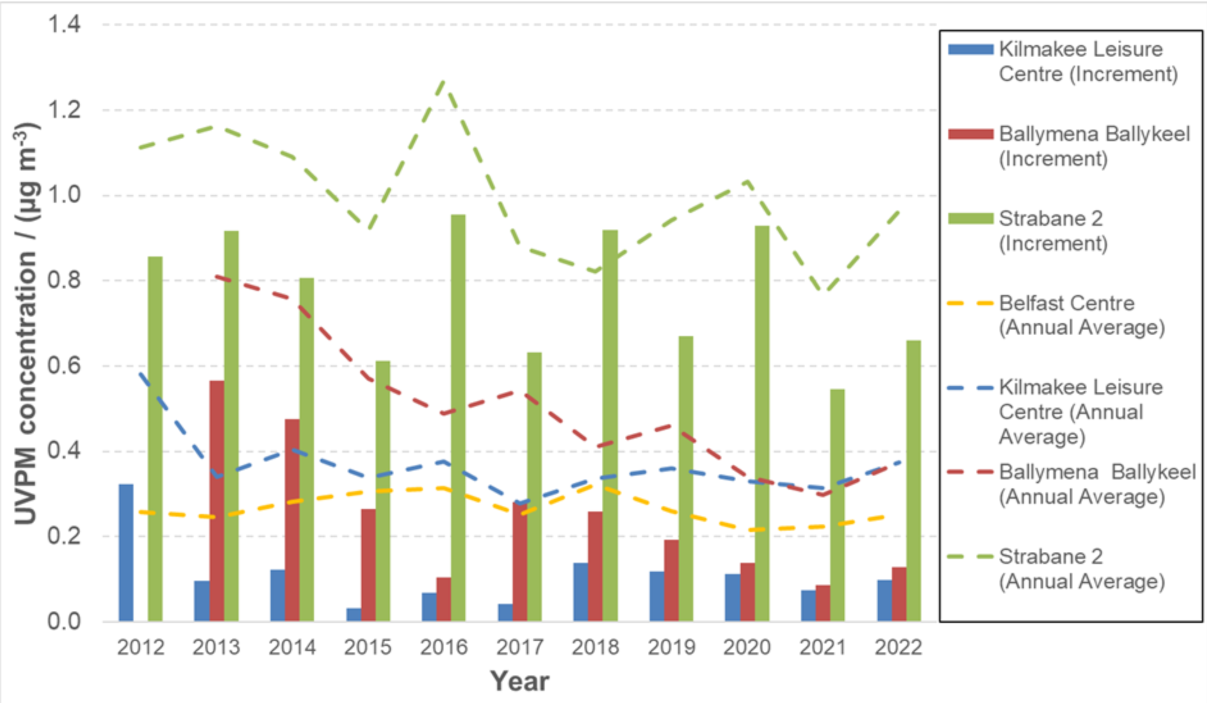

Figure 46 - Annual Mean UVPM concentrations and increments compared to Belfast Centre for 2012-2022

4.6.4 Diurnal, weekly, and monthly profiles - BC and UVPM

This section presents analysis of the temporal variation of BC and UVPM concentrations. All results have been grouped by site classification: roadside, urban background and rural background. The units on the y-axes are mass concentration in µg m^{-3} for BC and UVPM; the scales vary by site. The 2022 data are presented in Figure 47 to Figure 60.

Data from 2009-2022 are presented in Figure 61 to Figure 65. These 14-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 - 2022, are considered to be less biased when compared to the single year (2022) measurements presented in Figure 47 to Figure 60.

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 47 to Figure 60 is for display purposes only, to allow the uncertainty in the mean value to be seen more clearly. Figure 47 to Figure 65 are generated using the OpenAir Tools run on the R software platform[20,21].

At the roadside on weekdays the BC concentrations 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 BC concentrations, particularly at London Marylebone Road. There was little UVPM signature observed at any of the roadside sites.

At urban background sites BC 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.

At rural sites the 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.

BC and UVPM data at roadside sites for 2022

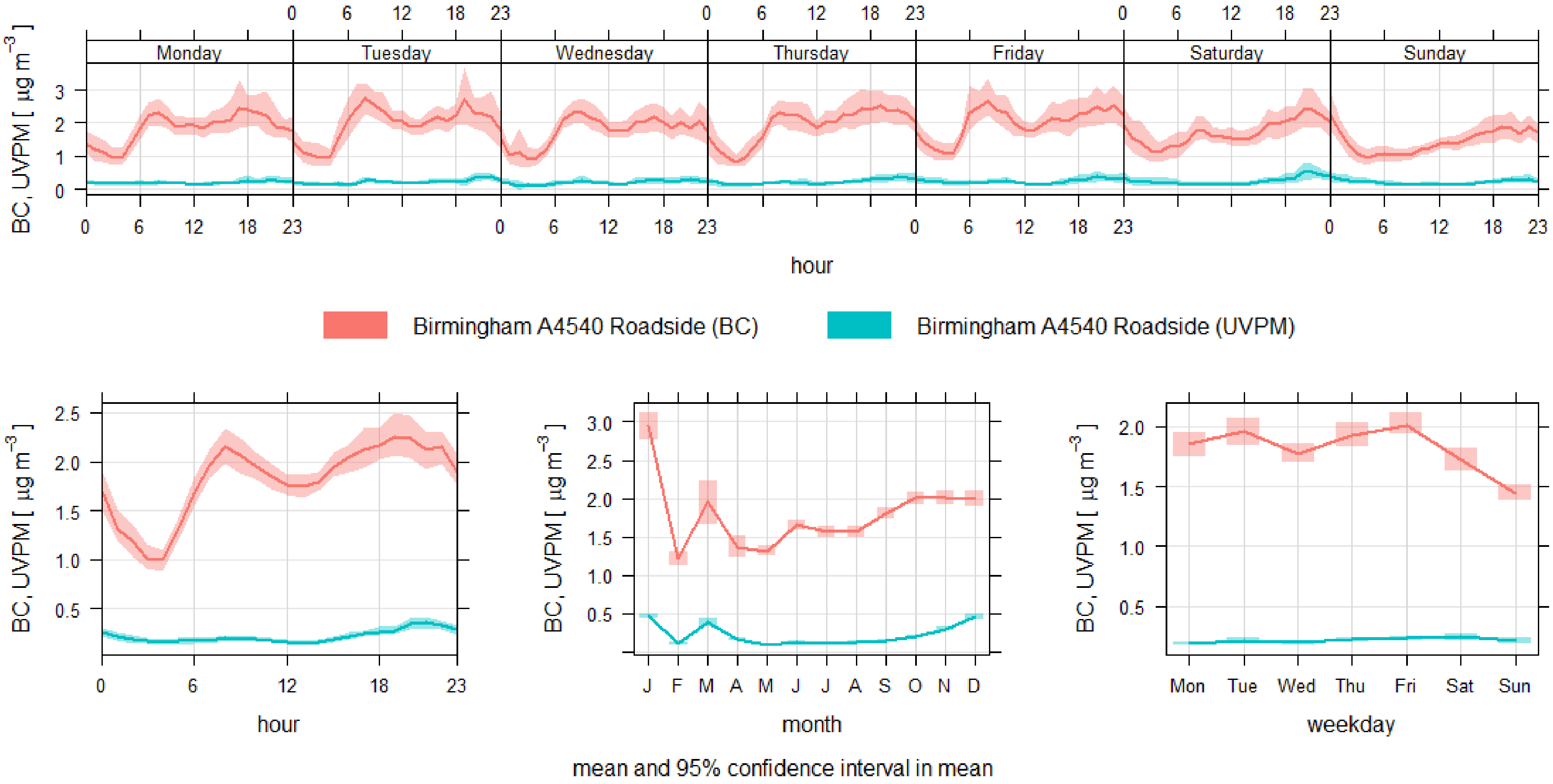

Figure 47 - Temporal variations of BC and UVPM concentrations at Birmingham A4540 Roadside for 2022

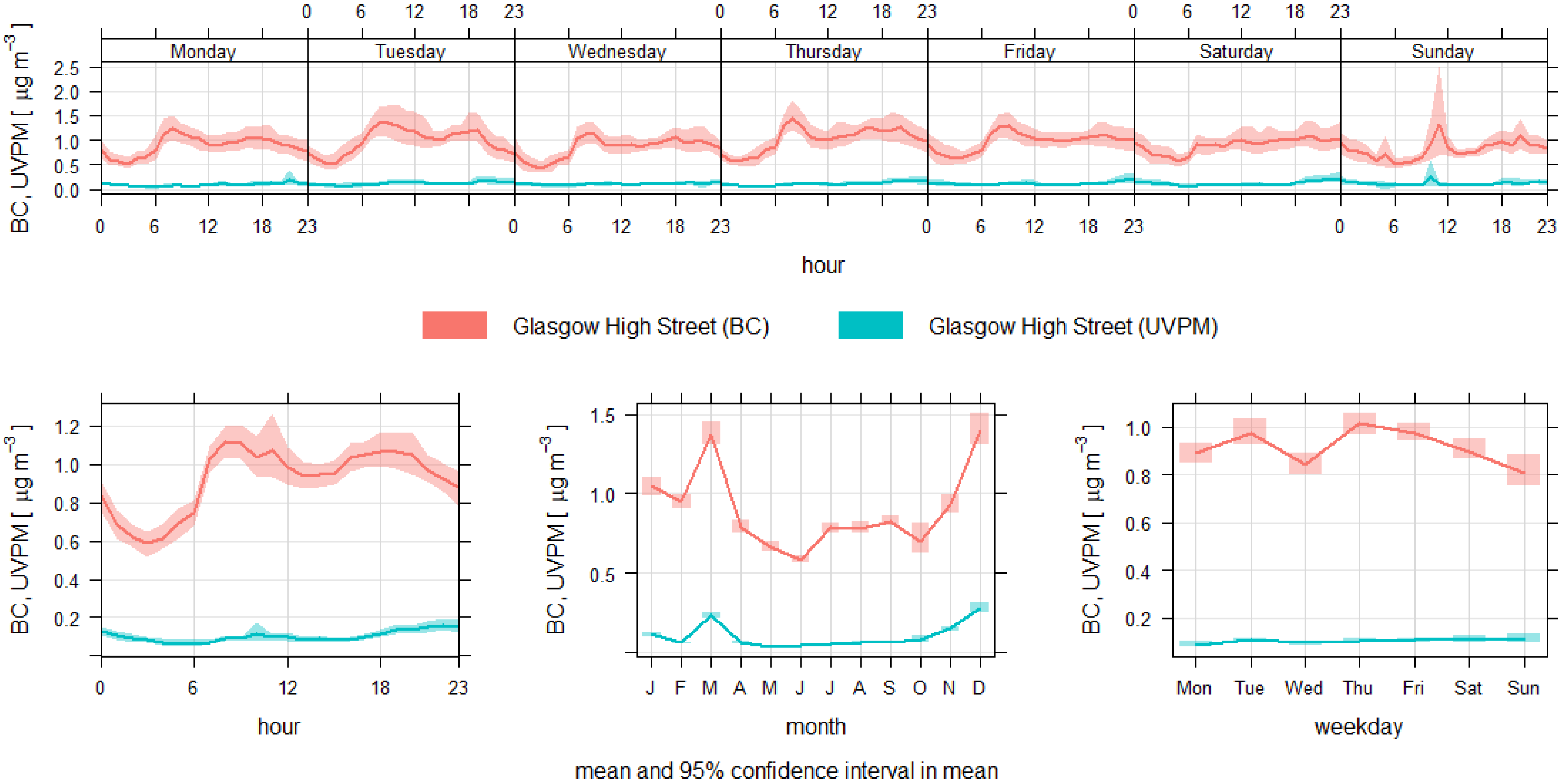

Figure 48 - Temporal variations of BC and UVPM concentrations at Glasgow High Street for 2022

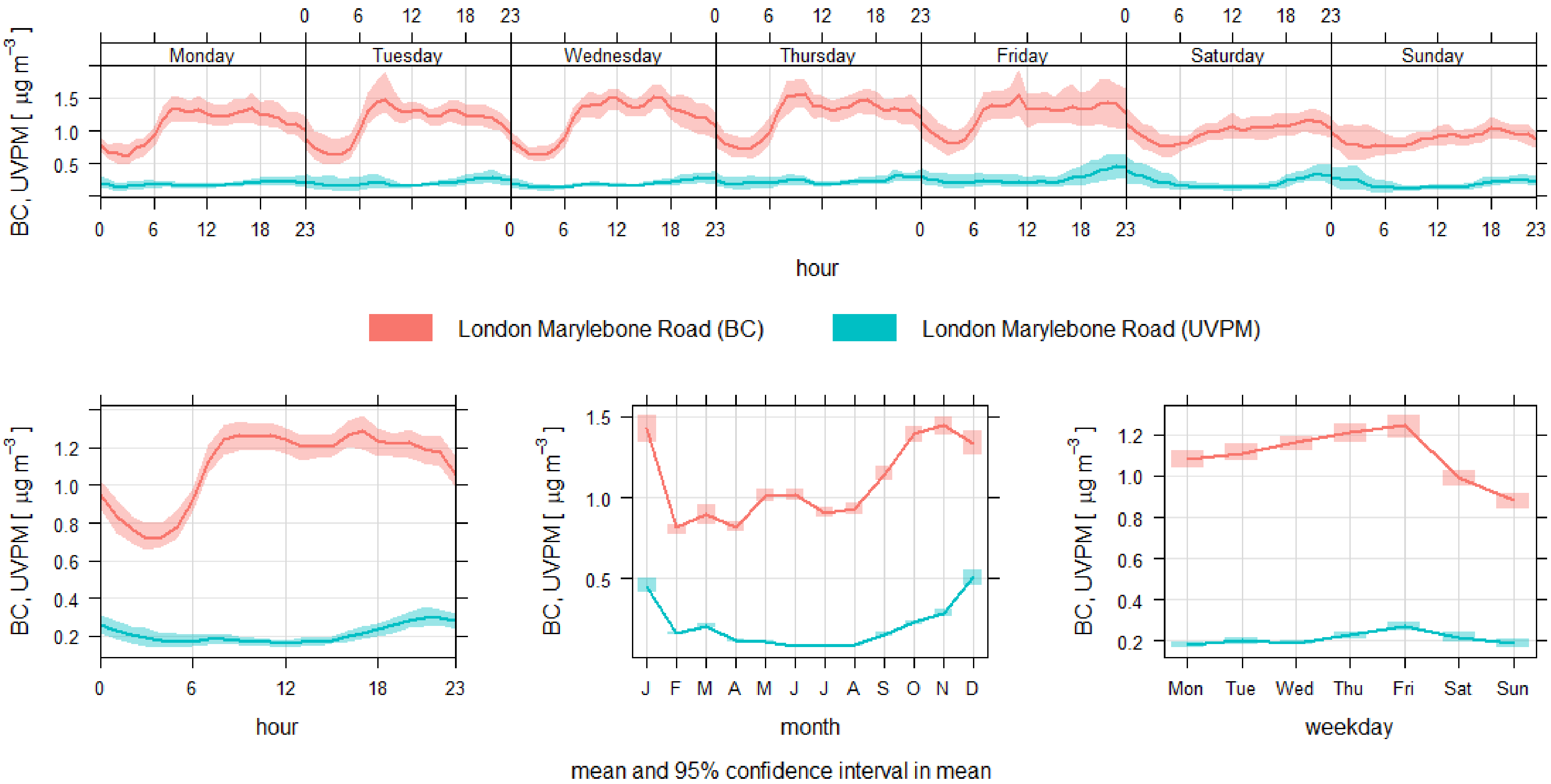

Figure 49 - Temporal variations of BC and UVPM concentrations at London Marylebone Road for 2022

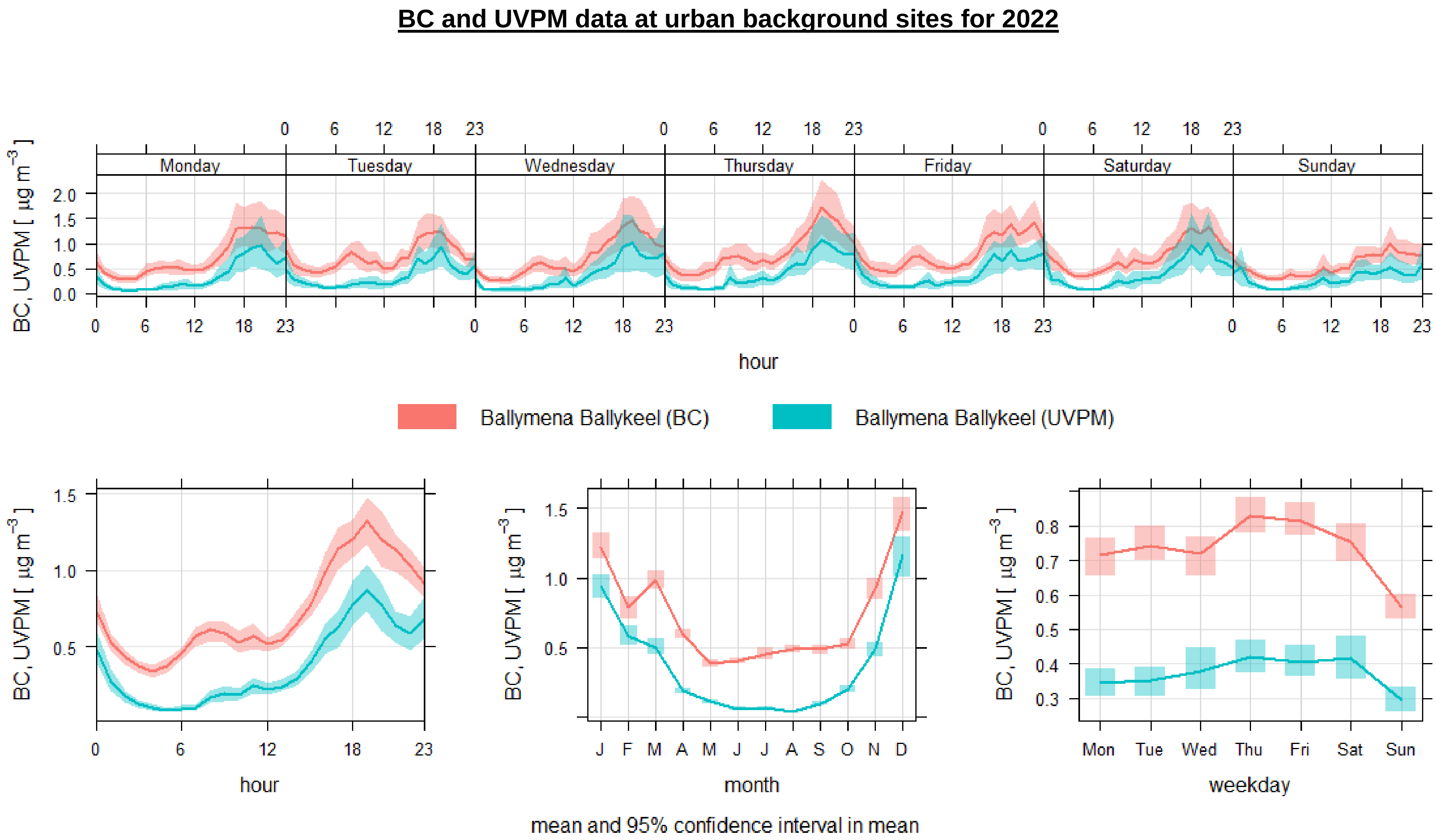

Figure 50 - Temporal variations of BC and UVPM concentrations at Ballymena Ballykeel for 2022

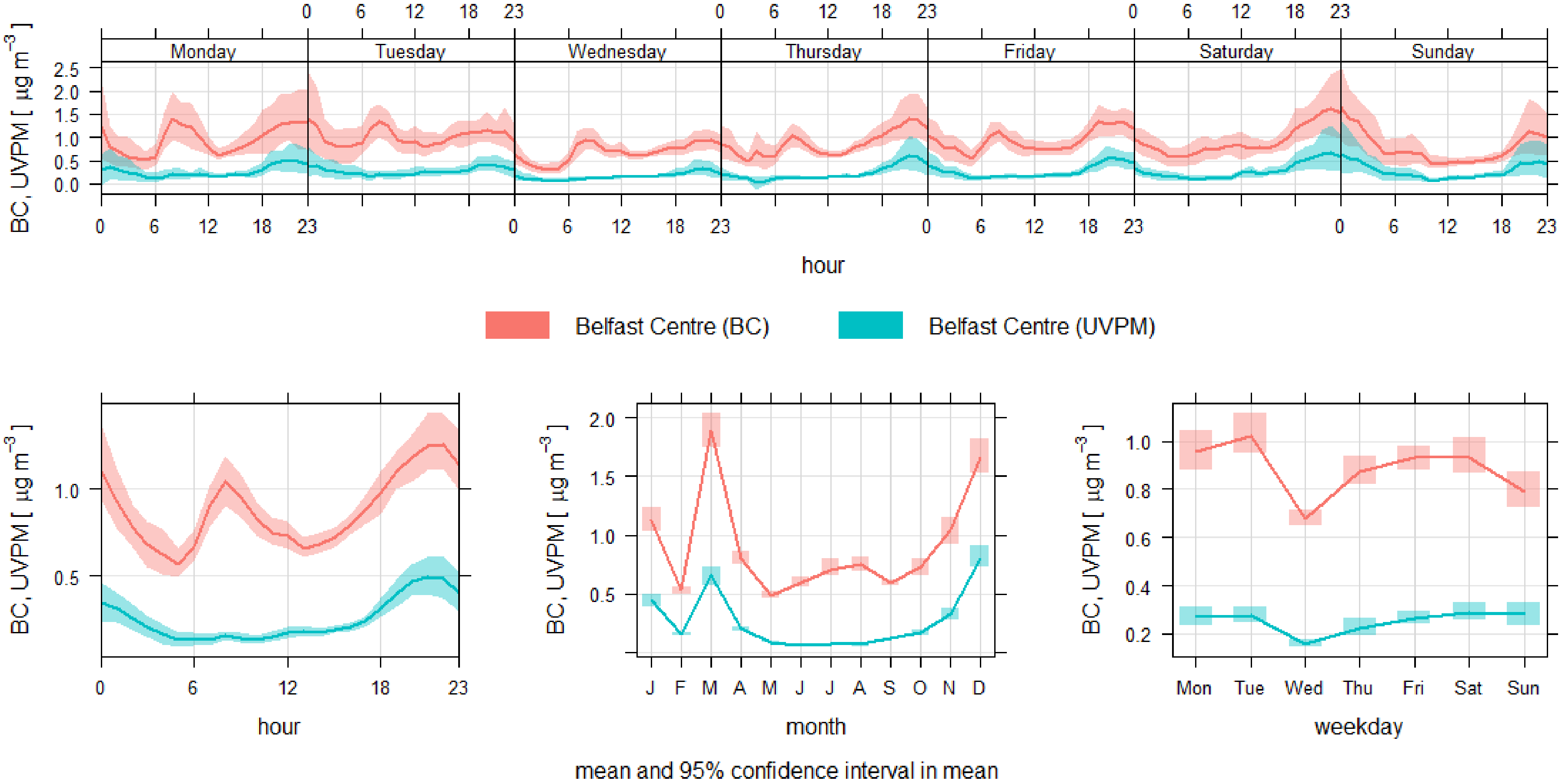

Figure 51 - Temporal variations of BC and UVPM concentrations at Belfast Centre for 2022

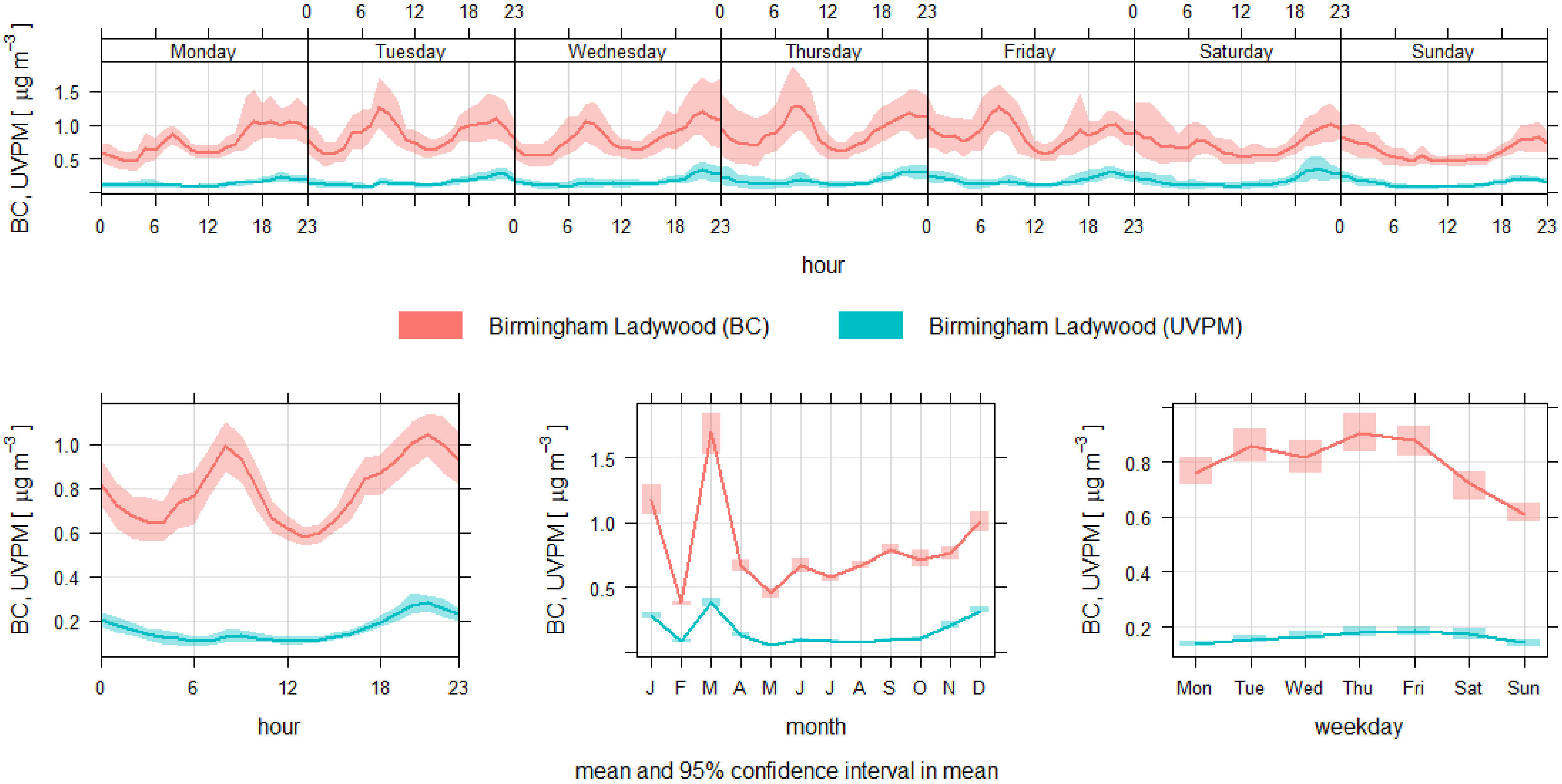

Figure 52 - Temporal variations of BC and UVPM concentrations at Birmingham Ladywood for 2022

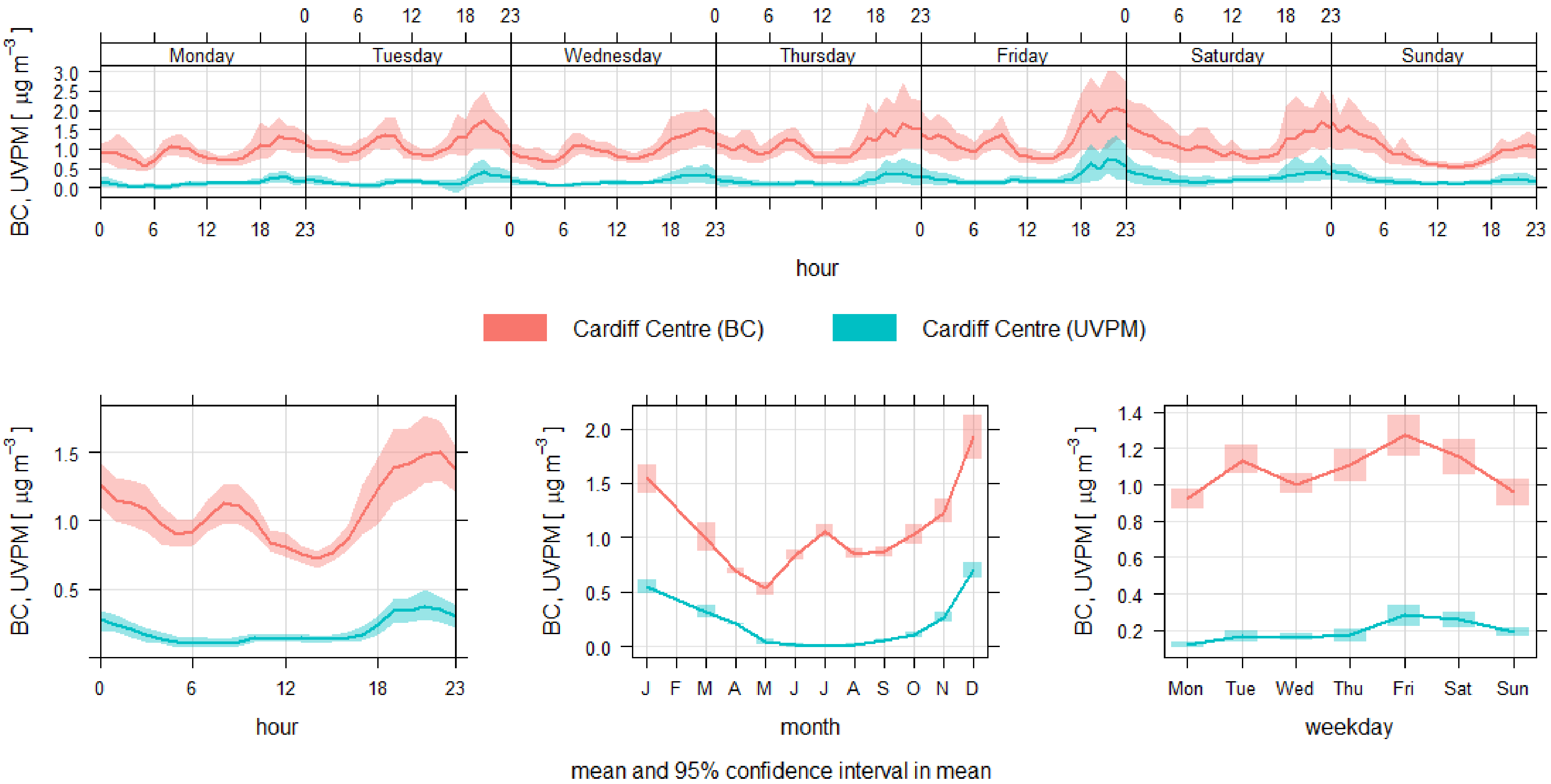

Figure 53 - Temporal variations of BC and UVPM concentrations at Cardiff Centre for 2022

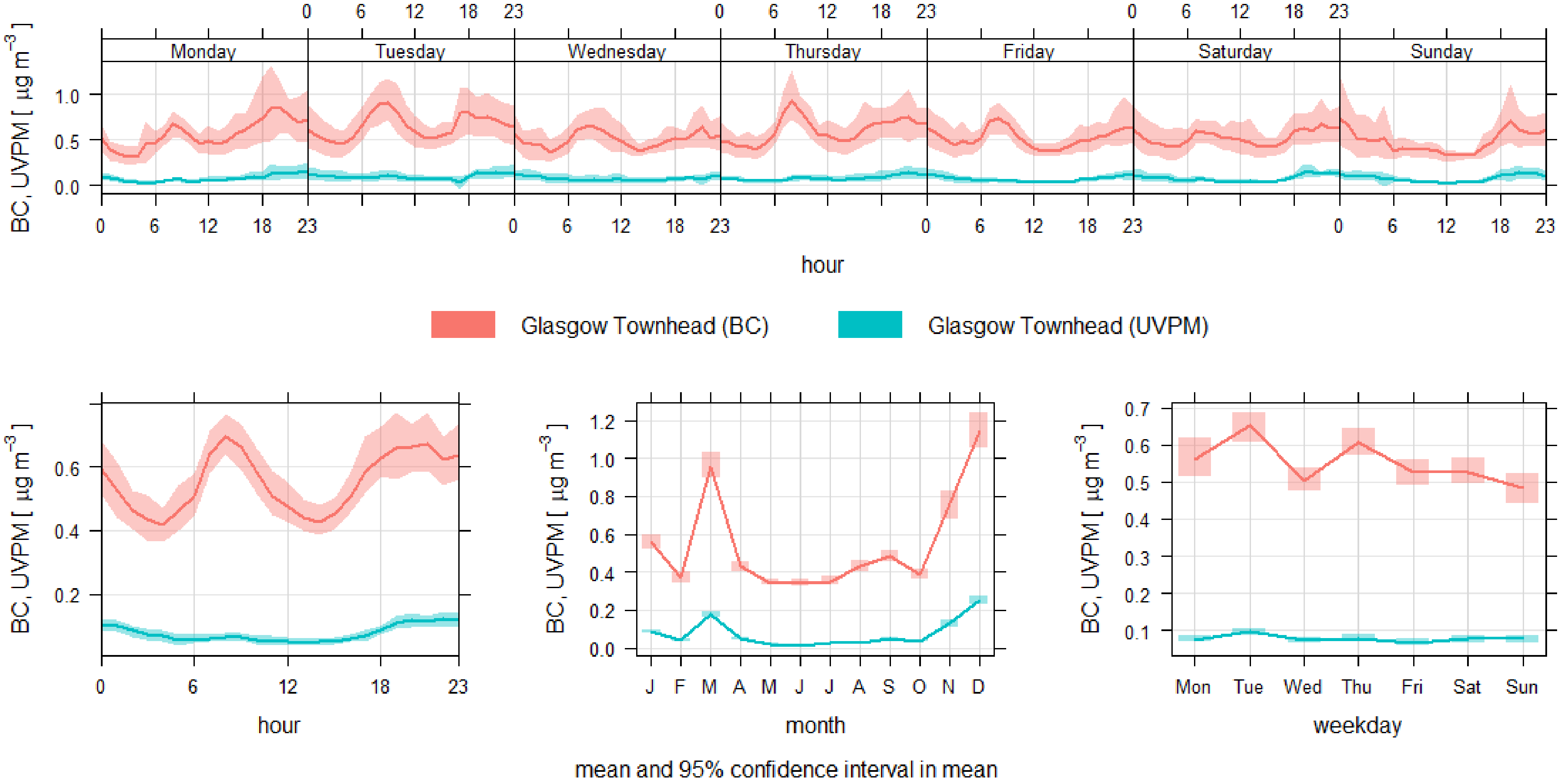

Figure 54 - Temporal variations of BC and UVPM concentrations at Glasgow Townhead for 2022

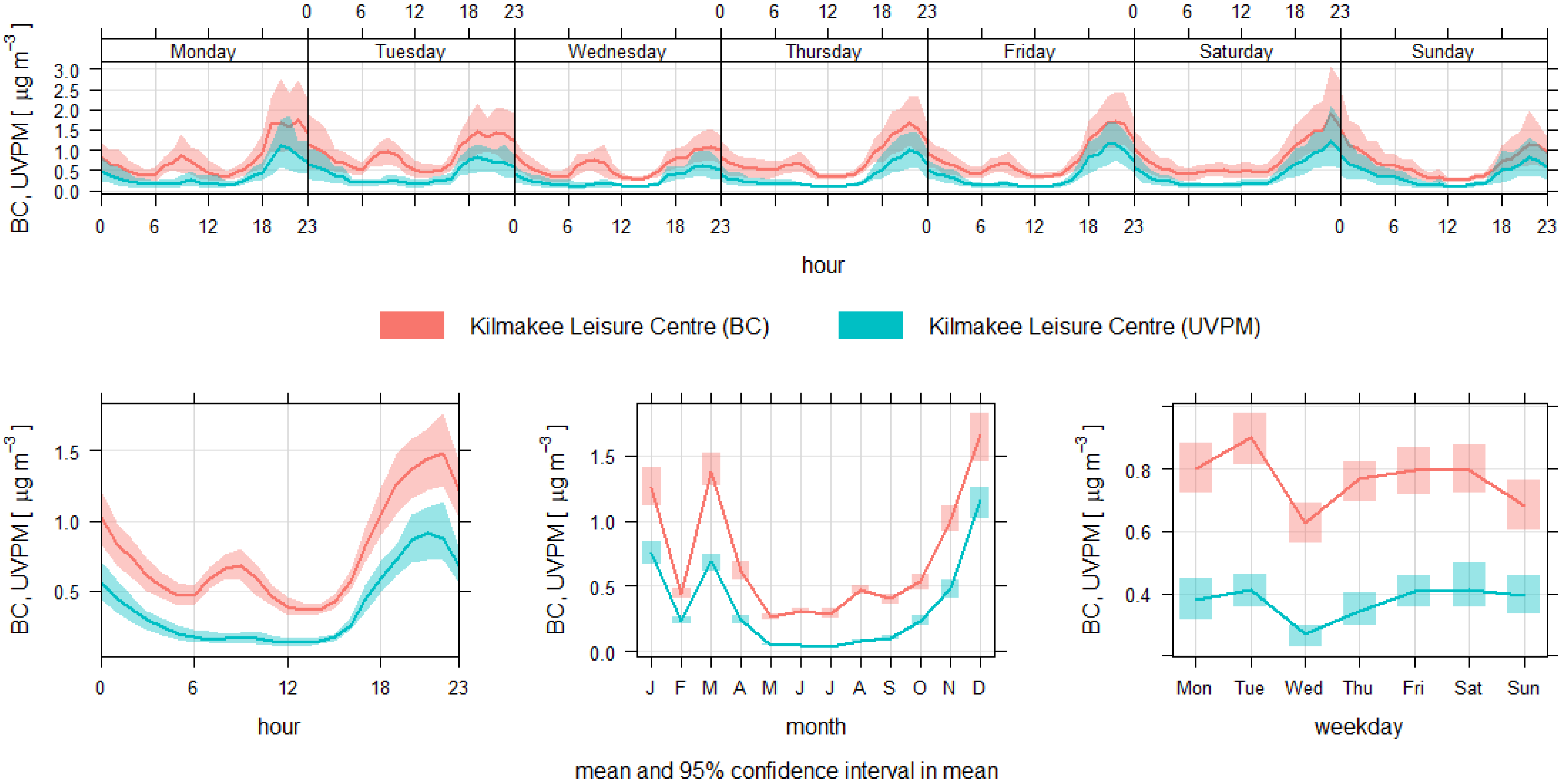

Figure 55 - Temporal variations of BC and UVPM concentrations at Kilmakee Leisure Centre for 2022

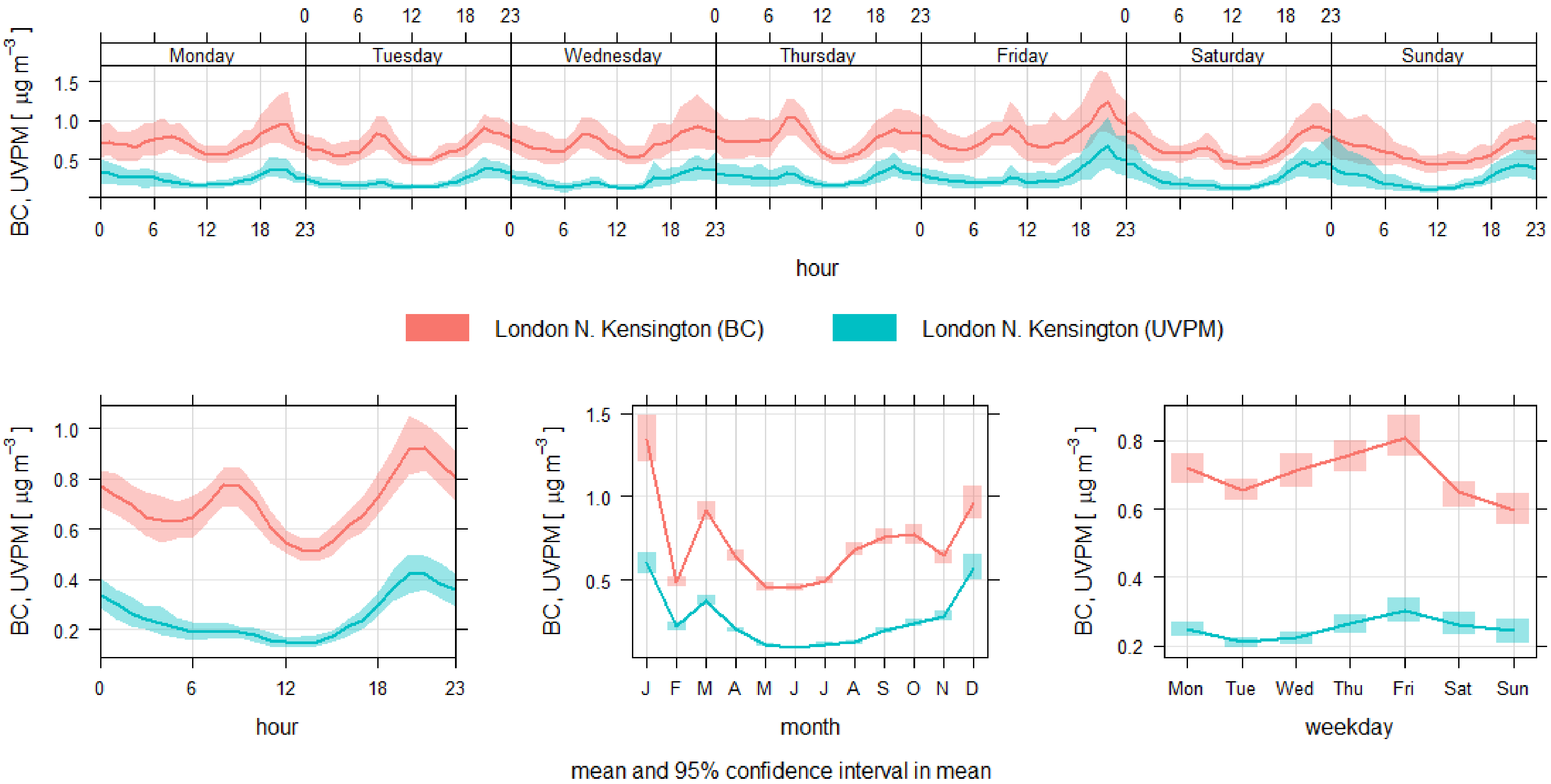

Figure 56 - Temporal variations of BC and UVPM concentrations at London North Kensington for 2022

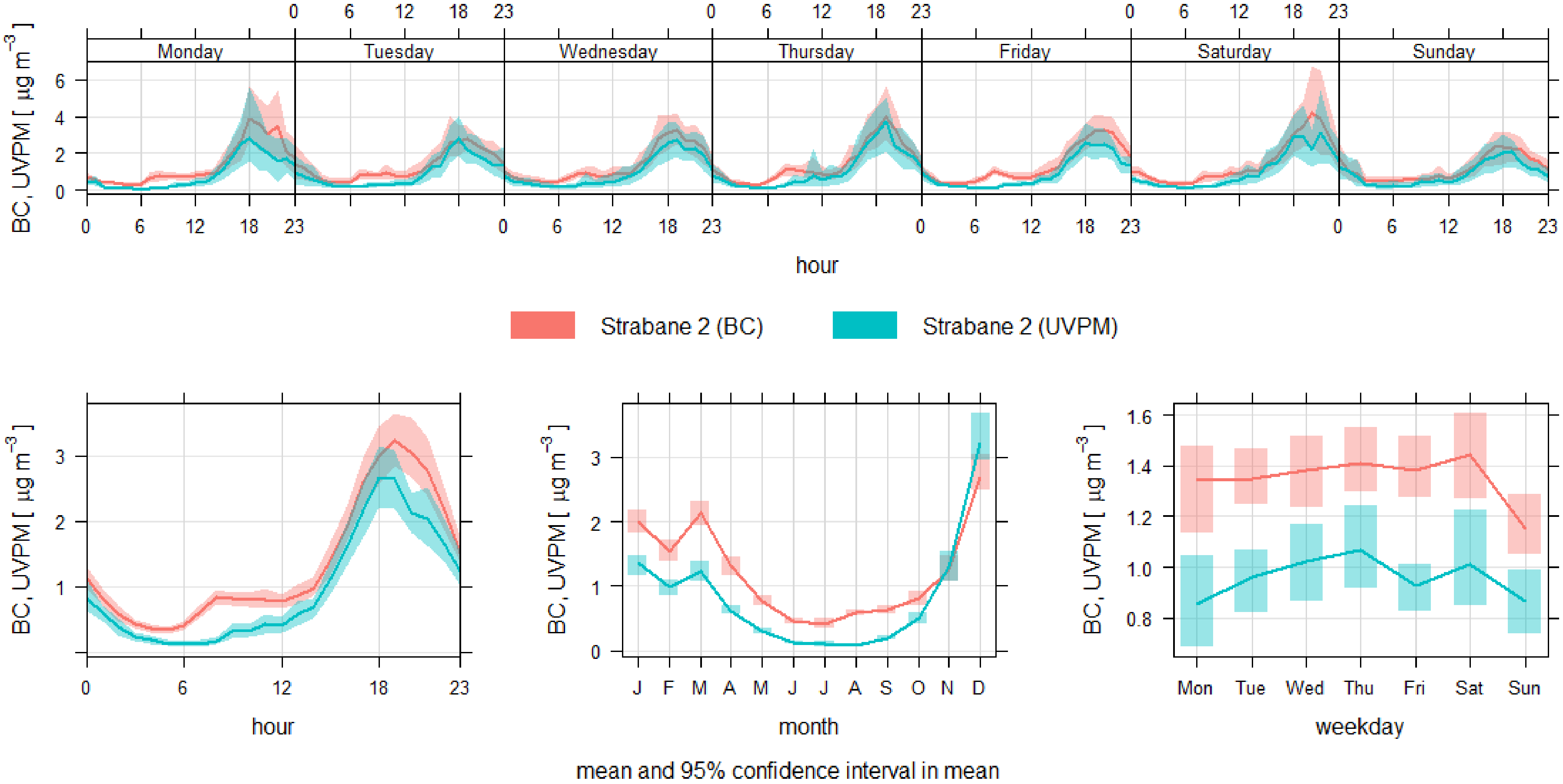

Figure 57 - Temporal variations of BC and UVPM concentrations at Strabane 2 for 2022

BC and UVPM data at rural background sites for 2022

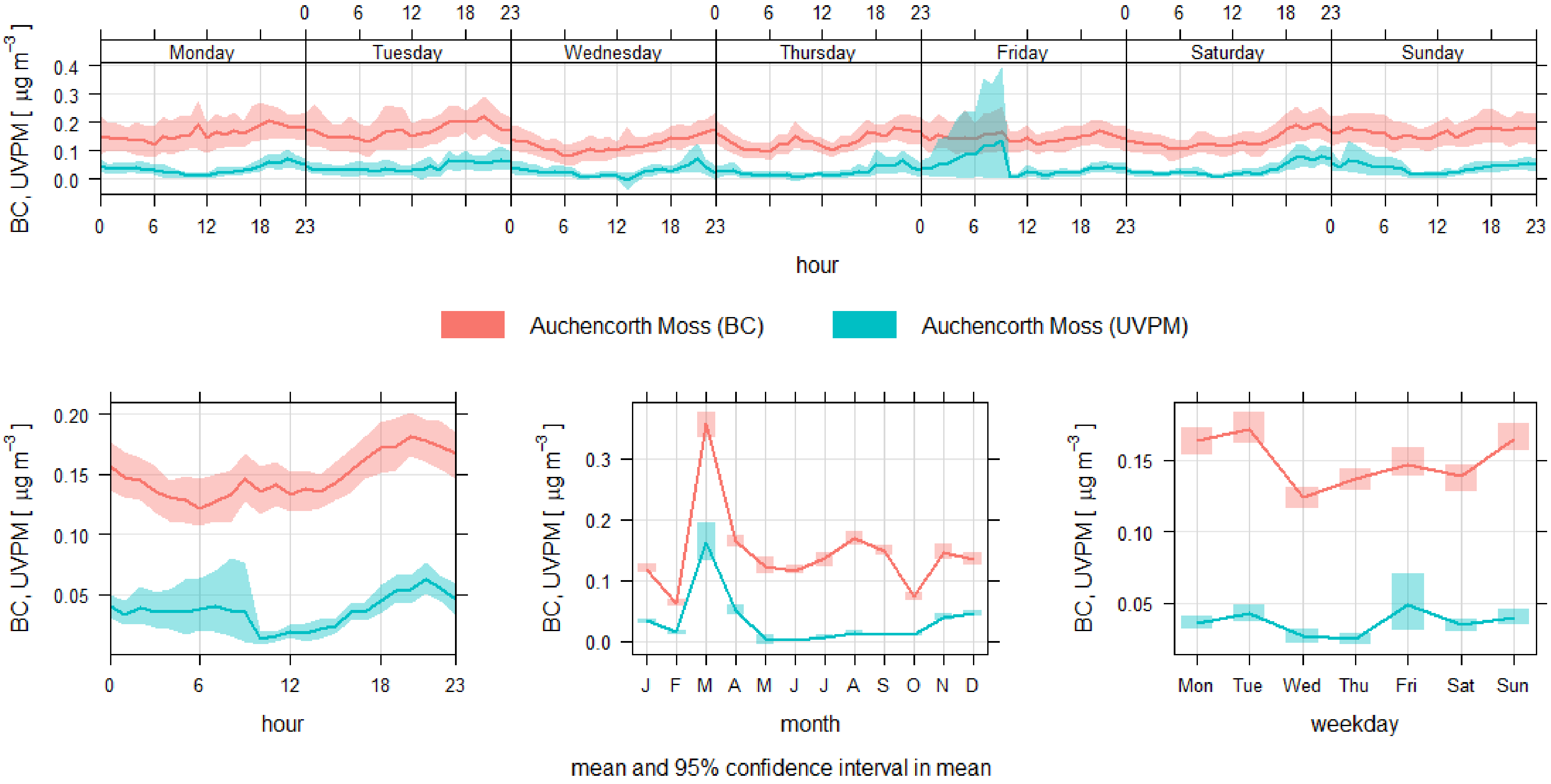

Figure 58 - Temporal variations of BC and UVPM concentrations at Auchencorth Moss for 2022

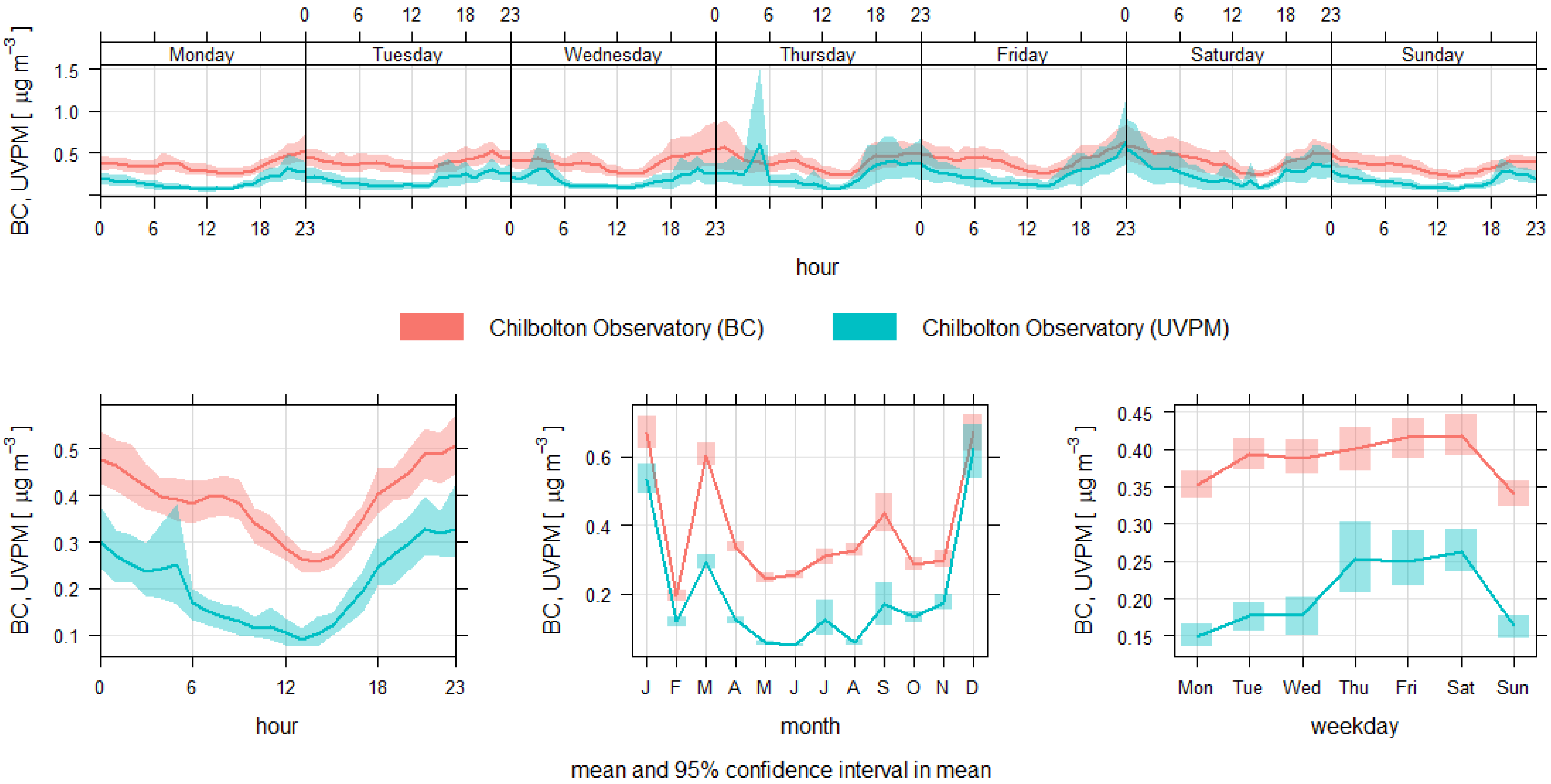

Figure 59 - Temporal variations of BC and UVPM concentrations at Chilbolton Observatory for 2022

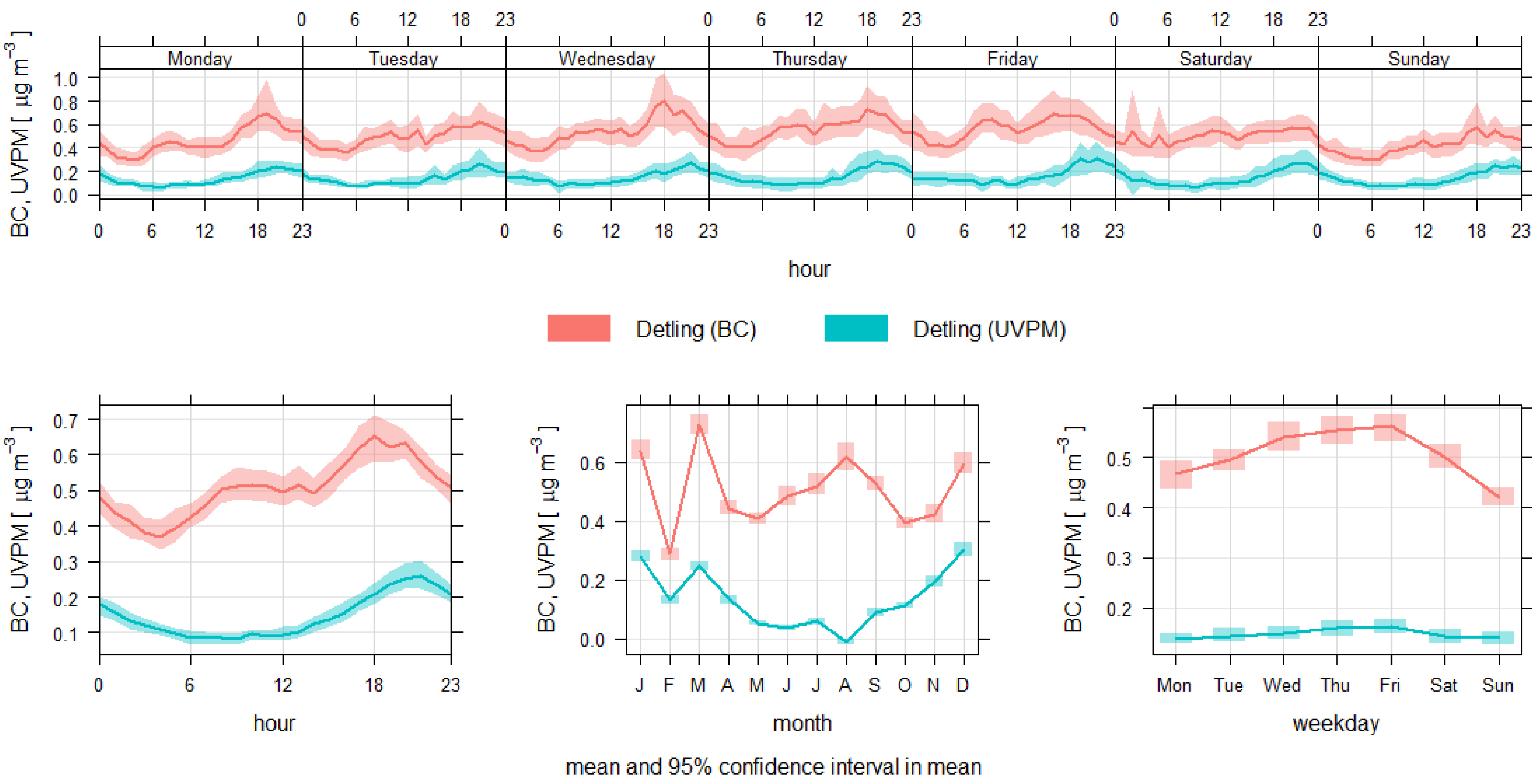

Figure 60 - Temporal variations of BC and UVPM concentrations at Detling for 2022

BC and UVPM data at roadside Sites for 2009 - 2022

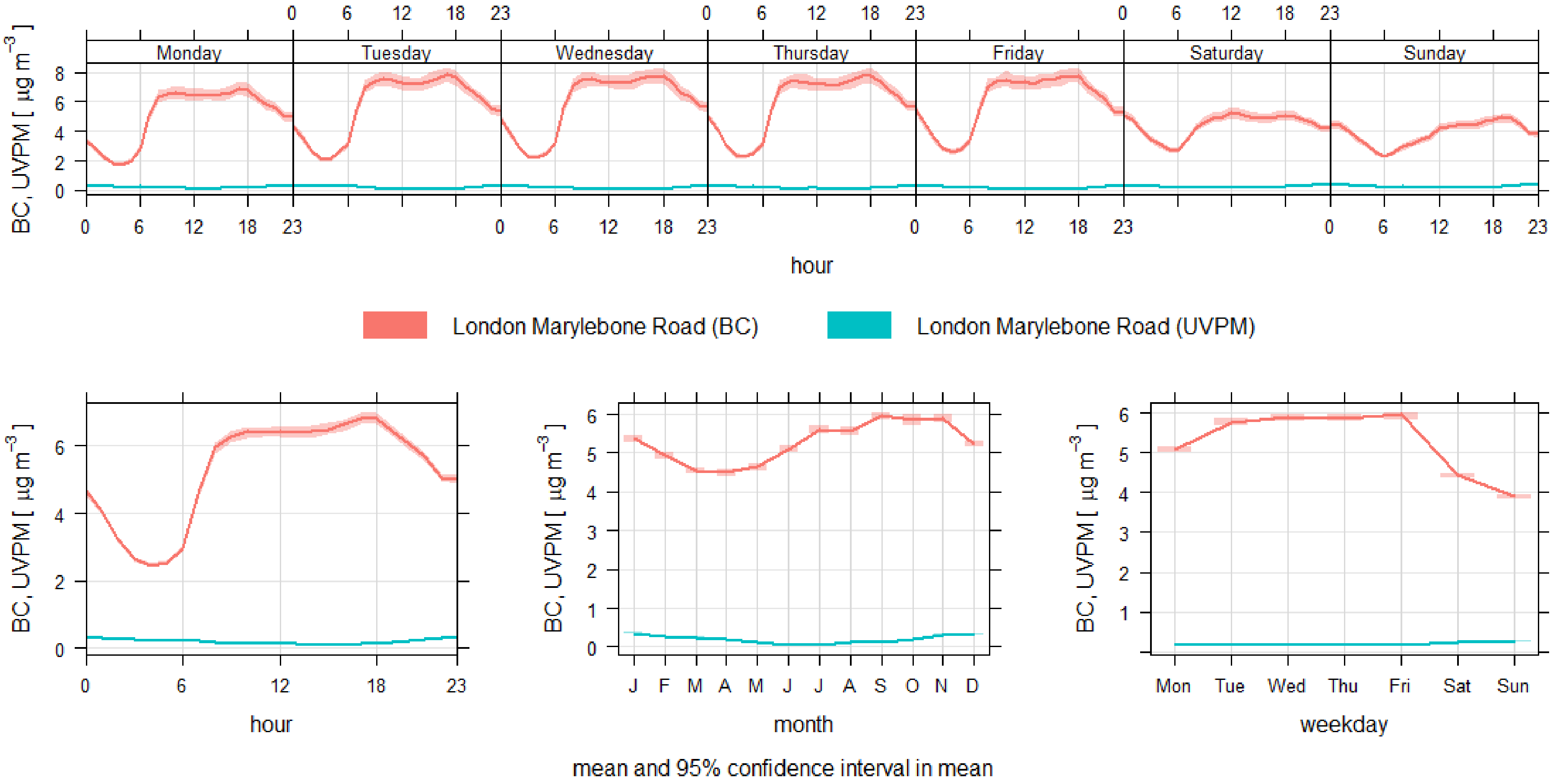

Figure 61 - Temporal variations of BC and UVPM concentrations at London Marylebone Road for 2009-2022

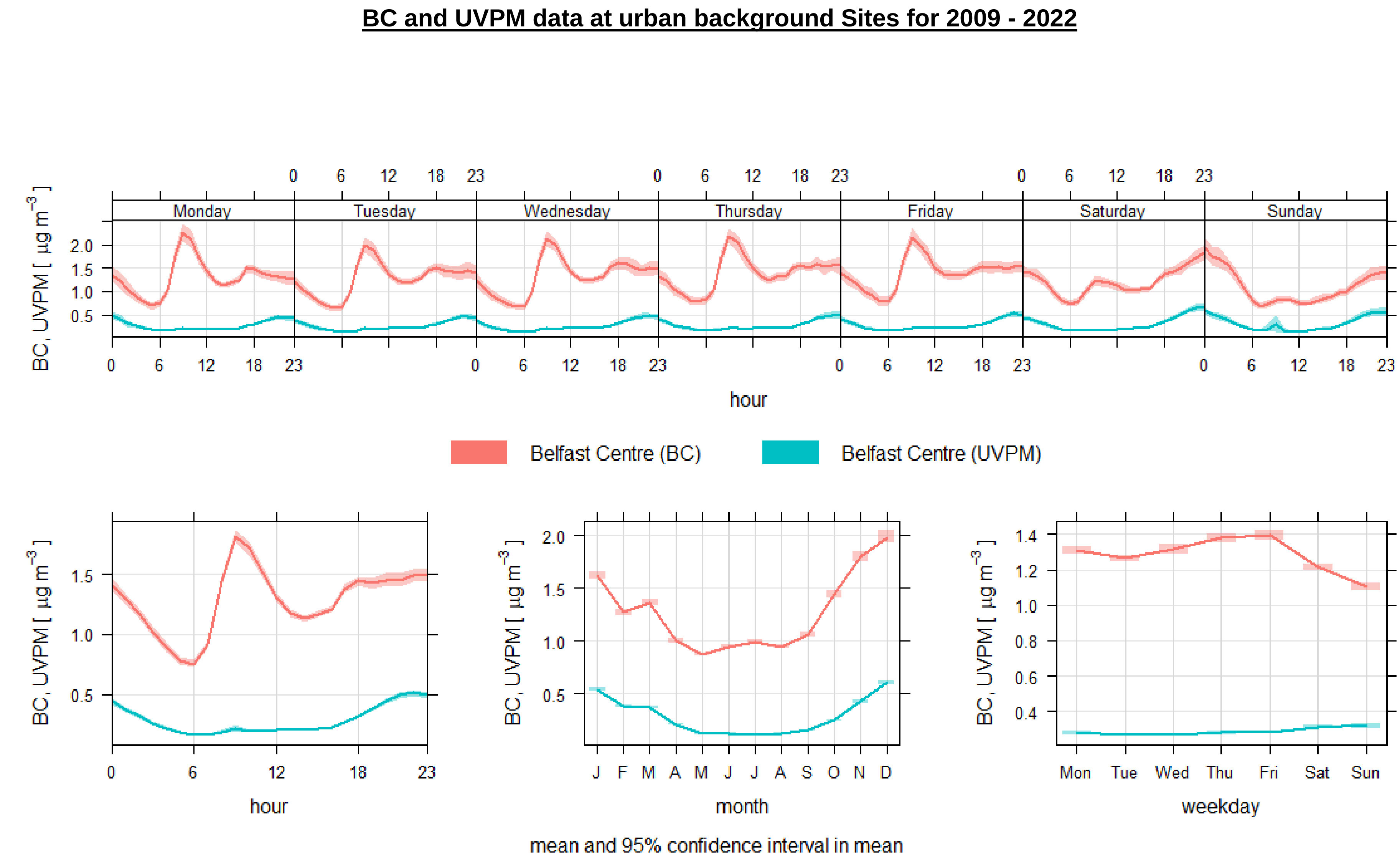

Figure 62 - Temporal variations of BC and UVPM concentrations at Belfast Centre for 2009-2022

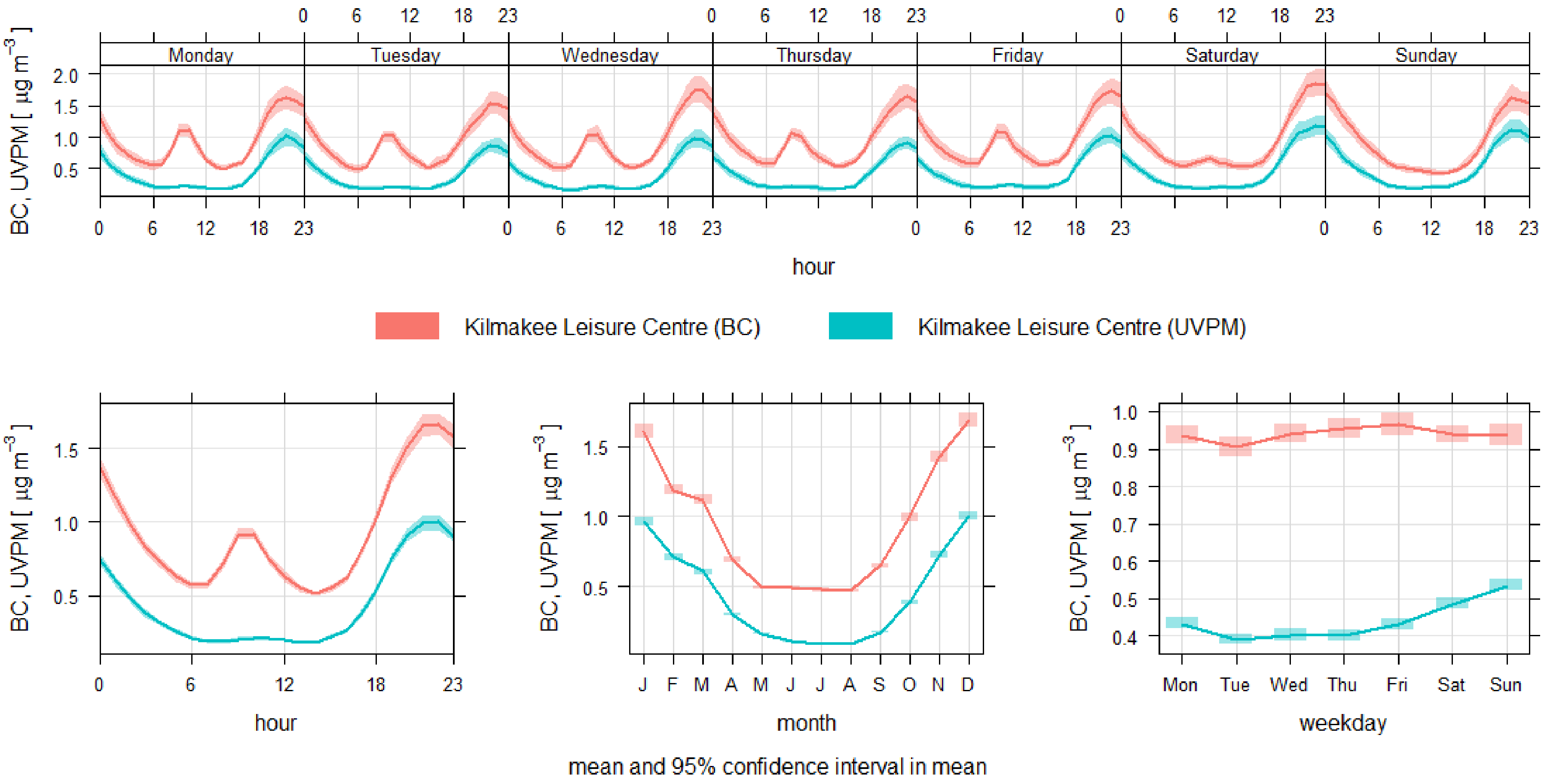

Figure 63 - Temporal variations of BC and UVPM concentrations at Kilmakee Leisure Centre for 2009-2022

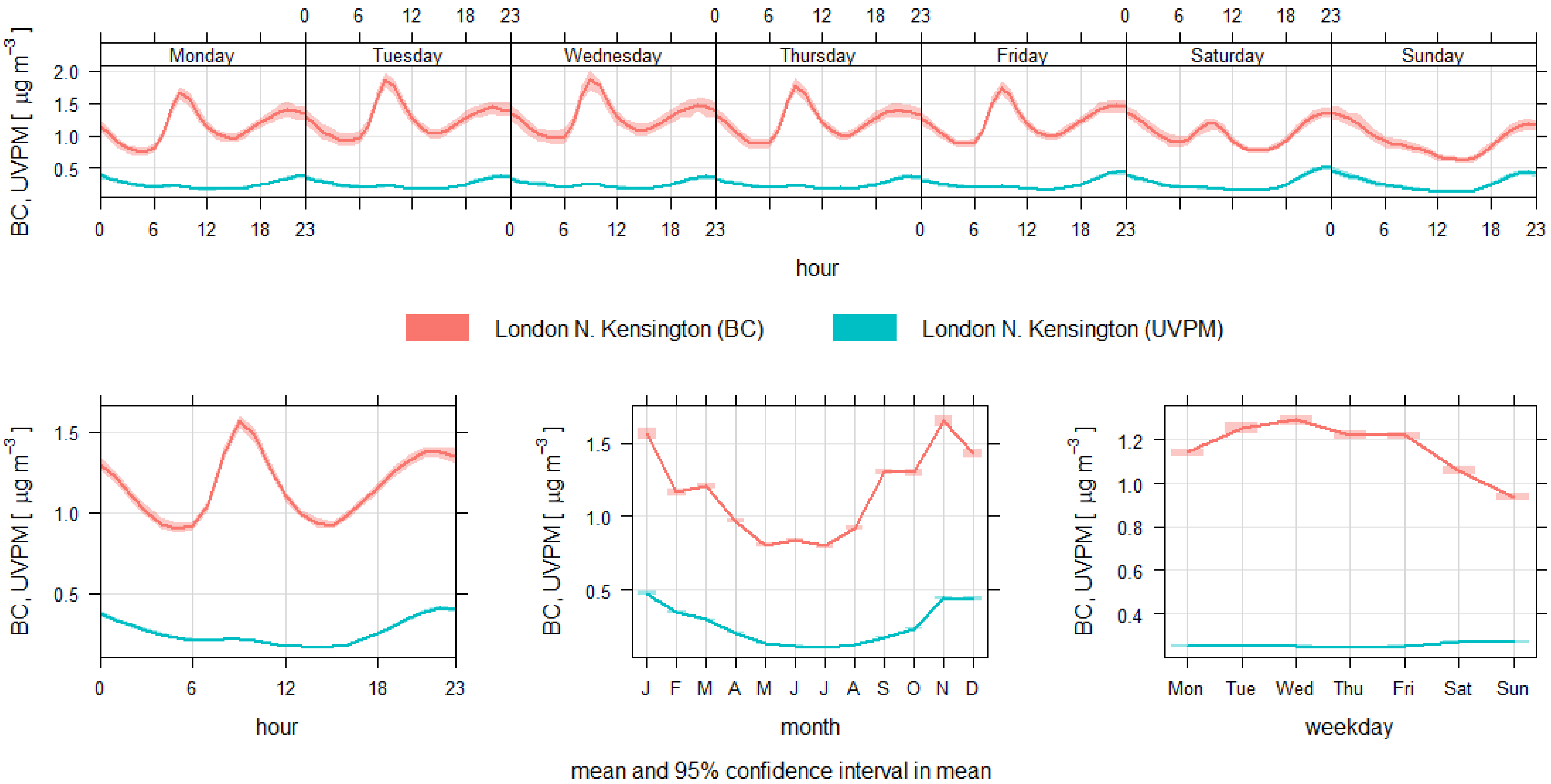

Figure 64 - Temporal variations of BC and UVPM concentrations at London North Kensington for 2009-2022

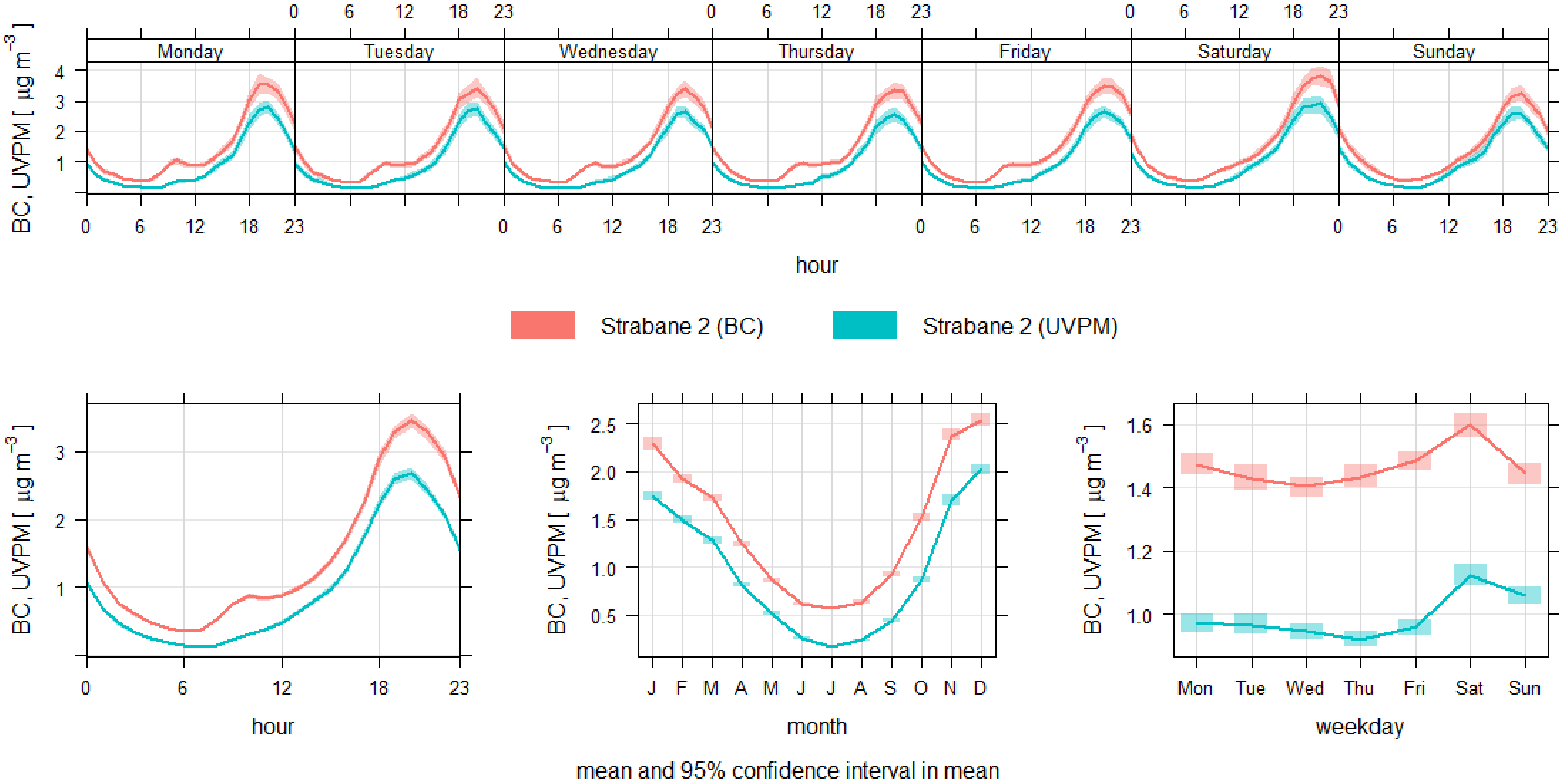

Figure 65 - Temporal variations of BC and UVPM concentrations at Strabane 2 for 2009-2022

4.6.5 Long-term trends

Figure 66 and Figure 67 show the trend in BC concentrations from the longest running sites in the Network, as monthly averages over the full calendar years 2009 to 2022.

The Theil-Sen method in OpenAir[20,21] was used to calculate the regression parameters including slope and uncertainty in the slope. This 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 shown as dashed lines with values provided in square brackets on each plot in Figure 66 and Figure 67. A statistically significant trend can be assumed when the probability value p is < 0.001 (as indicated by *** on the charts).

Over the period 2009 to 2022 all the long-running sites in the Network apart from Strabane 2 have shown a significant downward trend in BC concentrations. The decrease at London Marylebone Road is much larger than the other sites and BC concentrations have been falling consistently since 2011.

Figure 68 and Figure 69 show the long-term trends in UVPM concentration.

The London Marylebone Road UVPM concentration showed an upward trend over the period 2009 to 2022, this was probably due to the reduced BC concentrations over the latter years. As the Aethalometer measures the UVPM as the difference between the BC and UV channels. However, the trends determined for the London Marylebone Road and Belfast Centre sites should be treated with caution are they are not statistically significant.

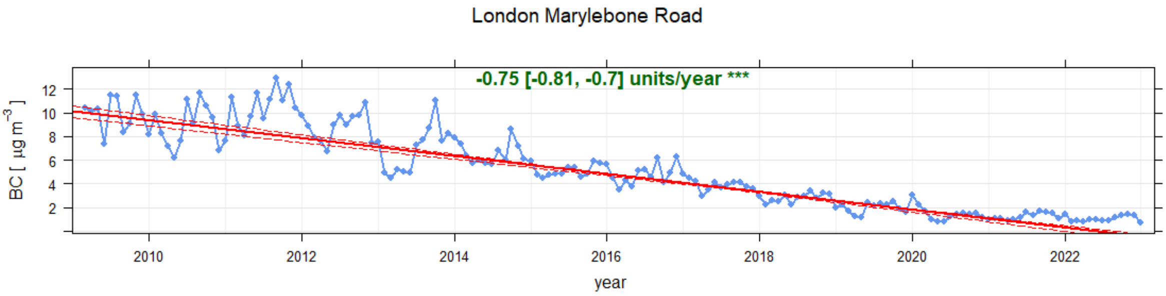

Figure 66 - BC trends measured at the London Marylebone Road roadside site, 2009 - 2022

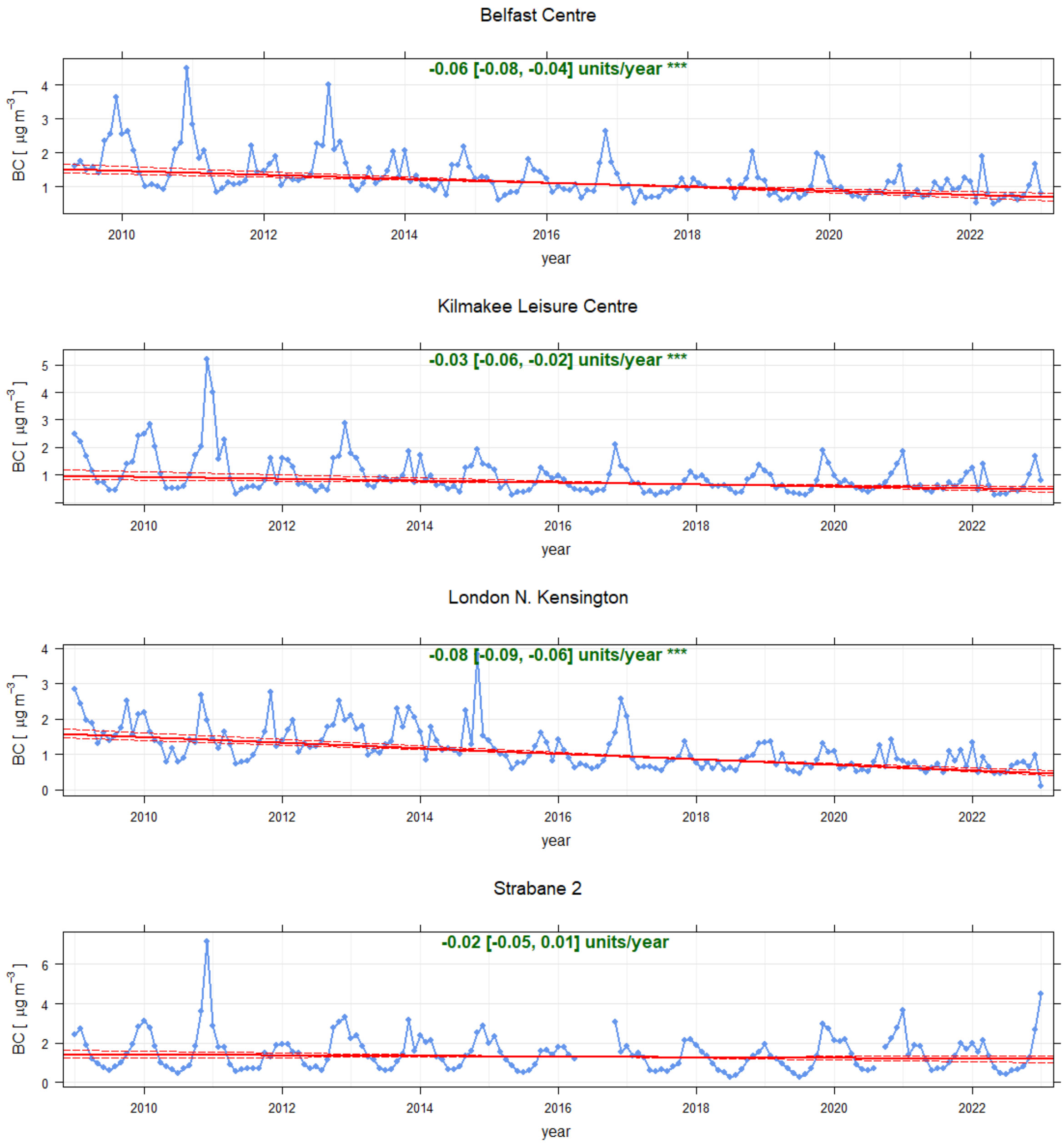

Figure 67 - BC trends measured at urban background sites, 2009 - 2022

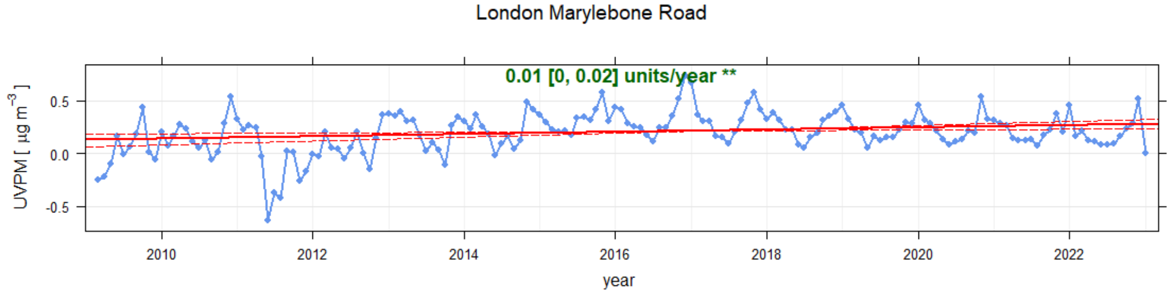

Figure 68 - UVPM concentrations measured at roadside sites, 2009 - 2022

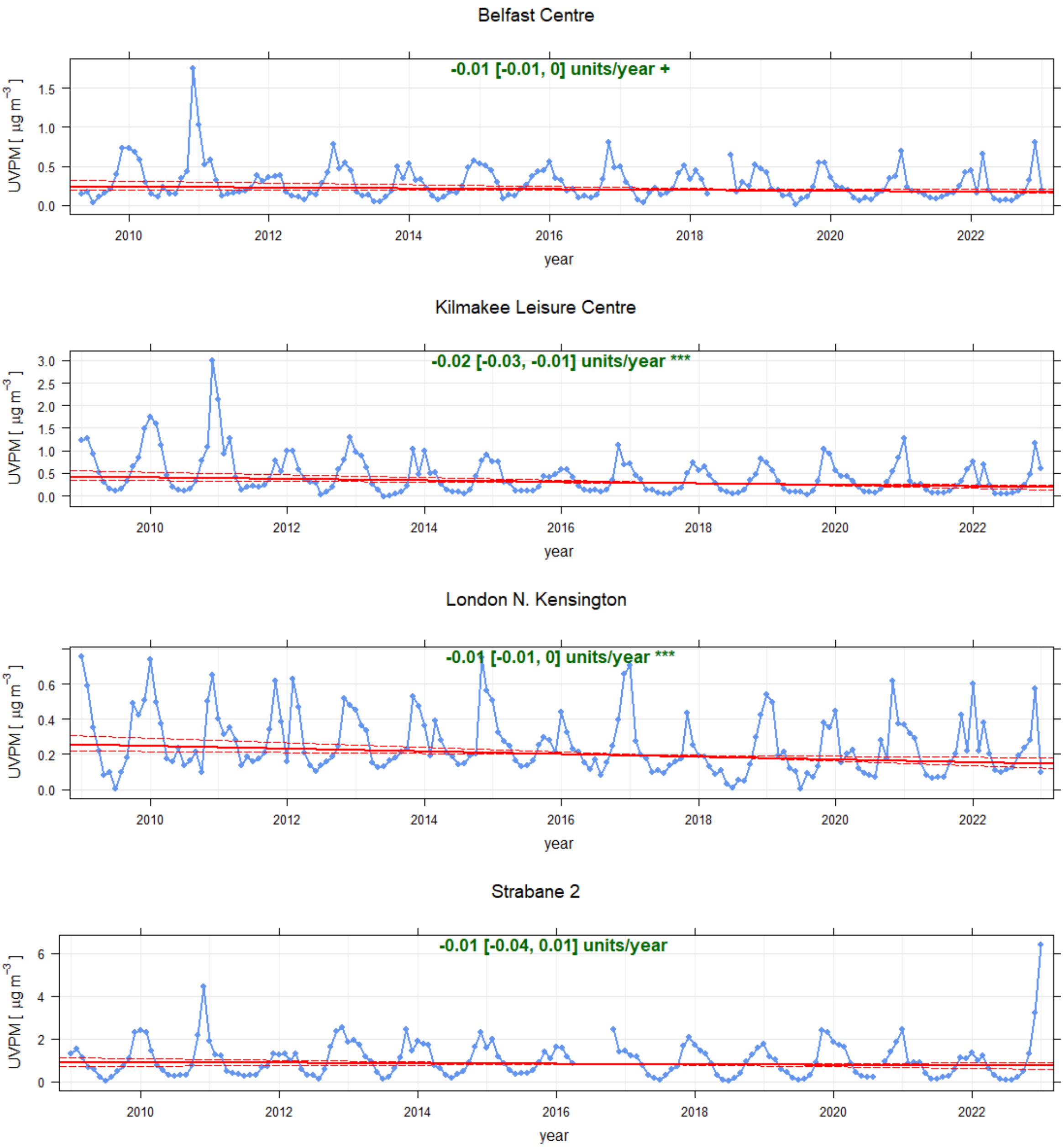

Figure 69 - UVPM concentrations measured at urban background sites, 2009 - 2022

4.6.6 Comparisons with other pollutants

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

4.6.6.1 EC

Daily EC measurements were made at London Marylebone Road and Chilbolton Observatory. Co-located measurements of BC (in $PM_{2.5}$) have been averaged into daily measurements and plotted as scatter plots against the EC concentrations in Figure 70. The regression is calculated according to the Reduced Major Axis (RMA) method[25] (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 EC metric and the optically based BC 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. However, quantifying carbonaceous material strongly depends on the measurement techniques and parameters used, thus differences between the absolute BC and EC measurements are often observed, even if an overall comparison of the data shows them to be linearly correlated[26].

There was a good linear correlation (R^2 ~ 0.8) between the EC and BC concentrations at the Chilbolton Observatory and London Marylebone Road sites in 2022 (see Table 14).

Table 14 - Relationship between BC ($PM_{2.5}$) and EC (PM_{10} & $PM_{2.5}$) and the three Network sites

	Chilbolton Observatory*		London Marylebone Road**	
Year	**Relationship**	**R^2**	**Relationship**	**R^2**
2020	1.91x - 0.05	0.906	1.69x - 0.02	0.880
2021	2.29x - 0.12	0.795	1.62x - 0.03	0.850
2022	1.77x - 0.11	0.782	1.36x - 0.01	0.780

<u>Notes</u>
* The Chilbolton Observatory data used in this comparison are from the $PM_{2.5}$ Leckel sampler which began daily measurements from June 2020 to January 2022. All other 2022 data are from the $PM_{2.5}$ Digitel sampler.
** The London Marylebone Road data for 2020 to early March 2022 are from the $PM_{2.5}$ Partisol sampler. All other 2022 data are from the $PM_{2.5}$ Digitel sampler.

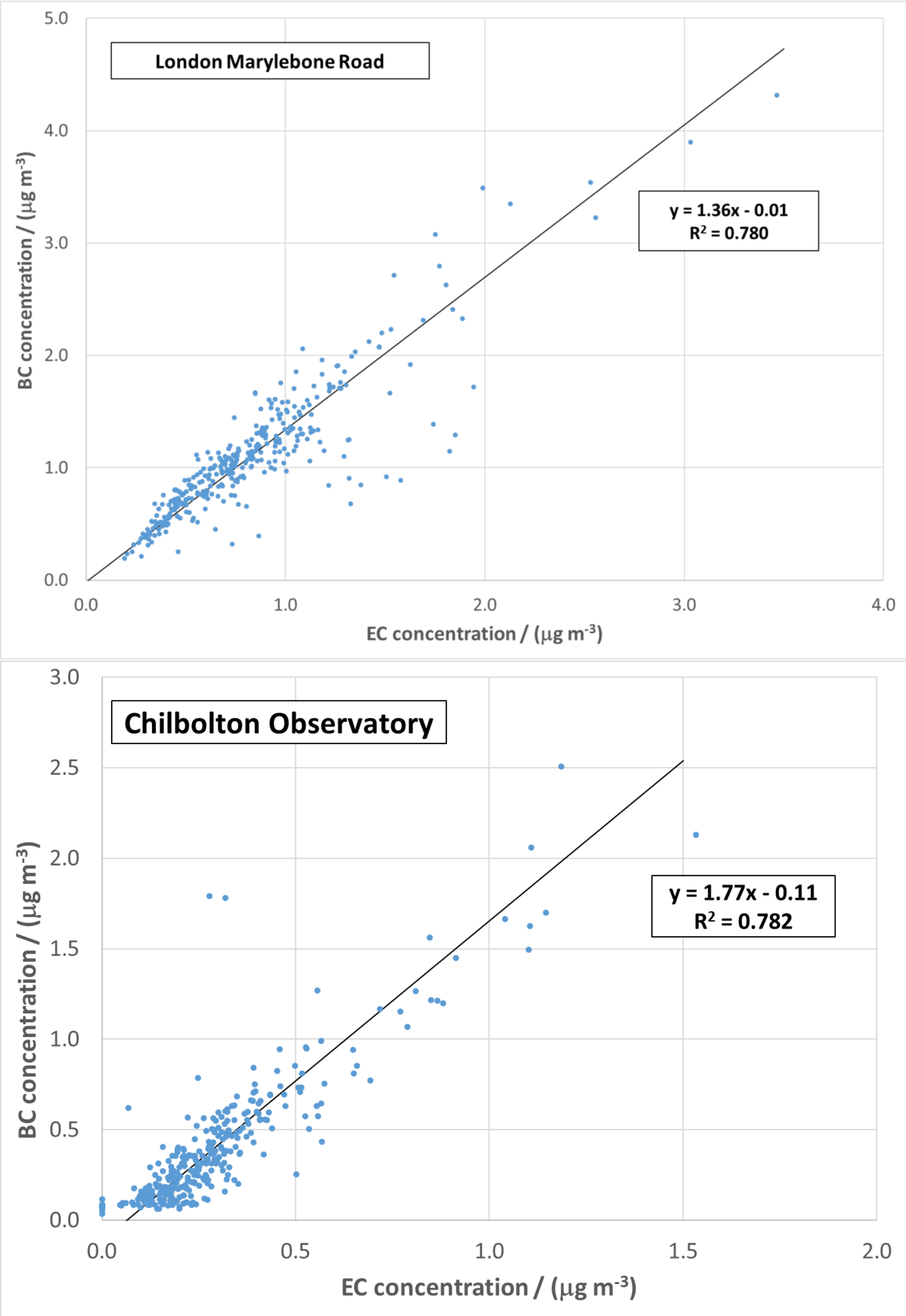

Figure 70 - Comparison between BC and EC at the London Marylebone Road and Chilbolton Observatory sites in 2022

4.6.6.2 Particle mass concentration

The annual average particulate mass concentration was compared with the BC concentration at co-located sites where automatic particulate mass instrumentation was installed. The results are shown in Table 15.

Table 15 - Comparison of annual BC 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	6 (FIDAS)	4 (FIDAS)	2	4
Belfast Centre	0.9	14 (FIDAS)	8 (FIDAS)	6	11
Birmingham A4540 Roadside	1.8	16 (FIDAS)	9 FIDAS)	11	20
Birmingham Ladywood	0.8	13 (FIDAS)	8 (FIDAS)	6	10
Cardiff Centre	1.1	16 (BAM)	11(BAM)	7	10
Chilbolton Observatory	0.4	12 (FIDAS)	8 (FIDAS)	3	5
Detling*	0.5	13 (TEOM FDMS)	-	4	-
Glasgow High Street	0.9	11 (FIDAS)	6 (FIDAS)	8	15
Glasgow Townhead	0.6	10 (FIDAS)	6 (FIDAS)	6	9
London Marylebone Road	1.1	21 (BAM)	11 (BAM)	5	10
London North Kensington	0.7	15 (FIDAS)	9 (FIDAS)	5	8
Strabane 2	1.4	12 (REF.EQ)	8 (FIDAS)	11	17

Notes:

- The techniques used for monitoring PM are:
  - (TEOM) - Tapered Element Oscillating Microbalance
  - (BAM) - Beta Attenuation Monitor
  - (FDMS) - Filter Dynamics Measurement System
  - (FIDAS) - Fine Dust Analysis System,
  - (REF.EQ) - the reference methods of measurement are defined in the relevant EU Directives
- The asterisk (*) for Detling 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 Birmingham A4540 Roadside and Glasgow High Street sites had a higher percentage of BC than the other sites. BC therefore represented a large proportion of the total particulate mass at sites influenced by road traffic emissions. However, this effect is less significant at other roadside stations: London Marylebone Road, Cardiff Centre and Belfast Centre. At the rural background sites BC made up 5 % or less of the PM mass. The high proportion of BC in PM at Strabane 2 site is most likely due to emissions from domestic heating.

5 RELATED RESEARCH PUBLICATIONS

The paper: ***Long-term trends in particulate matter from wood burning in the United Kingdom: Dependence on weather and social factors***[27] has been published in the *Environmental Pollution*.

In this paper, PM contributions from wood burning emissions (C_{wood}) at five locations in the UK between 2009 and 2021 were determined. Concentrations were greatest in the evenings in winter months, with larger evening concentrations in the weekends at the urban sites. Random-forest (RF) machine learning regression models were used to reconstruct C_{wood} concentrations using both meteorological and temporal explanatory variables at each site. The partial dependency plots indicated that temperature and wind speed were the meteorological variables explaining the greatest variability in C_{wood}, with larger concentrations during cold and calm conditions. Peaks of C_{wood} concentrations took place during and after events that are celebrated with bonfires, for example Bonfire Night events in urban areas and New Year's celebrations (which were observed on New Year's Day at the rural sites); the later probably related to long-range transport. Time series were built using the RF. Having removed weather influences, long-term trends of C_{wood} were estimated using the Theil Sen method. Trends for 2015-2021 were shown to be downwards at three locations (London, Glasgow and rural Scotland). The replacement of old fireplaces with lower emission wood stoves might explain the decrease in C_{wood} especially at the urban sites. The two rural sites in England observed positive trends for the same period but this was not statistically significant.

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