NPL REPORT ENV 57

AIRBORNE PARTICLE CONCENTRATIONS, PARTICLE NUMBERS, AND BLACK CARBON IN THE UNITED KINGDOM - ANNUAL REPORT 2023

KRZYSZTOF CIUPEK
JORDAN TOMPKINS
KATIE WILLIAMS
ANDREW BROWN
CHRIS ROBINS
JAMES ALLERTON
ELIZABETH McGHEE
VANDANA KANTILAL
DOUGLAS WALKER
CHRIS BRADSHAW
ADAM LILLEY
DAVID BUTTERFIELD
RICHARD BROWN
MAX PRIESTMAN
ANJA TREMPER
DAVID EK
DAVID GREEN

AUGUST 2024

Airborne Particle Concentrations, Particle Numbers, and Black Carbon in the United Kingdom - Annual report 2023

K. Ciupek, J. Tompkins, K. Williams, A. Brown, C. Robins, J. Allerton, E. McGhee, V. Kantilal, D. Walker, C. Bradshaw, A. Lilley, D. Butterfield, and R. Brown.

Atmospheric Environmental Science Department,
National Physical Laboratory.

M. Priestman, A. Tremper, D. Ek, and D. Green.

Environmental Research Group,
Imperial College London.

ISSN 2059-6030

https://doi.org/10.47120/npl.ENV57

National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

Approved on behalf of NPLML by
Craig Barnfield, Group Leader - Air Quality & Aerosol Metrology Group

CONTENTS

EXECUTIVE SUMMARY

The National Physical Laboratory is contracted to manage the UK Particle Concentrations and Numbers (PCN) and Black Carbon (BC) air quality Network. The PCN&BC Network measures and reports concentrations and chemical composition of particles in ambient air across the UK, with a focus on $PM_{2.5}$ (particulate matter with an aerodynamic diameter < 2.5 µm).

This report was prepared by the National Physical Laboratory and the Environmental Research Group at Imperial College London as part of the PCN&BC Networks contract. The contract is managed by the Environment Agency on behalf of the Department for the Environment, Food and Rural Affairs and the Devolved Administrations: the Scottish Government, the Welsh Government, and the Department of the Environment in Northern Ireland.

This 2023 annual report 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 2023.

And, where applicable:
- Plots of the diurnal, weekly, and monthly trends in ratified Network data in 2023.
- Plots of the long-term trends in ratified Network data.
- Comparisons between pollutants measured by the Network.
- Activities associated with the UK $PM_{2.5}$ monitoring expansion programme, which will to provide additional particulate matter (PM) speciation data to enhance the measurement evidence base associated with the $PM_{2.5}$ targets from the Environmental Targets (Fine Particulate Matter) (England) Regulations 2023[1].

In 2023, 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 2023, the Network reported data for:

Analyte	Instrument(s)	Frequency	Sites
Particle number concentrations in $PM_{2.5}$	Condensation Particle Counter (CPC)	Hourly	3
Particle size distributions in $PM_{2.5}$	Scanning Mobility Particle Sizer (SMPS)	15 min	3
Mass concentrations of ammonium, nitrate, sulfate, and organic compounds in $PM_{2.5}$ or PM_1*	Aerosol Chemical Speciation Monitor (ACSM)	Hourly	3
40 elements in $PM_{2.5}$ and PM_{10}*	X-ray fluorescence instrument (XRF)	Hourly	2
Mass concentrations of organic carbon and elemental carbon (OC/EC) in $PM_{2.5}$	Ambient air sampler and thermal/optical carbon analyser	Weekly or daily	4
Mass concentrations of BC and ultraviolet particulate matter (UVPM) in $PM_{2.5}$	Aethalometer	Hourly	14

* PM_1 and PM_{10} is particulate matter with an aerodynamic diameter < 1 µm and <10 µm respectively.

Fully ratified data from the Network can be downloaded from the Defra UK-AIR website[2].

Some notable features from the Network data in 2023 are:

- The annual average particle number concentrations for 2023 at London Marylebone Road and London Honor Oak Park showed a slight increase from the 2022 annual average. The particle number concentrations at both of these sites however remain lower than the pre-coronavirus pandemic values suggesting that there has been a sustained reduction compared to the 2019 annual average values.

- The introduction of the newer model of SMPS at the sites has shown a broadening of the particle size distribution. It has also shown a shift of the peak to larger mobility diameters at a both London Honor Oak Park and London Marylebone Road. This, however, is most likely an artifact of the change in instrument rather than a shift in the particle size distribution of the ambient aerosol.

- 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 2022.

- Of the 40 elements measured via XRF, is it noted that chlorine reported the highest annual average concentration at both London Marylebone Road and London Honor Oak Park sites, in both $PM_{2.5}$ and PM_{10}. In summary, the elements that reported the highest annual average concentrations in PM_{10} were (in order) chlorine, iron, and sulfur at London Marylebone Road, and chlorine, sulfur, and iron at London Honor Oak Park.

- The annual average mass concentrations of EC for all sites decreased by around 20 % when compared to 2022. The OC mass concentrations at London Marylebone Road site increased slightly from 2022. At Auchencorth Moss, the annual average mass concentrations of OC, EC, and total carbon (TC) decreased since previous year.

- Annual average mass concentrations of BC and UVPM were measured at all 14 sites in 2023 and the concentrations for both components were broadly lower to those measured in 2022. The largest decrease of UVPM was observed at the Cardiff Centre site from 0.19 µg m^{-3} in 2022 to 0.11 µg m^{-3} in 2023, whereas the largest decrease of BC was observed at the Strabane 2 site from 1.36 µg m^{-3} in 2022 to 0.91 µg m^{-3} in 2023.

- The significant downward trend in measured BC mass concentrations since 2009 observed at all the long-running sites in the Network (apart from Strabane 2), continued into 2023. The relative decrease in BC measured 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:

- 59 % for particle number concentration measurements
- 46 % for particle size distribution measurements
- 90 % for aerosol mass and chemical composition measurements
- 90 % for elemental measurements
- 93 % for OC/EC measurements
- 89 % for BC measurements

1 INTRODUCTION

The UK 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
- aerosol mass and chemical compositions
- elemental concentrations
- organic carbon and elemental carbon (OC/EC)
- black carbon (BC) and ultraviolet particulate matter (UVPM) 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 under this Network, 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 2010 (AQSR)[3,4,5,6], and all associated amendments, which reference the EU Ambient Air Quality Directive 2008[7,8], and support objectives set out in the UK's Clean Air Strategy 2019[9] and Environmental Improvement Plan 2023[10].

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).

Following the Environment Act 2021[11] and the new legally binding $PM_{2.5}$ targets published through The Environmental Targets (Fine Particulate Matter) (England) Regulations 2023[1], Defra has requested an expansion of the PCN&BC Network to provide additional particulate matter (PM) speciation data to enhance the measurement evidence base associated with the $PM_{2.5}$ environmental targets. In 2023, the PCN&BC Network team were involved in various activities in preparation of expanding the networks.

This report presents: a summary of the 2023 data; key findings from the data; a comparison with previous years and, where relevant, a comparison with data from other networks; and other related activities.

2 NETWORK INFRASTRUCTURE AND OPERATION

2.1 NETWORK OVERVIEW

In 2023, the Network 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.

- The capture vaporisers on the aerosol chemical speciation monitors (ACSMs) were replaced with standard vaporisers at all three sites to standardise organic fragmentation patterns and source profiles. The standard vaporisers were installed at London Marylebone Road and London Honor Oak Park in April 2023 and at Chilbolton Observatory in December 2023.

- A new TSI 3938W50-CEN scanning mobility particle sizer (SMPS) was installed at Chilbolton Observatory and London Honor Oak Park to replace the previous TSI 3936 SMPS, in April and March respectively. At the same time, a new TSI 3750200 sampling system was also installed at these sites to supply the SMPS and stand-alone condensation particle counter (CPC). This replaced the previous sampling system. This follows the same replacement at London Marylebone Road in November 2022, so now all three sites have the same model of SMPS and sampling system.

The instrumentation used for all other measurements performed by the Network remained unchanged throughout 2023.

Also of note are that:

- The CPC at Birmingham Ladywood continued to not be operational during 2023. Discussions about preparing the site for the re-installation of the equipment are currently on hold.

NPL has continued its role as the primary contractor, central management and control unit (CMCU) and quality assurance / quality control (QA/QC) unit, 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 2023 is shown in Table 1. Site locations are shown in Figure 1. Site details are available through the UK AIR website[2].

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[3,4,5,6] (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 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), which includes a CMCU and a QA/QC unit. In 2023, NPL has continued its role as CMCU and QA/QC unit, with significant support from ERG.

CMCU activities include management of equipment, consumables, and health and safety; management of subcontractors such as local site operators (LSOs) and equipment support units (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 CPC, SMPS, OC/EC, and Aethalometers, NPL perform the majority of the CMCU and QA/QC duties, with support from ERG, who are responsible for collecting and storing the CPC, SMPS, and BC data; and manage the ESU emergency callouts and scheduled services and calibration for Aethalometers. NPL have continued to undertake OC/EC analyses in-house, including associated QA/QC activities.

ERG have continued to undertake the majority of the CMCU and QA/QC activities for the ACSM and X-ray fluorescence (XRF) equipment, with support from NPL.

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 2023
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 [1]	Hourly $PM_{2.5}$ or PM_{10} elements [2]	Daily or Weekly $PM_{2.5}$ OC/EC [3]	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			X	3
Birmingham A4540 Roadside	Urban roadside						X	4
Birmingham Ladywood	Urban background						X	5
Chilbolton Observatory	Rural background	X		X	X	X [4]	X	6
London North Kensington	Urban background						X	7
London Marylebone Road	Urban roadside	X	X	X	X	X	X	8
London Honor Oak Park	Urban background	X	X	X	X	X [5]		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

Notes
[1] The Chilbolton Observatory and London Honor Oak Park ACSMs sample $PM_{2.5}$; the London Marylebone Road ACSM samples PM_1 (particulate matter with an aerodynamic diameter < 1 µm). In 2023, the capture vaporisers were replaced with standard vaporisers at all three sites (London Marylebone Road and London Honor Oak Park in April, and Chilbolton Observatory in December).
[2] The XRFs have a size fraction sampling switching inlet, measuring $PM_{2.5}$ and PM_{10} (particulate matter with an aerodynamic diameter < 10 µm) on alternate hours.
[3] Weekly samples are taken at Auchencorth Moss for OC/EC; daily samples are taken at the other three sites.
[4] The TSI 3936 SMPS was replaced with a TSI 3938W50-CEN SMPS in April 2023.
[5] The TSI 3936 SMPS was replaced with a TSI 3938W50-CEN SMPS in March 2023.

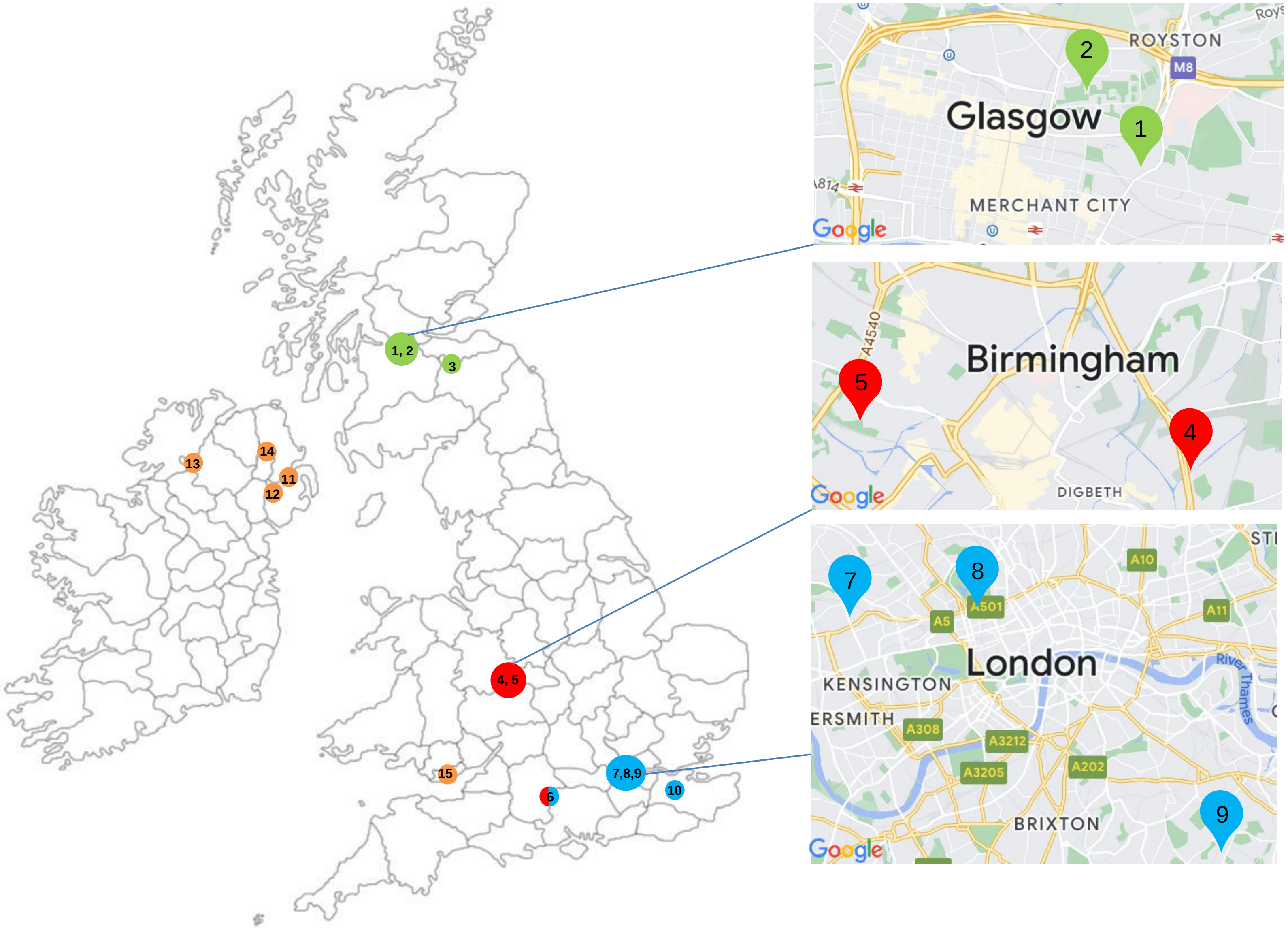


Figure 1 - Network sites in 2023. The colour key indicates the emissions sources representative of each site: Green = Glasgow Urban; Red = Birmingham Urban; Blue = London Urban; Orange = solid fuel use / domestic emissions.

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 2023 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

The very low data capture seen at the Chilbolton Observatory site was due to a fault in the dryer inlet system, which supplies both CPC and SMPS, which caused both instruments to sample cabin air. Mitigation measures have been put in place to more thoroughly leak check the new dryer systems at the point of installation.

Table 2 - Data capture for particle number concentration measurements

Site Name	Data capture / %
Chilbolton Observatory	15
London Marylebone Road	82
London Honor Oak Park	81
Average	**59**

2.3.2 Particle size distribution

The very low data capture seen at the Chilbolton Observatory site was due to a fault in the dryer inlet system as explained in section 2.3.1. The data capture loss at London Marylebone Road was due to a fault in the differential mobility analyser (DMA) column of the SMPS, where it over-read the particle number concentrations above 200 nm. This instrument had to be sent to the manufacturer (TSI) for repair. The first six months of the year were also affected by this issue but the particle number concentrations for size bins at 200 nm and below could be used and that data were submitted. The data capture loss at London Honor Oak Park was due to a contaminated DMA column on the SMPS. The DMA was cleaned at NPL and returned to site.

Table 3 - Data capture for particle size distribution measurements

Site Name	Data capture / %
Chilbolton Observatory	8
London Marylebone Road	54
London Honor Oak Park	76
Average	**46**

2.3.3 Aerosol mass and chemical composition

All three ACSMs operated without any major issues throughout 2023. At London Marylebone Road and London Honor Oak Park the main cause of data loss occurred due to PC connection issues and software crashes. At London Honor Oak Park there was a further loss of seven days due to a motor and motherboard failure.

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

Site Name	Data capture / %
Chilbolton Observatory	95
London Marylebone Road	90
London Honor Oak Park	85
Average	**90**

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 x-ray tube failure, 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	90
Average	**90**

2.3.5 OC/EC

The main cause of data loss at Auchencorth Moss and Chilbolton Observatory sites was due to temperature and pressure sensor failures, and subsequent long turnaround time for their delivery and replacement.

Table 6 - Data capture for OC/EC measurements

Site Name	Data capture / %
Auchencorth Moss	87
Chilbolton Observatory	91
London Marylebone Road	99
London Honor Oak Park	97
Average	**93**

2.3.6 BC and UVPM

The main cause of data loss at Birmingham Ladywood was due to wrong tape being installed on 7 September 2023. This was reported during service visit in 2024 thus data from September to December 2023 were not valid. At Ballymena Ballykeel there were a number of power cuts, which resulted in the instrument being sent for a technical review and servicing. There is limited data in May and June 2023 for this site.

Table 7 - Data capture for BC measurements

Site Name	Data capture / %
Auchencorth Moss	93
Ballymena Ballykeel	71
Belfast Centre	90
Birmingham A4540 Roadside	91
Birmingham Ladywood	64
Cardiff Centre	96
Chilbolton Observatory	96
Detling	97
Glasgow High Street	90
Glasgow Townhead	95
Kilmakee Leisure Centre	87
London Marylebone Road	93
London North Kensington	96
Strabane 2	86
Average	**89**

2.4 INSTRUMENTATION

2.4.1 Particle number concentration

Particle number concentrations are measured using TSI 3772-CEN-7 CPCs (Figure 2).

The CPCs operate by drawing a continuous airborne particle sample through a heated saturator, in which butanol is vapourised and diffuses into the sample stream. The particle sample and butanol vapour pass into a cooled condenser, where the butanol vapour becomes supersaturated. Under this condition, the butanol vapour condenses on the particles (down to 7 nm in size), growing quickly into larger droplets and enabling them to be counted optically via an optical detector. These CPCs are sensitive to particles from 7 nm up to a few micrometres in size and have a concentration measurement range from zero to 50,000 cm^{-3}. The TSI 3772-CEN-7 CPC was developed to comply with the requirements of the Technical Specification CEN/TS 16976:2016[12], (which has since been superseded by EN 16976:2024[13]). The CPC operates in single particle counting mode with continuous live-time coincidence correction for particle concentrations up to 50,000 cm^{-3}. CEN/TS 16976:2016[12] (which has since been superseded by EN 16976:2024[13]) outlines the measurement criteria for the control of humidity in the sampled aerosol.

When the TSI 3772-CEN-7 CPCs were installed in 2017, dryer systems manufactured by TSI were installed with them. After some initial teething problems, a solution of a TSI 3772200 Nafion dryer sampling system (Figure 2, left-top) for the stand-alone CPC and a separate NPL-designed Nafion dryer sampling system (Figure 3, left) for the SMPS were employed. As part of the installation of new Network SMPS systems in 2022/3, a new TSI 3750200 sampling system (Figure 2, right), shared between the SMPS and stand-alone CPC, replaced the older separate dryer systems. This system was installed at London Marylebone Road in August 2022, London Honor Oak Park in March 2023, and Chilbolton Observatory in April 2023. The main difference between the old and new dryer systems is that the new system does not dilute the particle number concentration of the ambient air sampled.

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

2.4.2 Particle size distribution

Particle size distributions were measured using a TSI 3938W50-CEN-7 SMPS (Figure 4) at all sites, except for the first two months of 2023 at London Honor Oak Park and Chilbolton Observatory which used the old TSI 3936 SMPS (Figure 3).

The new TSI 3938W50-CEN SMPS was installed at London Honor Oak Park and Chilbolton Observatory to replace the previous TSI 3936 SMPS, in March and April 2023, respectively. At the same time, a new TSI 3750200 sampling system was also installed at these sites to supply the SMPS and stand-alone CPC. This replaced the previous sampling and dryer system. This follows the same replacement at London Marylebone Road in 2022, so now all three sites have the same model of SMPS and sampling system.

A 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 TSI 3936 SMPS (nominally 16 - 600 nm). The new model consists of a TSI 3750-CEN-7 CPC combined with a TSI 3082 electrostatic classifier and a new TSI 3083 Vienna-type DMA. The charge neutralizer in the electrostatic classifier brings the particles in the airborne particles in the sample to a known steady state charge distribution and, at specific voltage, the DMA allows particles of a specific 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 of particles obtained. This new 3083 DMA is designed to cover a particle size range from 10 - 800 nm. This SMPS is compliant with CEN Technical Specification CEN TS 17434:2020[14].

With the new TSI 3938W50-CEN-7 SMPSs on the network, it is possible to reliably determine the SMPS particle number concentration (TNC-SMPS) from the weighted combination of the concentrations from all SMPS size bins. This therefore allows the TNC-SMPS to be reported to UK-Air[2], along with the expanded range of size bins. Previously, the only TNC data reported was for TNC-CPC (using data from the standalone CPC). It should be noted that the EN 16976:2024[13] standard method for determining TNC stipulates the use of a CPC. Variations between TNC-SMPS and TNC-CPC may be due to the effects of differing proportions of sub-20 nm particles in the sample – this is currently under further investigation in CEN TC264 WG32.

Figure 4 shows the new configuration of the SMPS, CPC, and sampling system. Note that instead of a TSI 3772-CEN-7 CPC, a TSI 3750-CEN-7 CPC is shown in the figure.

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, consisting of:

- 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 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.

This comparison between the two SMPS systems will be published in a separate NPL report in due course.

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/drying 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 Aerodyne Research Inc. (ARI) quadrupole Q-ACSM measures in real-time the mass and chemical composition of non-refractory sub-micrometre aerosol particles in ambient air. It uses established aerosol mass spectroscopy 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 aerodynamic lens focuses particles into a narrow beam which is directed to a resistively heated particle vaporiser, typically operated at 600 °C, mounted inside the electron impact ionisation chamber of a mass spectrometer, where non-refractory components in/on the particle flash vaporise. The vaporised constituents are ionised by electron impact and subsequently analysed with a quadrupole mass spectrometer which reports aerosol mass spectra (< 200 amu). These spectra are used to extract the chemically speciated aerosol mass loadings. Figure 5 shows a schematic diagram of the set up.

The 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.

Following the acquisition of two ToF (Time of Flight) ACSMs with standard vaporisers, due to be installed at two new rural supersites in 2024/25 as part of the upcoming Network expansion, the decision was made to harmonise vaporiser types across the Network and thereby mitigate fragmentation anomalies in the organic mass fraction and improve source apportionment. The ToF ACSM is very similar to the Q ACSM except it uses a time-of-flight detector with the additional advantages of increased mass resolution and lower detection limits. In 2023, all the capture vaporisers were replaced with standard vaporisers (London Marylebone Road and London Honor Oak Park in April 2023, and Chilbolton Observatory in December 2023).

Table 8 summarises the configuration of the three current Network ACSMs in 2023.

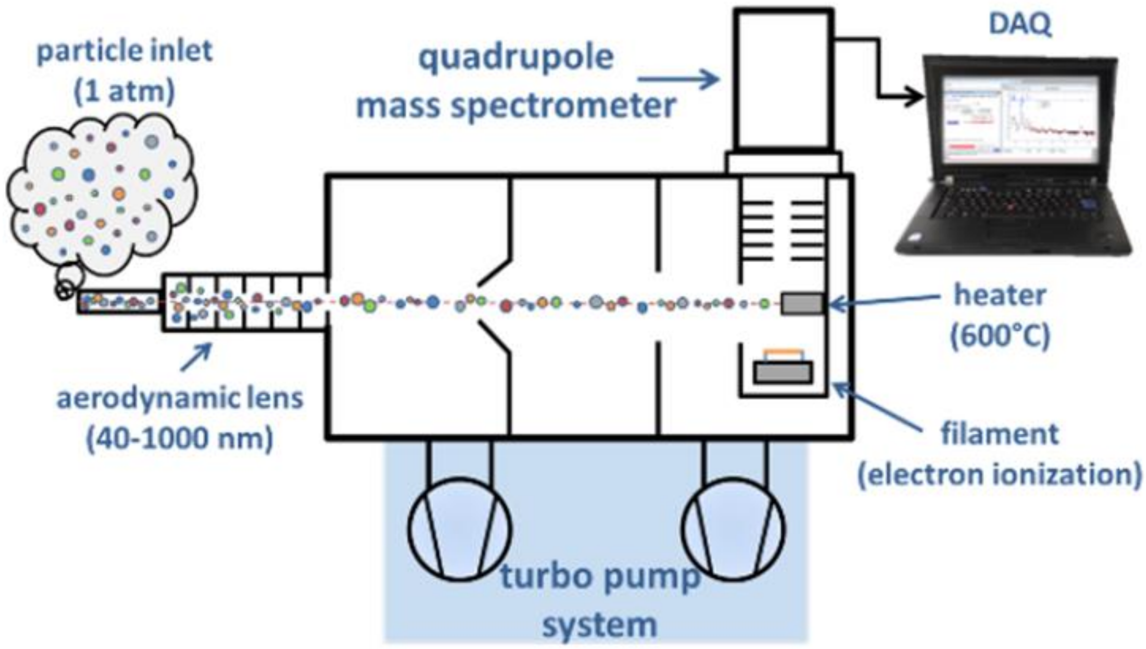


Figure 5 - ARI Q-ACSM schematic diagram (DAQ = Data acquisition [control]). Image copyright of Deutscher Wetterdienst (DWD).

Table 8 - Configuration of Network ACSM instruments

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

2.4.4 Elemental analysis

The Cooper Environmental Xact® 625i XRF analyser (Figure 6) continuously and simultaneously measures the ambient concentration of 40 elements: Ag, Al, As, Ba, Bi, Br, Ca, Cd, Ce, Cl, Co, Cr, Cu, Fe, Ga, Ge, Hg, In, K, La, Mn, Mo, Ni, P, Pb, Pd, Pt, S, Sb, Se, Si, Sn, Sr, Te, Ti, Tl, V, Y, Zn, Zn and Zr. 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. Both instruments use a switching valve, which alternates between sampling PM_{10} and $PM_{2.5}$ on an hourly basis. The sampling is only interrupted during tape advances and during internal QA/QC checks at midnight daily.

More information and evaluations of the instrumentation can be found in Furger *et al*., 2017[15] and Tremper *et al*., 2018[16].

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 2022.

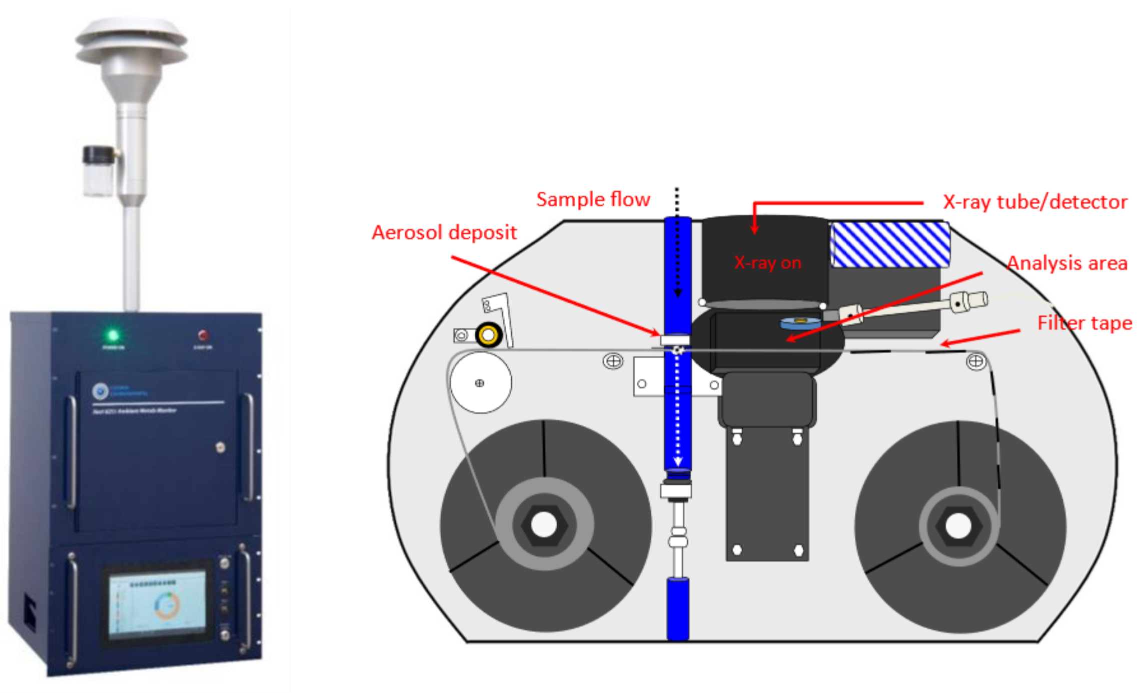


Figure 6 - Xact 625i instrument (left) and sampling schematic (right). Images courtesy of Cooper Environmental Services.

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 2023, sampling of $PM_{2.5}$ continued at all four sites using Digitel DPA14 samplers (Figure 7).

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[17]. 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 - Digitel DPA14 sampler, photograph courtesy of Digitel AG.

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 flow), are used to calculate attenuation. The rate of change of the attenuation of light, together with flow rate, spot 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*.[18]. The results from the 880 nm channel (BC) give the quantitative concentration of 'black' carbon, and those from 370 nm channel (UV) 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 of both models is, 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 2023 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[19].

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[20]. NPL is accredited to International Standard ISO/IEC 17025:2017[21] 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 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 perform repeat measurements every 15 minutes, providing verified data.
- NPL is accredited by UKAS to ISO 17025 to perform the calibration of CPCs directly against the UK primary reference electrometer. 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 factors are then applied during ratification to give the best estimate of the particle number concentrations.
- The CPC instruments undergo annual servicing: replacing the saturator wick, cleaning the critical orifice, and replacing any discoloured or damaged tubing.

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, an aerosol containing a single size of polystyrene latex nanospheres is used to check the sizing accuracy. This aerosol is generated using a nebuliser and conditioned with a diffusion dryer.
- The SMPS instruments undergo annual servicing where the DMA column is cleaned,

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 ACTRIS standard operating procedures (SOPs) developed for the ACSM[22].
- 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 ACSM ACTRIS SOPs[22]. 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 inlet cleaning and tape changes (as required).
- Flow rate checks and calibration checks are performed every quarter by trained technical users. For the calibration checks, five thin film standards covering different analysis conditions of the instrument are used to verify the instrument operates within its parameters.
- Annual 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 12341:2023[23]. 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 NPL Teddington 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 rate, tape life and data from the other five channels are remotely downloaded by ERG's 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"[24].

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

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[25]. 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 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).

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 2023 were 3.5 % in $PM_{2.5}$ and 3.2 % in PM_{10} at London Marylebone Road, and 6.2 % in $PM_{2.5}$ and 4.5 % 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 7.4 % in $PM_{2.5}$ and 4.9 % in PM_{10} at London Marylebone Road, and 8.1 % in $PM_{2.5}$ and 7.2 % in PM_{10} at London Honor Oak Park.

3.2.5 OC/EC

The uncertainty in the measured TC concentrations is a combination of the analytical uncertainty and the uncertainty in the measured sample volume. The expanded analytical uncertainty for TC has been found to be 6 % relative. EN 12341:2023[23] requires the consistency of the average volumetric flow rate 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

A method for the determination of the uncertainty of BC mass concentration has not yet standardised, but this is one of the deliverables in the European Partnership of Metrology project STANBC[26]. However, NPL's current uncertainty budget estimates the expanded uncertainty for the annual concentration of BC measured using the AE33 Aethalometer to be 9 %, with the dominant uncertainty contribution being the measurement of the flow rate. Uncertainties related to the default parameters used in the Aethalometer are not yet taken into account.

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 CPC

NPL holds ISO 17025[21] accreditation for CPC calibration. The Network CPCs are serviced and calibrated at NPL on an annual basis. Details of the calibration are provided in section 3.1.1.

3.3.2 SMPS

The SMPS instruments have been serviced and calibrated at NPL on an annual basis. Details of the calibration are provided in section 3.1.2.

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* callouts and repairs.

3.3.5 Digitel 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. The 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 Sunset Laboratory Inc. L5 thermal/optical carbon analyser is serviced annually by a Sunset Laboratory Inc. service 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 CONCENTRATION

4.1.1 2023 time series

Time series of hourly particle number concentrations (between approximately 7 nm and 2.5 µm in diameter) measured at Network sites during 2023 are shown in Figure 10. As described in section 2.3.1, minimal data was recorded for Chilbolton Observatory due to a fault in the dryer inlet system.

4.1.2 2023 diurnal, weekly, and monthly profiles

The diurnal, weekly, and monthly profiles for particle number concentrations in 2023 are shown for the London Honor Oak Park and London Marylebone Road sites in Figure 11 and Figure 12 respectively (plots generated using the OpenAir Tools run on the R software platform[27,28]). There was insufficient data capture to generate a plot for Chilbolton Observatory in 2023 due to a fault in the dryer inlet system, which caused the CPC instrument to sample cabin air.

At both sites there are higher concentrations during the working week and lower concentrations on a Sunday. The concentrations remain higher on a Saturday at London Marylebone Road compared to London Honor Oak Park which follows the same trend as the 2022 particle number concentration data. There is also a clear increase in particle number concentration at both sites during the evening, although this is less significant at London Marylebone Road.

4.1.3 Long-term trends

Figure 13 and Figure 14 show long-term annual trends for CPC measurements at all sites. The 2017 data are omitted due to the installation of new CPCs in that year. As discussed in section 4.1.2, there was also insufficient data capture to generate a datapoint for Chilbolton Observatory in 2023.

The London Ultra Low Emission Zone (ULEZ) was introduced in April 2019 and encompassed the London Marylebone Site. The ULEZ was expanded so to also cover the London Honor Oak Park site in October 2021. The effect of the ULEZ on measured annual particle number concentrations at London Marylebone for 2020 and 2021 was difficult to determine, predominantly due to the potential influence of the Covid-19 lockdown in those years. The 2022 and 2023 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[29,30,31] in 2021.

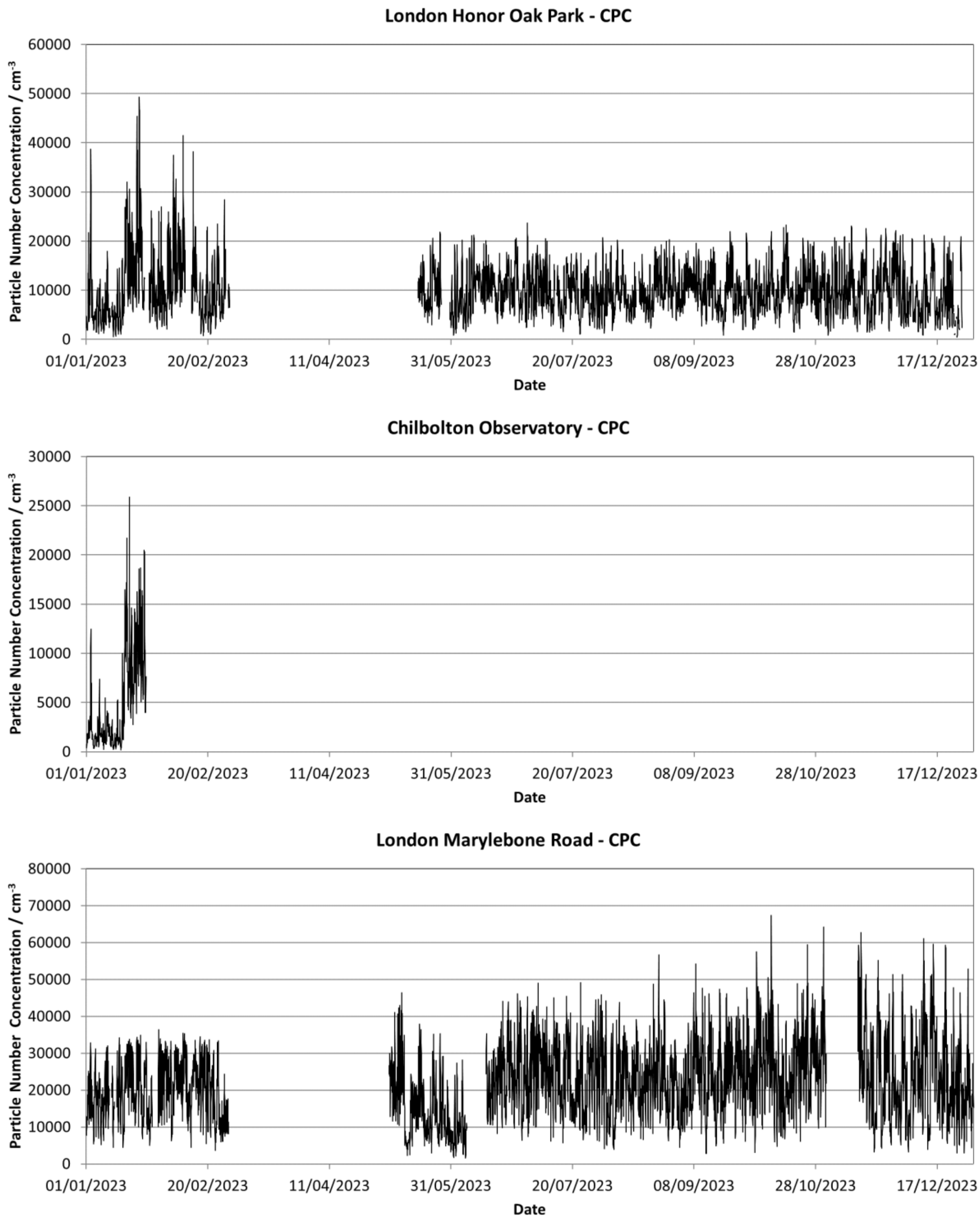


Figure 10 - Hourly particle number concentrations at London Honor Oak Park, London Marylebone Road, and Chilbolton Observatory in 2023.

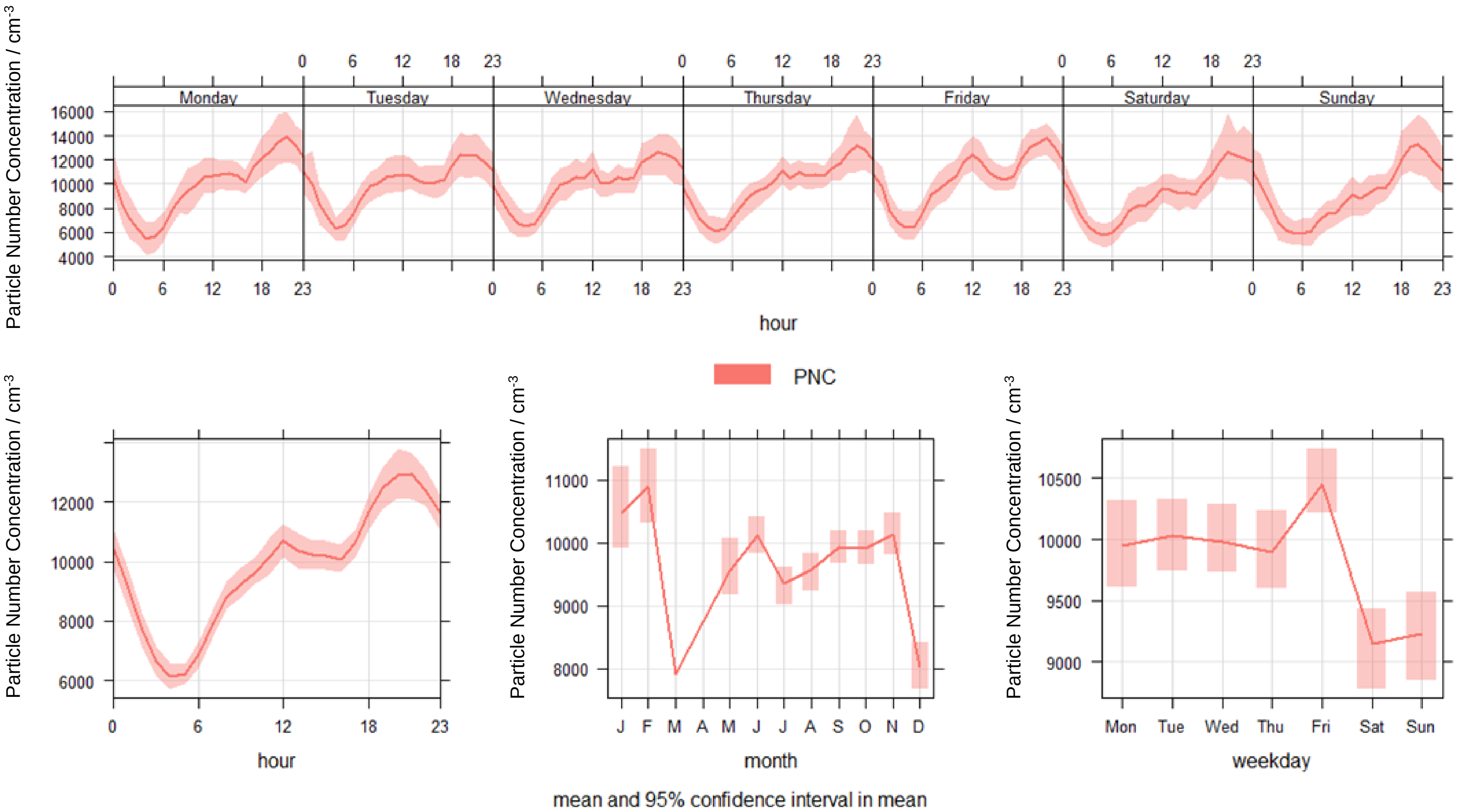


Figure 11 – Diurnal, weekly and monthly variations of particle number concentrations in 2023 at London Honor Oak Park. The solid lines represent the mean particle number concentration, and the shaded areas represent the 95% confidence interval in the mean. Note that any line joining non-consecutive months 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).

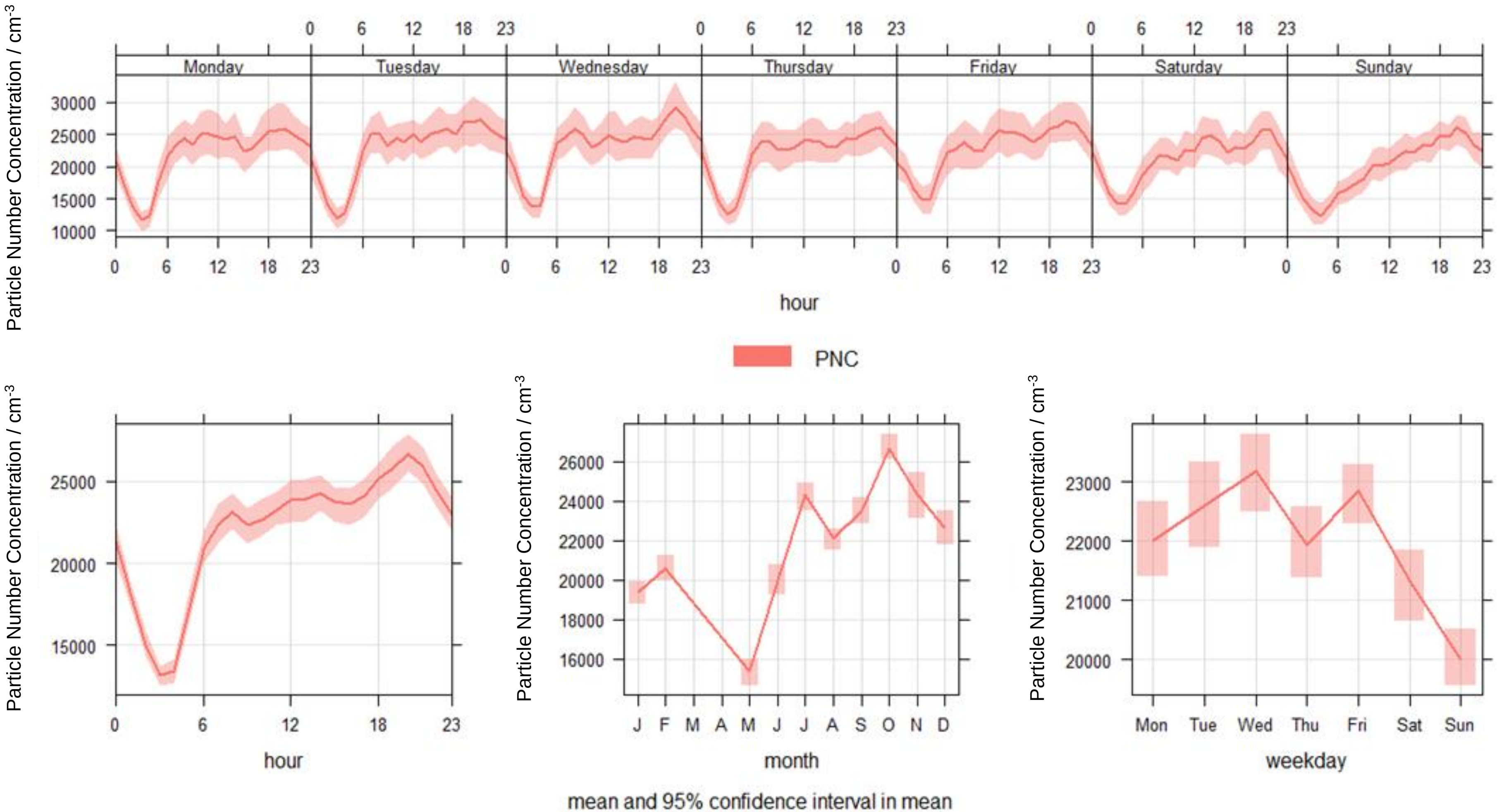


Figure 12 – Diurnal, weekly and monthly variations of particle number concentrations in 2023 at London Marylebone Road. The solid lines represent the mean particle number concentration, and the shaded areas represent the 95% confidence interval in the mean. Note that any line joining non-consecutive 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).

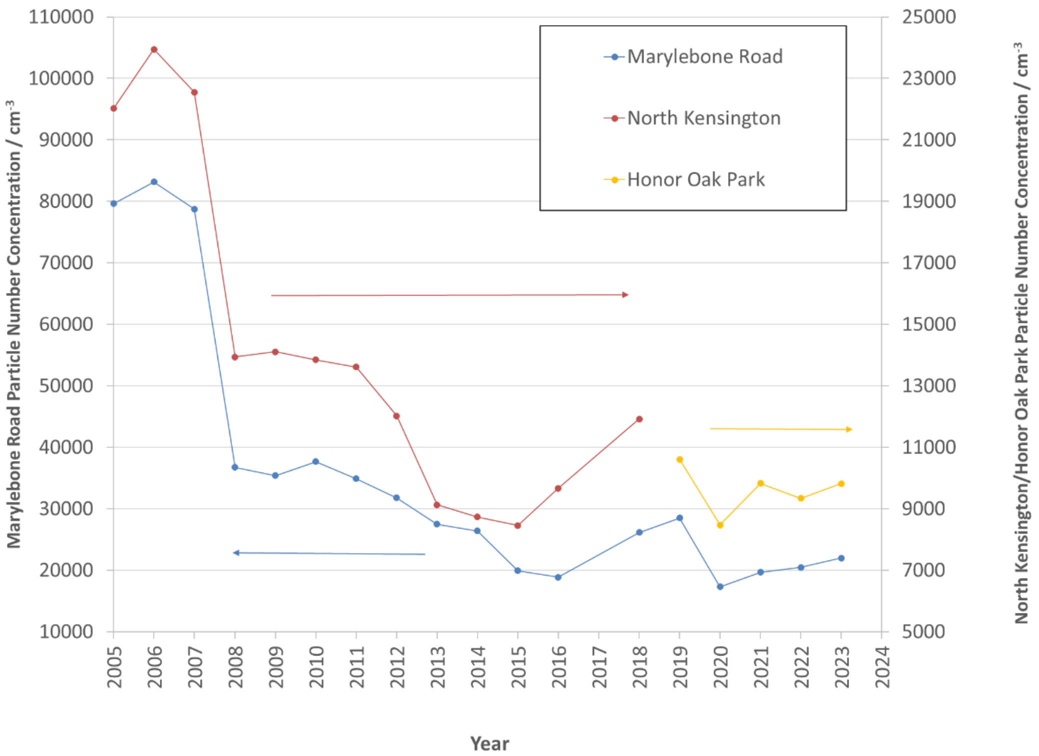


Figure 13 - Long-term particle number concentrations annual trends at all London sites. The London North Kensington site moved to London Honor Oak Park in November 2018.

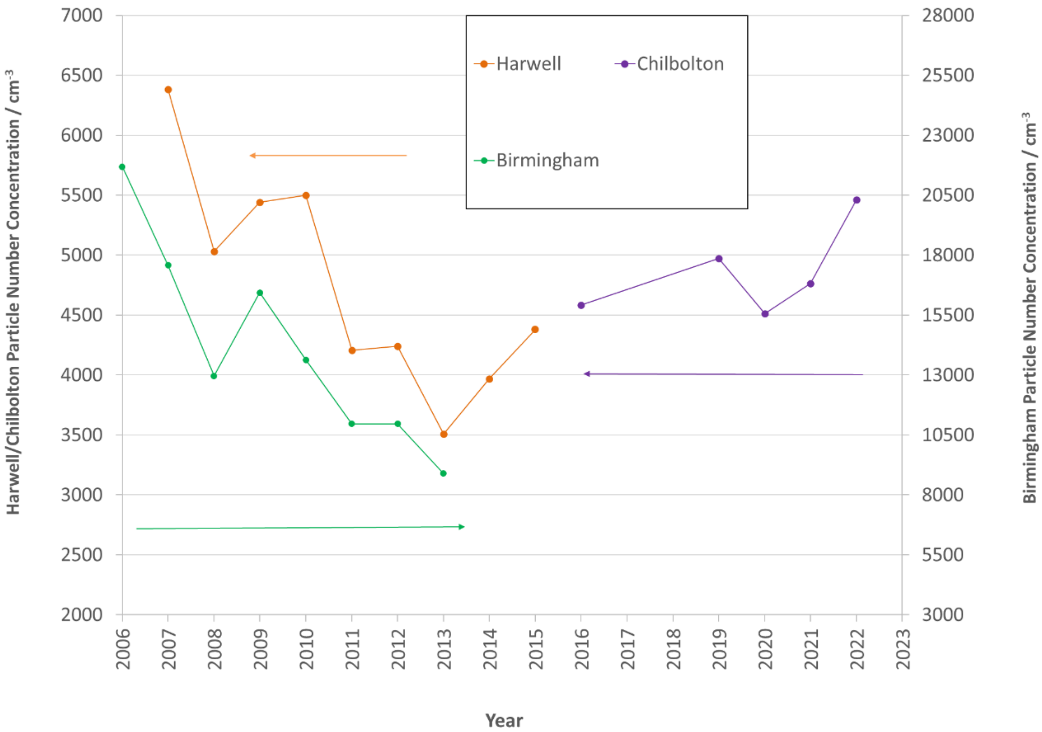


Figure 14 - Long-term particle number concentrations annual trends at all sites outside London. The Harwell site moved to Chilbolton Observatory in 2016. Note: there was insufficient data capture to include data from 2023.

4.2 PARTICLE SIZE DISTRIBUTION

4.2.1 2023 time series

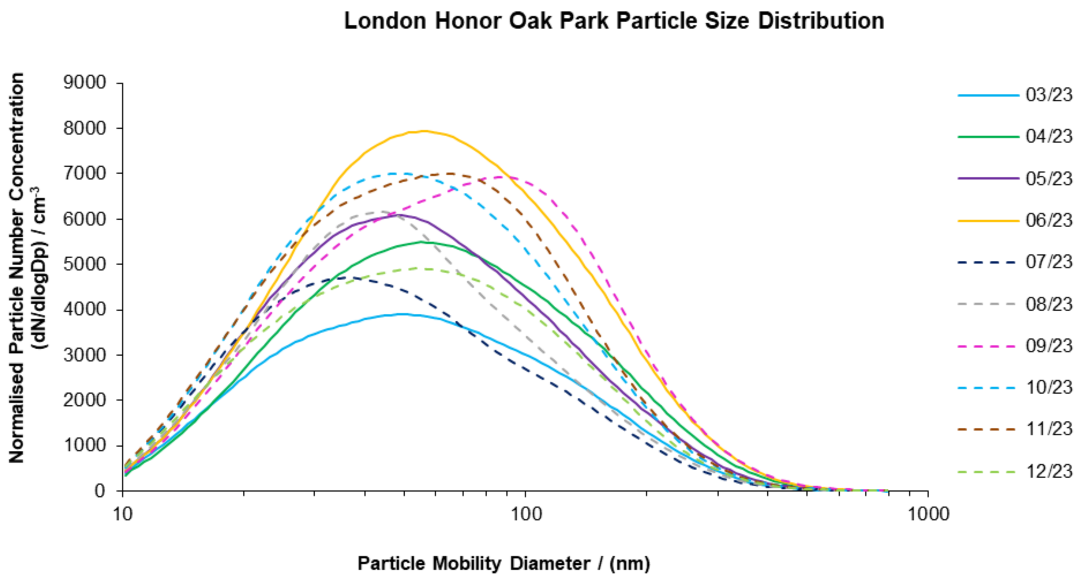
Time series of monthly particle size distributions measured at Network sites during 2023 are shown in Figure 15. The plots show both the variation in particle number concentration and the shape of the particle size distribution across 2023 at each site. For Chilbolton Observatory, there was insufficient valid data to generate a meaningful plot.

4.2.2 2023 diurnal, weekly, and monthly profiles

The diurnal, weekly, and monthly profiles for particle number concentrations as an integral over the collected SMPS particle size range in 2023 are shown for the London Honor Oak Park and London Marylebone Road sites in Figure 16 and Figure 17 respectively (plots generated using the Open Air Tools run on the R software platform[27,28]). There was insufficient data capture generate a plot for Chilbolton Observatory in 2023.

4.2.3 Long-term trends

Time series of annual particle size distributions measured at Network sites from 2019 to 2023 are shown in Figure 18. The plots show both the variation in particle number concentration and particle size distribution. The plot for Chilbolton Observatory is only up to 2022 due to low data capture in 2023 at this site. The introduction of the newer model of SMPS at the sites in 2023 has shown a broadening of the particle size distribution. It has also shown a shift of the peak to larger mobility diameters at a both London Honor Oak Park and London Marylebone Road. This, however, is most likely an artefact of the change in instrument rather than a shift in the particle size distribution of the ambient aerosol. This will be explored further in the SMPS comparison report.



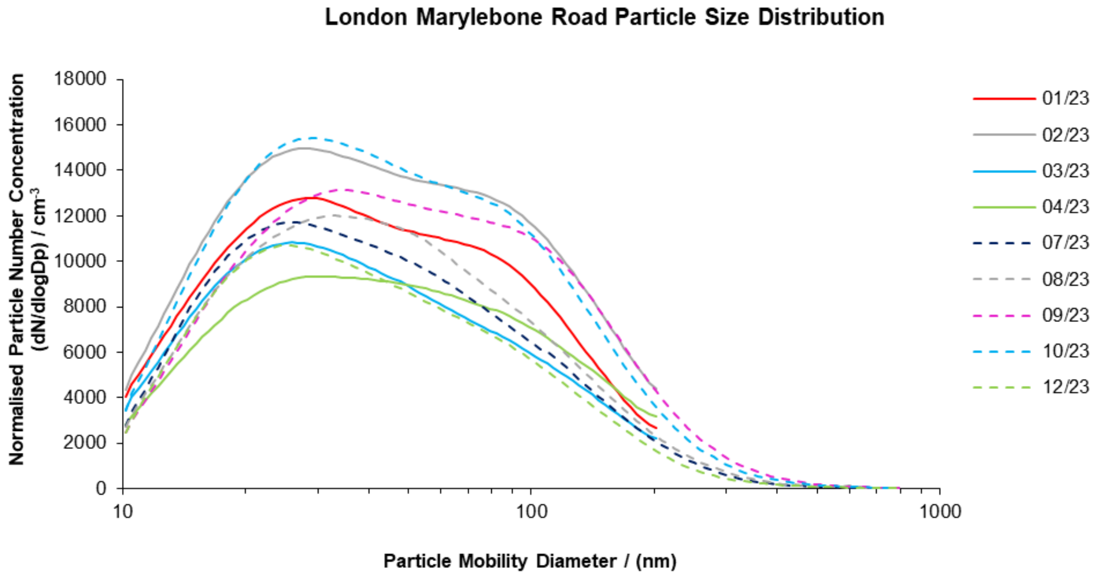


Figure 15 - Monthly averaged particle size distributions at the Network sites for each month during 2023. There was no TSI 3938W50-CEN-7 data from Chilbolton Observatory for 2023. Data for January and February 2023 at the London Honor Oak Park and Chilbolton Observatory sites are not included as this data was from the TSI 3936 SMPS and the rest of the data was from the new TSI 3938W50-CEN-7 SMPS.

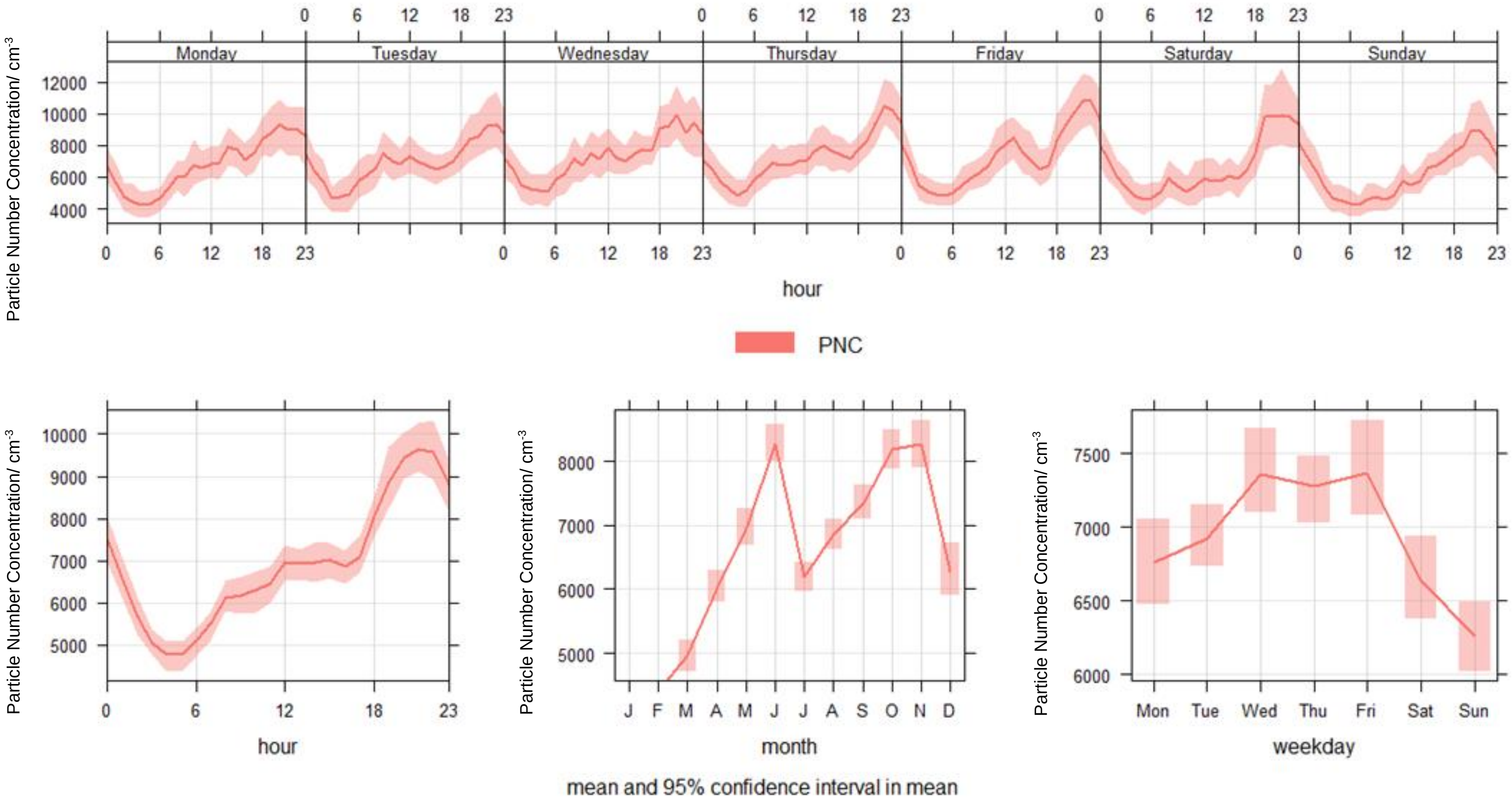


Figure 16 – Diurnal, weekly and monthly variations of particle number concentrations from SMPS averages in 2023 at London Honor Oak Park. The solid lines represent the mean particle number concentration, and the shaded areas represent the 95% confidence interval in the mean. Note that any line joining 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).

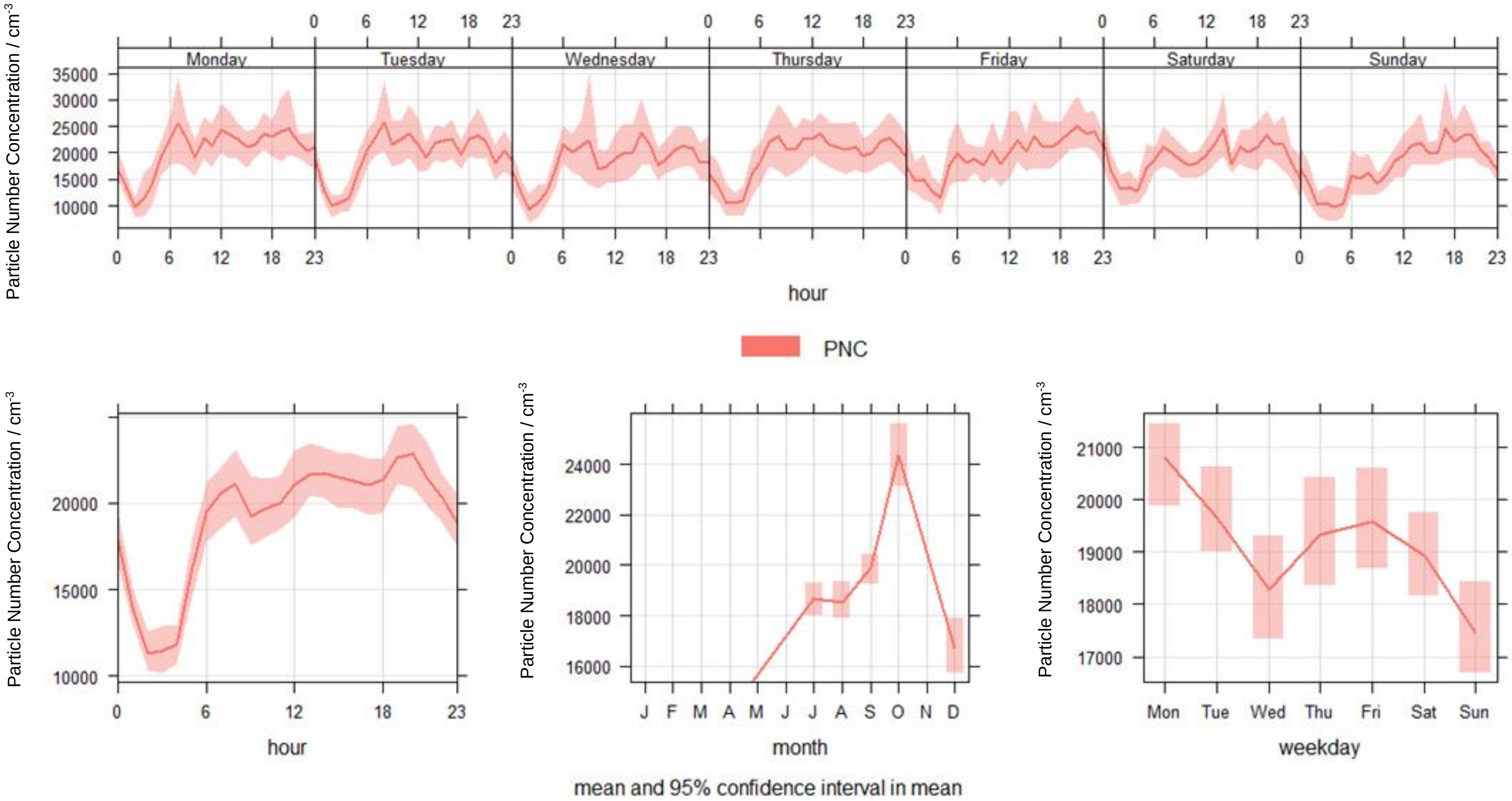


Figure 17 – Diurnal, weekly and monthly variations of particle number concentrations from SMPS averages in 2023 at London Marylebone Road. The solid lines represent the mean particle number concentration, and the shaded areas represent the 95% confidence interval in the mean. The first six months of the year have been excluded from these plots as a full particle size distribution was not recorded, due to an instrument error only the size bins of 200 nm and below were useable. 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).

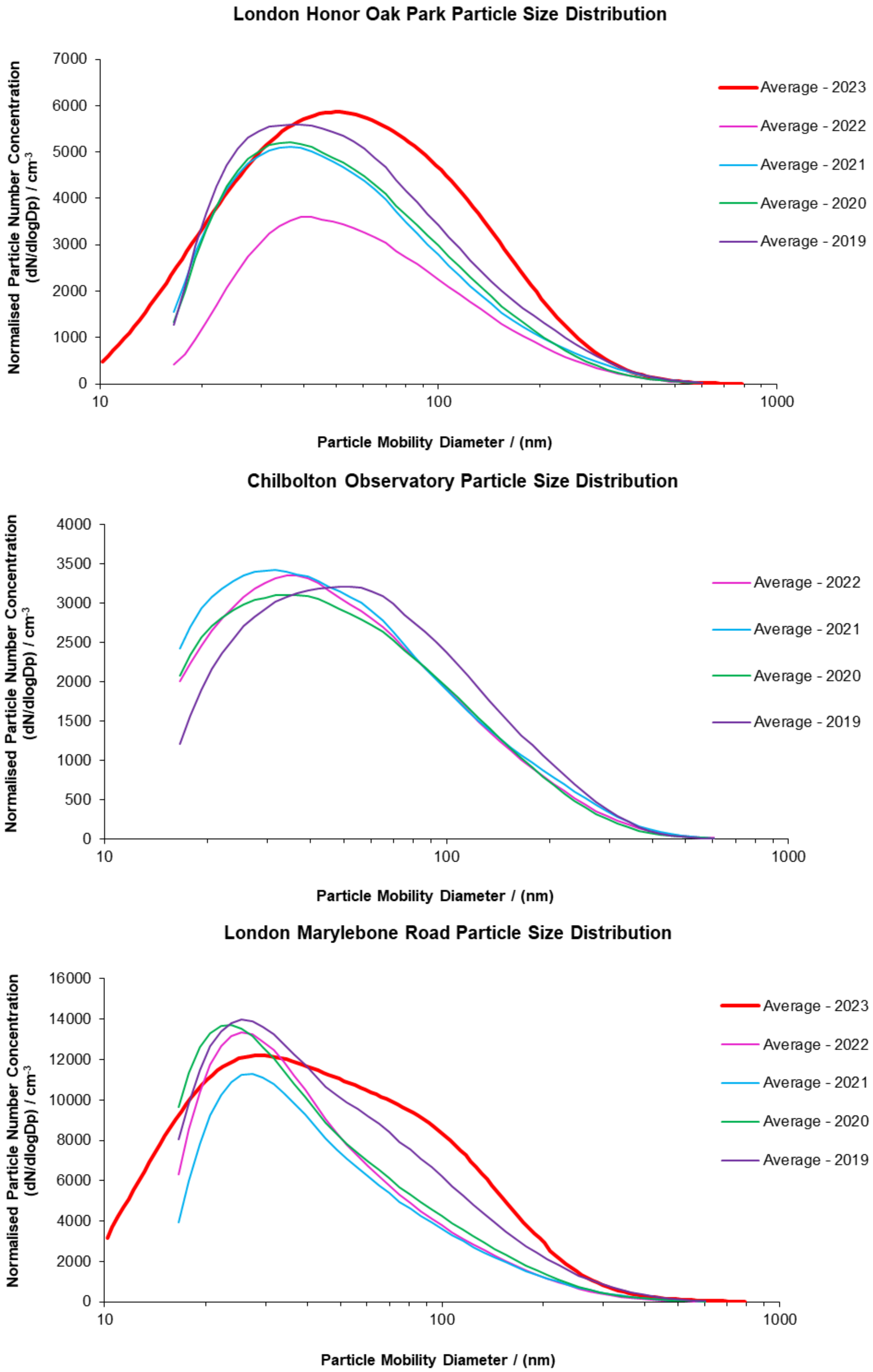


Figure 18 - Comparison of the 2019 to 2023 annual average size distribution. Note that measurements have only taken place at London Honor Oak Park since 2019 and at Chilbolton Observatory since 2016. The data for January and February 2023 from the old TSI 3936 SMPS at the London Honor Oak Park site are not included here. The data for Chilbolton Observatory is only up to 2022 due to low data capture in 2023 at this site.

4.3 AEROSOL MASS AND CHEMICAL COMPOSITION

4.3.1 2023 time series

Figure 19 to Figure 21 (plots generated using the OpenAir Tools run on the R software platform[27,28]) 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 2023. In 2023, all the capture vaporisers were replaced with standard vaporisers (London Marylebone Road and London Honor Oak Park in April 2023, and Chilbolton Observatory in December 2023).

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 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 Observatory.

Figure 22 to Figure 25 (plots generated using the Open-Air Tools run on the R software platform[27,28]) 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.

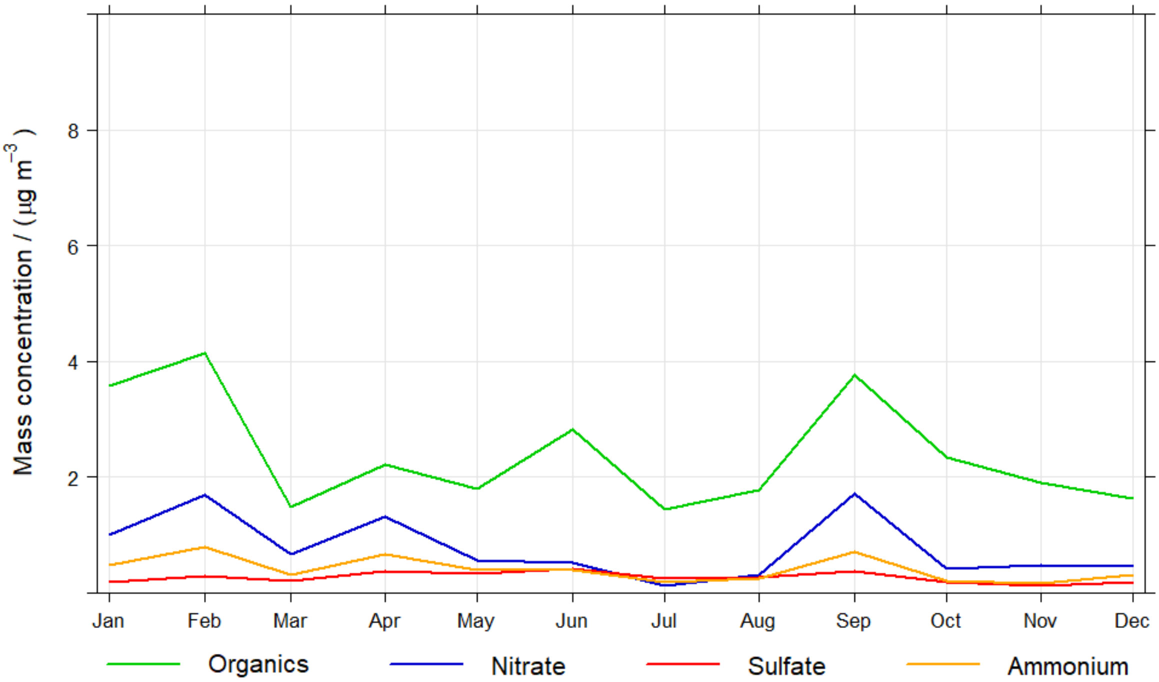


Figure 19 - Monthly average mass concentrations of organics, nitrate, sulfate, and ammonium in $PM_{2.5}$ measured by ACSM in 2023 at London Honor Oak Park.

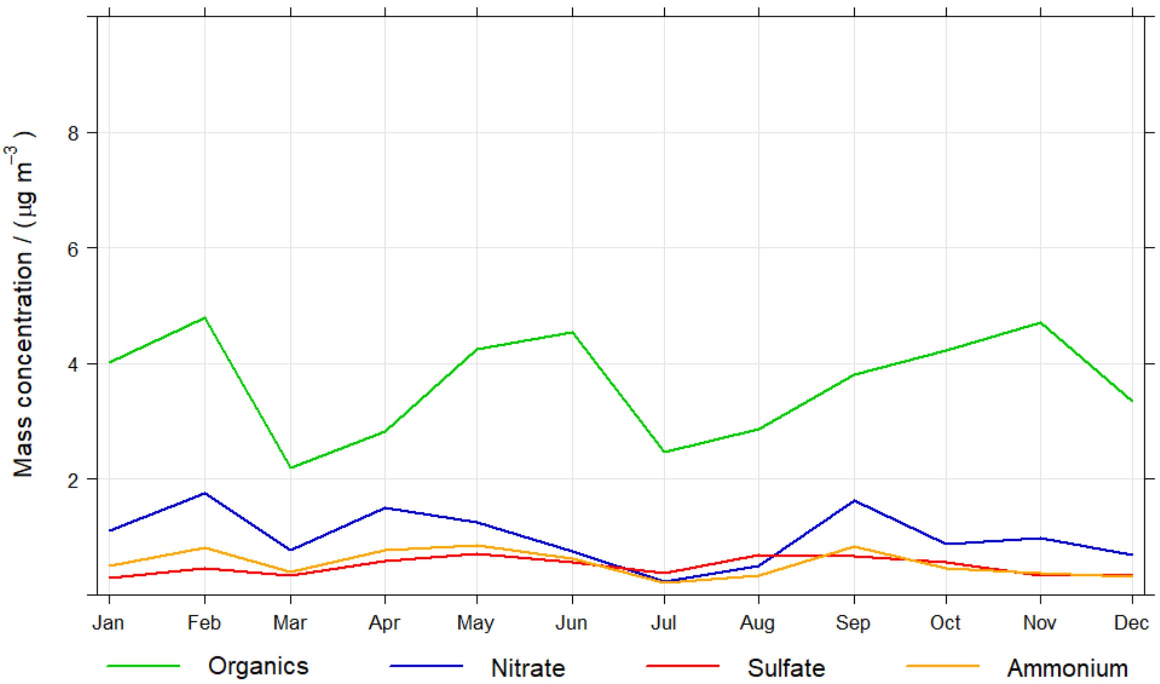


Figure 20 - Monthly average mass concentrations of organics, nitrate, sulfate, and ammonium in PM_1 measured by ACSM in 2023 at London Marylebone Road.

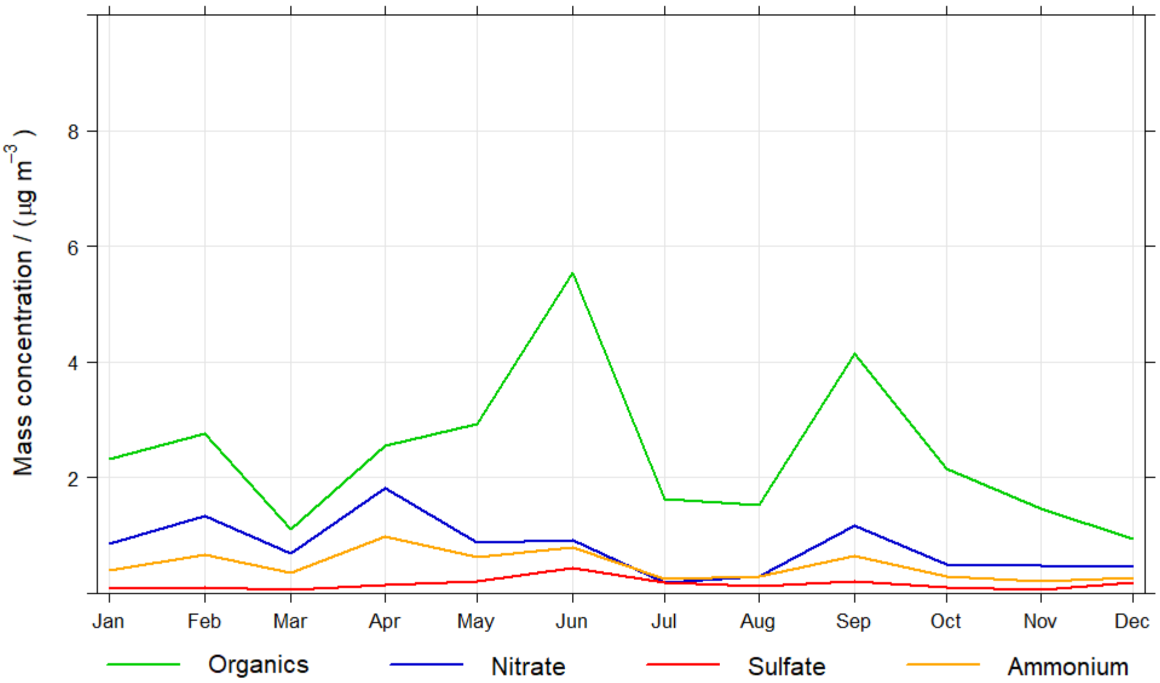


Figure 21 - Monthly average mass concentrations of organics, nitrate, sulfate, and ammonium in $PM_{2.5}$ measured by ACSM in 2023 at Chilbolton Observatory.

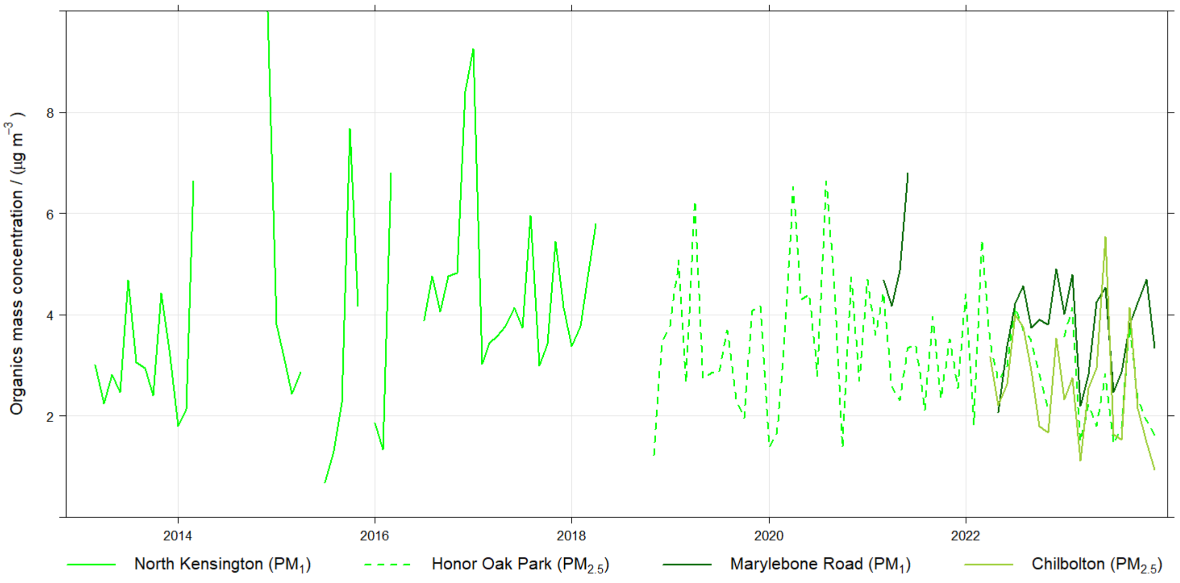


Figure 22 - Long-term mass concentration trends of organics at the rural background site Chilbolton Observatory, urban background site London Honor Oak Park (London North Kensington before 2019) and roadside site London Marylebone Road. The tick marks on the x-axis indicate the start of each year.

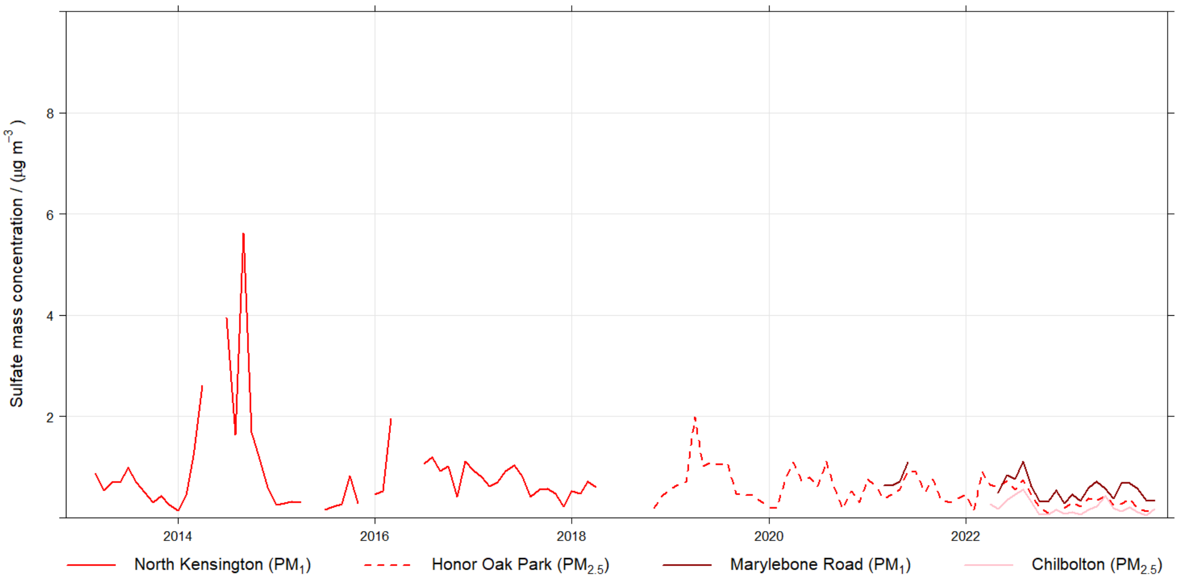


Figure 23 - Long-term mass concentration trends of sulfate at the rural background site Chilbolton Observatory, urban background site London Honor Oak Park (London North Kensington before 2019) and roadside site London Marylebone Road. The tick marks on the x-axis indicate the start of each year.

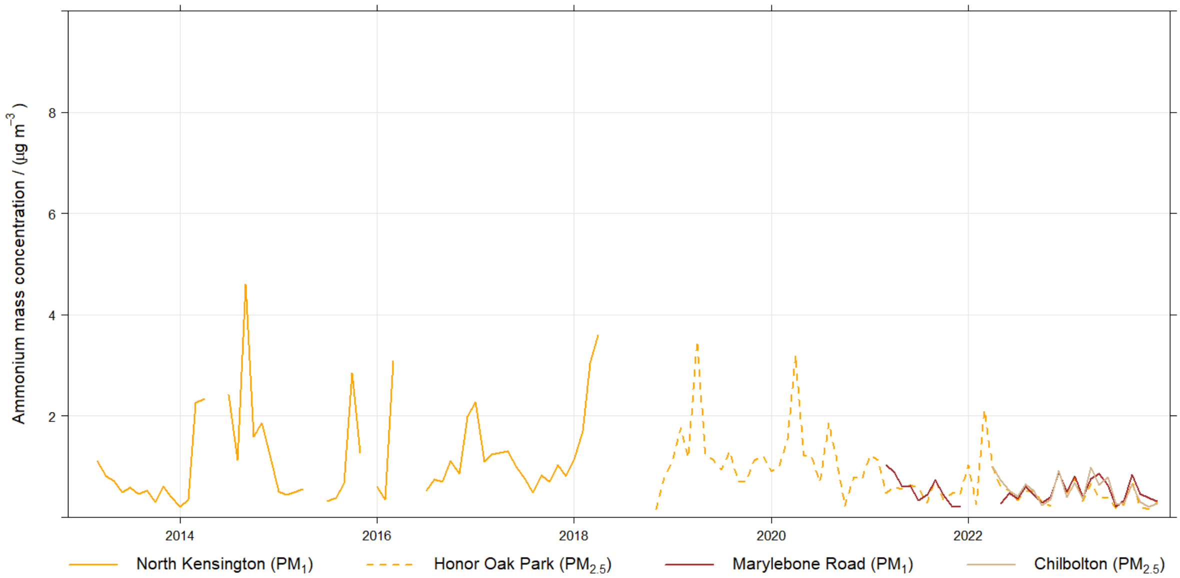


Figure 24 - Long-term mass concentration trends of ammonium at the rural background site Chilbolton Observatory, urban background site London Honor Oak Park (London North Kensington before 2019) and roadside site London Marylebone Road. The tick marks on the x-axis indicate the start of each year.

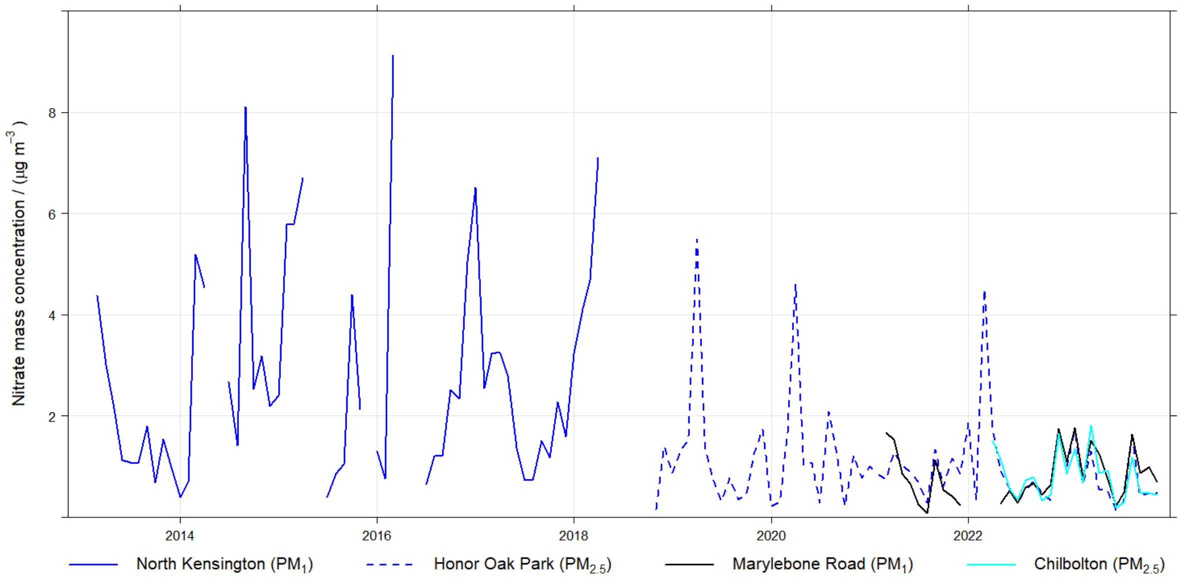


Figure 25 - Long-term mass concentration trends of nitrate at the rural background site Chilbolton Observatory, urban background site London Honor Oak Park (London North Kensington before 2019) and roadside site London Marylebone Road. The tick marks on the x-axis indicate the start of each year.

4.4 ELEMENTAL ANALYSIS

4.4.1 2022-23 time series

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

Figure 26 to Figure 28 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 and 2023 for both $PM_{2.5}$ and PM_{10}. These six elements were chosen from the 40 measured as examples, because for these elements a significant proportion (more than 90 %) 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 2023. 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.

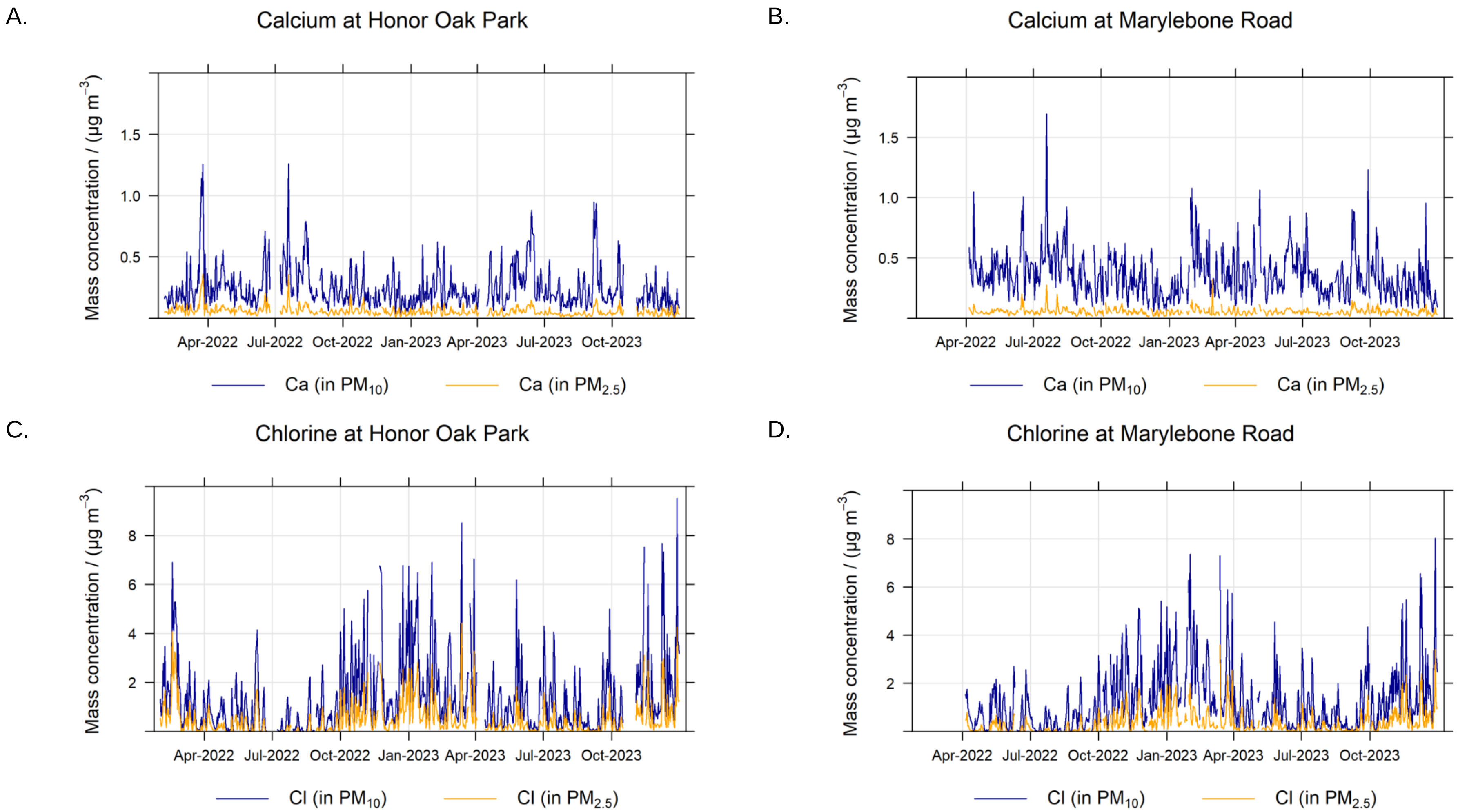


Figure 26 - Daily calcium (A, B) and chlorine (C, D) concentrations in 2022-23 at London Honor Oak Park (A, C) and London Marylebone Road (B, D) based on interpolated bihourly data. The tick marks on the x-axes indicate the start of every third month.

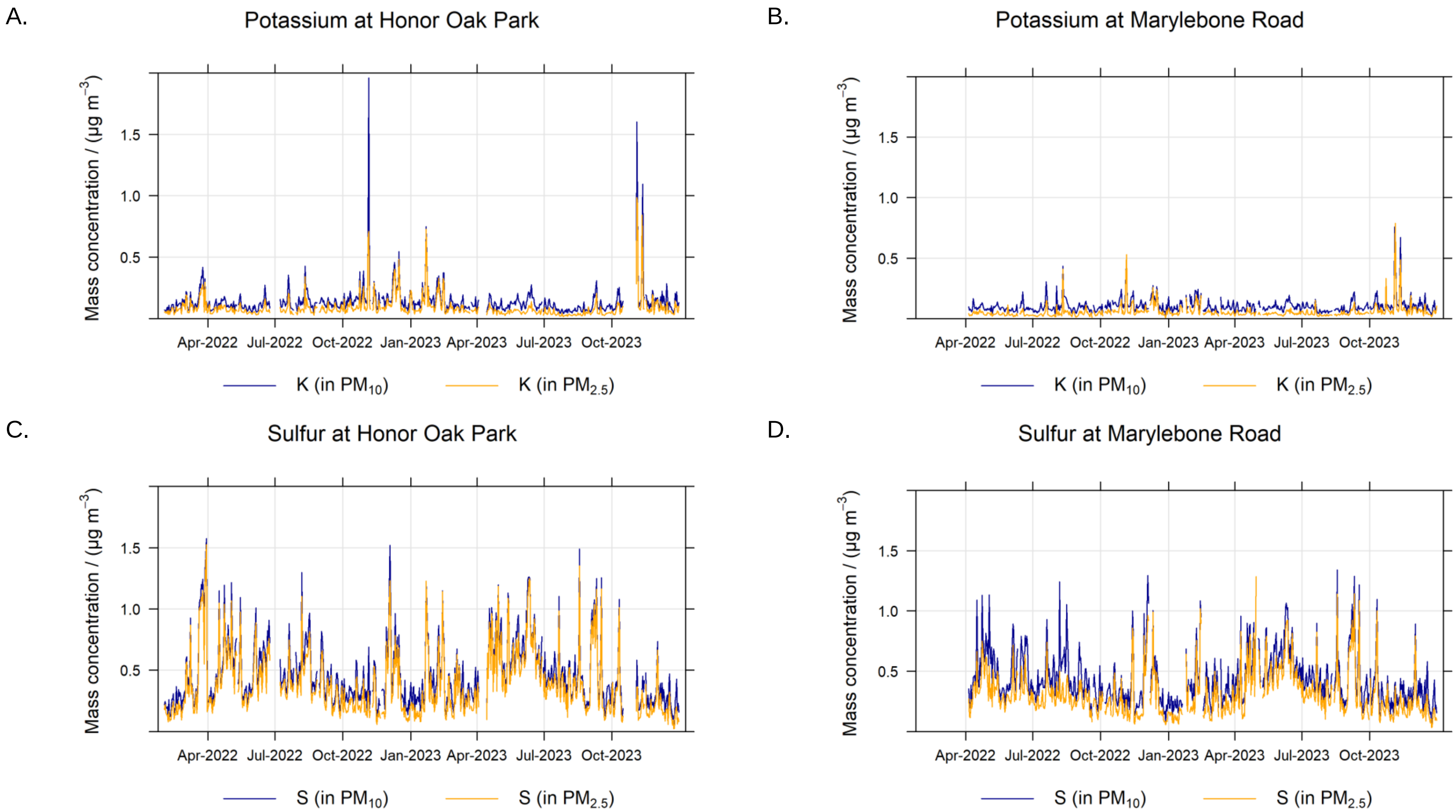


Figure 27 - Daily potassium (A, B) and sulfur (C, D) concentrations in 2022-23 at London Honor Oak Park (A, C) and London Marylebone Road (B, D) based on interpolated bihourly data. The tick marks on the x-axes indicate the start of every third month.

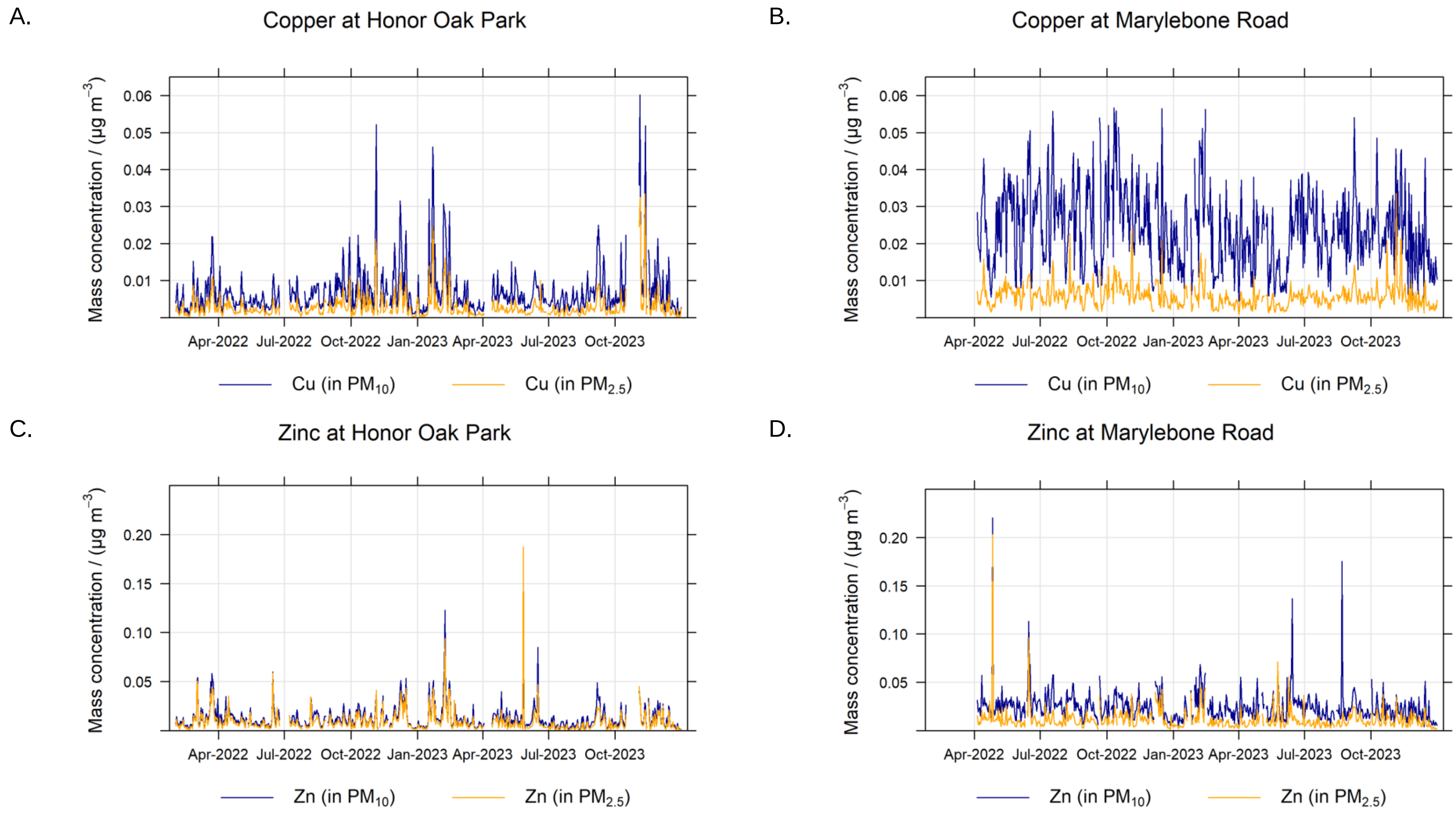


Figure 28 - Daily copper (A, B) and zinc (C, D) concentrations in 2022-23 at London Honor Oak Park (A, C) and London Marylebone Road (B, D), based on interpolated bihourly data. The tick marks on the x-axes indicate the start of every third month.

Table 9 - Mean mass concentration, 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 2023. The data are based on bihourly sampling, which is taken into account for the data capture calculation.

		London Honor Oak Park				London Marylebone Road			
Element	LoD for metals in PM / (µg m^{-3})	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	0.00067	93	0.0007	93	0.0013	88	0.0012	88
Al	0.17	0.06	87	0.085	83	0.36	24	0.35	30
As	0.00011	0.0016	16	0.0019	15	0.0021	7.2	0.0025	4
Ba	0.00067	0.001	82	0.003	52	0.0017	43	0.0095	7.9
Bi	0.00023	0.00021	97	0.00029	97	0.00016	98	0.00016	97
Br	0.00018	0.0034	2.3	0.0049	1	0.0034	1.5	0.0049	0.7
Ca	0.00052	0.047	0.4	0.23	0	0.052	0	0.34	0
Cd	0.0044	0.01	48	0.01	48	0.00014	100	0.00018	99
Ce	0.00052	0.000023	99	0.000022	99	0.0000016	100	0.0000002	100
Cl	0.003	0.53	3	1.6	0.2	0.41	4.7	1.4	0.5
Co	0.00024	0.000021	98	0.000011	99	0.0000022	100	0.0000021	100
Cr	0.0002	0.00021	74	0.0009	33	0.00068	34	0.0048	2.9
Cu	0.00014	0.0029	7.1	0.0071	1.8	0.0053	0.2	0.022	0
Fe	0.0003	0.08	0	0.26	0	0.21	0	0.89	0
Ga	0.0001	0.000013	95	0.000011	96	0.0000022	100	0.0000004	100
Ge	0.0001	0.000004	99	0.0000031	100	0.0000004	100	0.0000005	100
Hg	0.00021	0.0000047	100	0.0000039	100	0.0000038	100	0.0000021	100
In	0.0054	0.001	96	0.001	96	0.00019	100	0.00022	99
K	0.002	0.084	0	0.13	0	0.057	0.2	0.1	0.1
La	0.00063	0.000011	100	0.0000063	100	0.0000004	100	0.0000005	100
Mn	0.00025	0.0005	67	0.0022	26	0.00088	43	0.0058	2.6
Mo	0.00084	0.000024	100	0.000039	99	0.000044	99	0.00026	92
Ni	0.00017	0.00035	56	0.00044	49	0.0002	74	0.00038	48
P	0.009	0.00016	100	0.000072	100	0.00014	100	0.000031	100
Pb	0.00022	0.0027	74	0.003	70	0.0022	46	0.003	32
Pd	0.0038	0.0063	44	0.0061	46	0	100	0.000005	100
Pt	0.0002	0.0000009	100	0.0000002	100	0.0000001	100	0	100
S	0.0055	0.39	0.6	0.47	0.3	0.32	0	0.43	0
Sb	0.009	0.0013	96	0.0014	96	0.00044	99	0.0006	99
Se	0.00014	0.00015	71	0.00017	66	0.00011	83	0.00011	80
Si	0.031	0.0097	94	0.16	59	0.0035	98	0.19	46
Sn	0.0071	0.0021	91	0.0021	90	0.0014	96	0.0024	90
Sr	0.00038	0.00048	78	0.0013	41	0.00034	89	0.0014	31
Te	0.001	0.0063	39	0.0063	39	0.0044	36	0.0047	34
Ti	0.00028	0.0018	19	0.0077	4.8	0.0022	10	0.014	0.4
Tl	0.0002	0.0000041	100	0.0000031	100	0.0000003	100	0	100
V	0.00021	0.0006	61	0.00069	57	0.00032	76	0.00038	73
Y	0.00048	0.00054	70	0.00056	70	0.000053	97	0.000055	97
Zn	0.00012	0.0086	9.8	0.012	3.3	0.01	0	0.022	0
Zr	0.00057	0.00014	92	0.0004	77	0.00014	91	0.0021	28

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 combustion of fossil fuels, predominantly from heavy hydrocarbons (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 AQSR[3,4,5,6] (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 2023 time series

The time series of OC, EC, and TC (the sum of OC and EC) are displayed in Figure 29 to Figure 32 for each site. The plots for London Marylebone Road, London Honor Oak Park, and Chilbolton Observatory comprise daily data; the plot for Auchencorth Moss comprises weekly data.

4.5.2 Long-term trends

Figure 33 and Figure 34 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 2023) is plotted continuously with the data from the former Harwell site and its daily data is plotted continuously with the former weekly data.

Figure 35 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).

The London Marylebone Road OC, EC and TC concentrations showed a downward trend over the period 2008 to 2020. The period after 2020 shows more stable concentrations for EC and upward trend for OC and TC concentrations at all London sites.

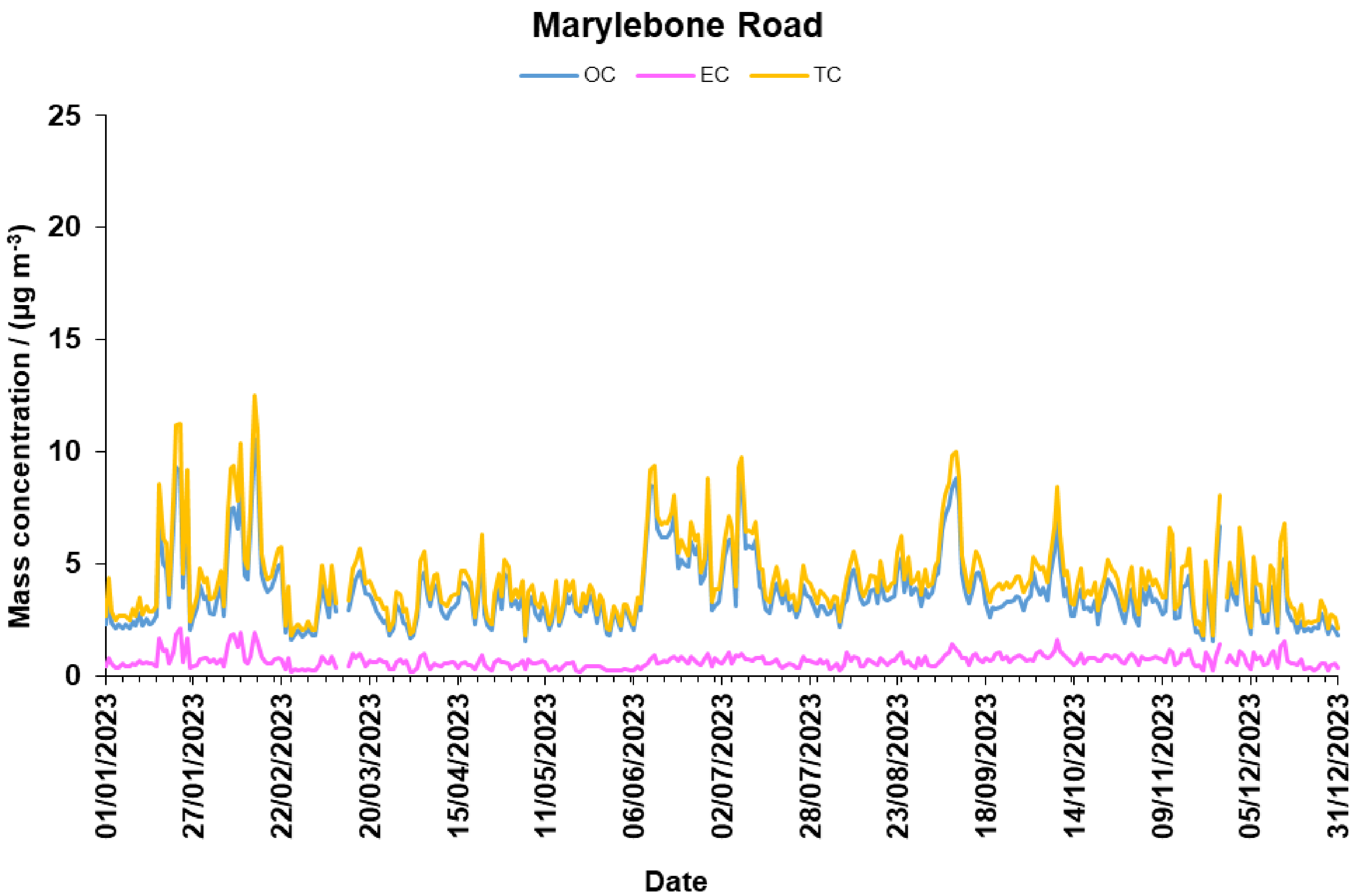


Figure 29 - Daily OC, EC, and TC mass concentrations in $PM_{2.5}$ measured at London Marylebone Road during 2023.

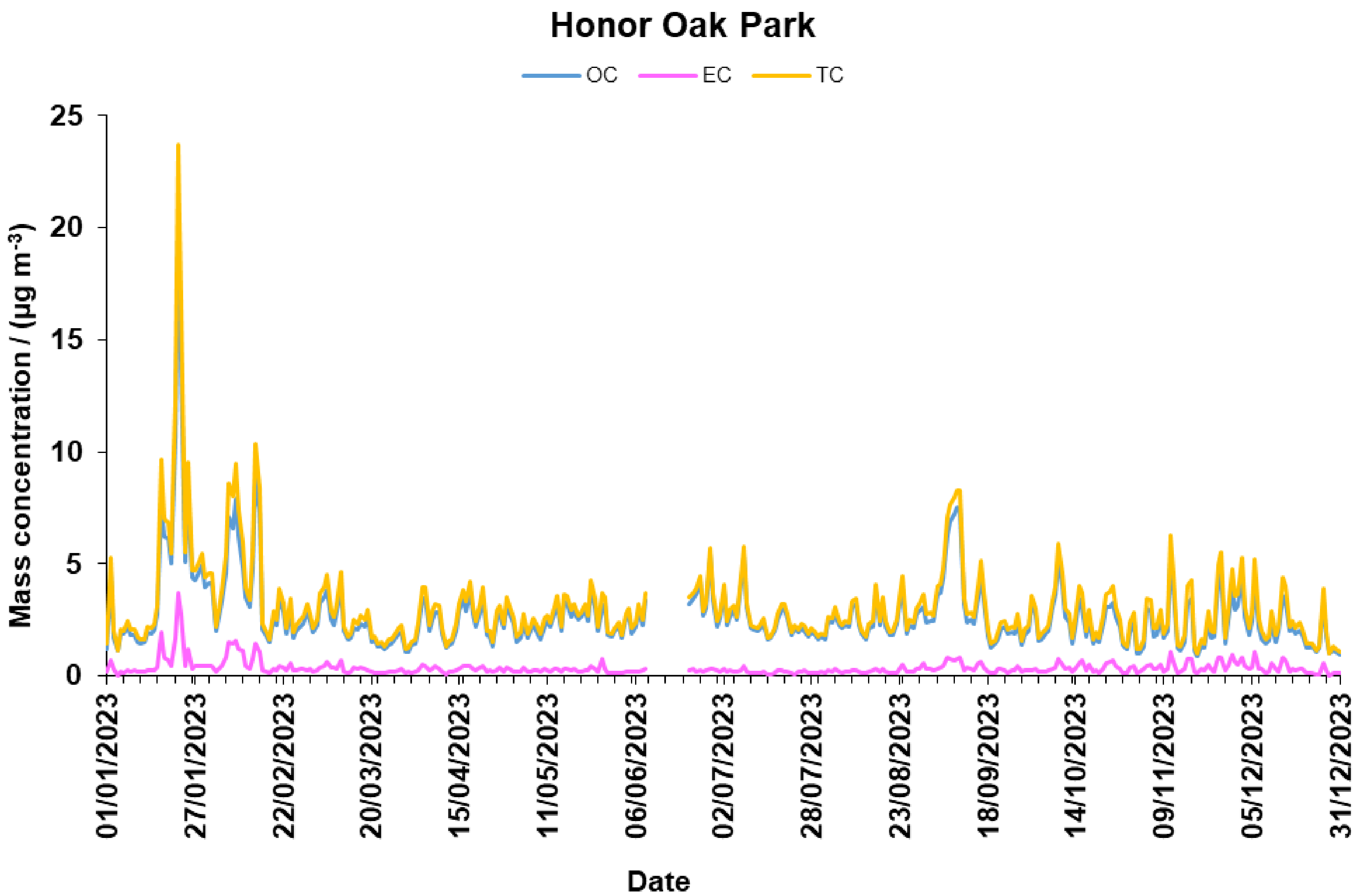


Figure 30 - Daily OC, EC, and TC mass concentrations in $PM_{2.5}$ measured at London Honor Oak Park during 2023.

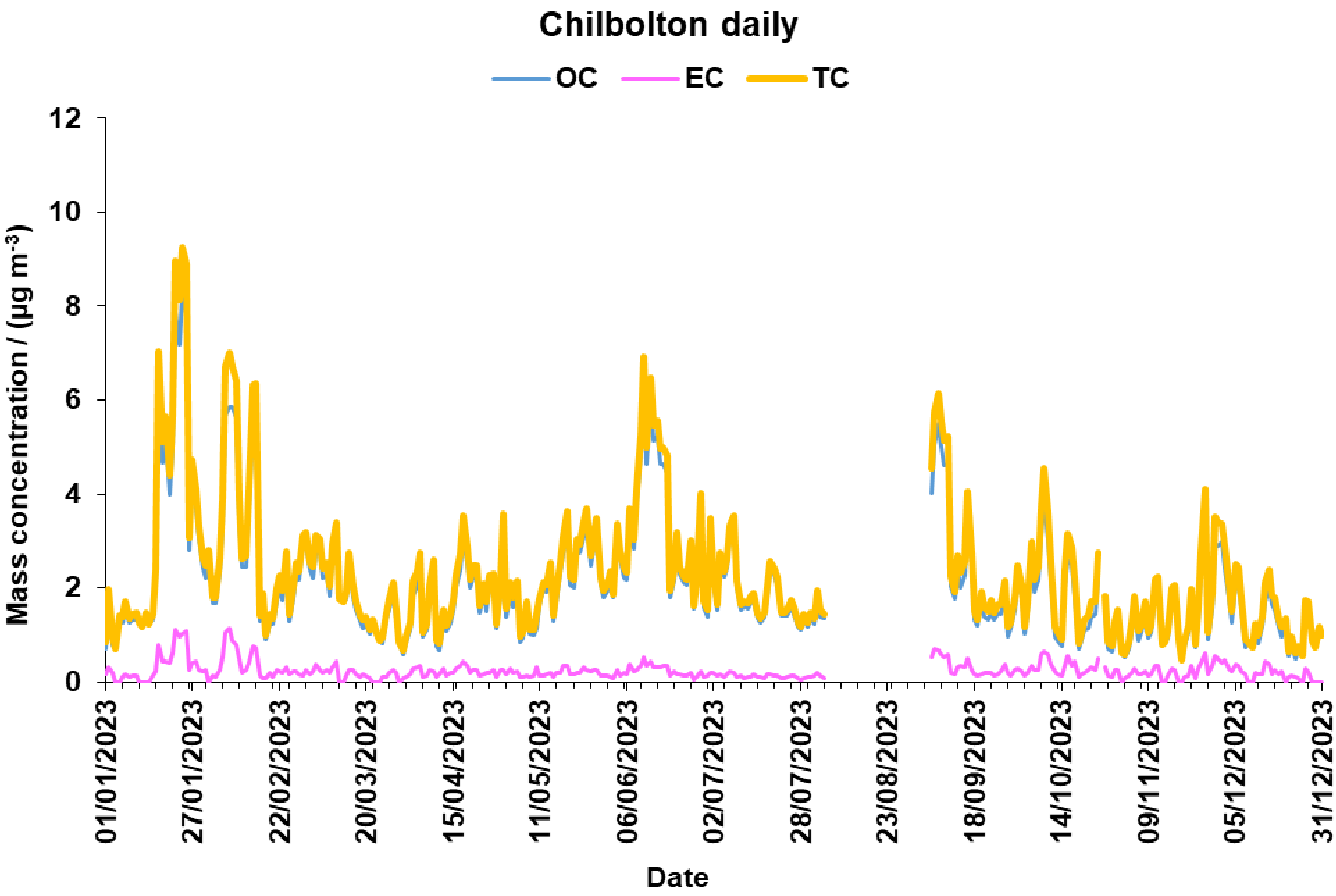


Figure 31 - Daily OC, EC, and TC mass concentrations in $PM_{2.5}$ measured at Chilbolton Observatory during 2023.

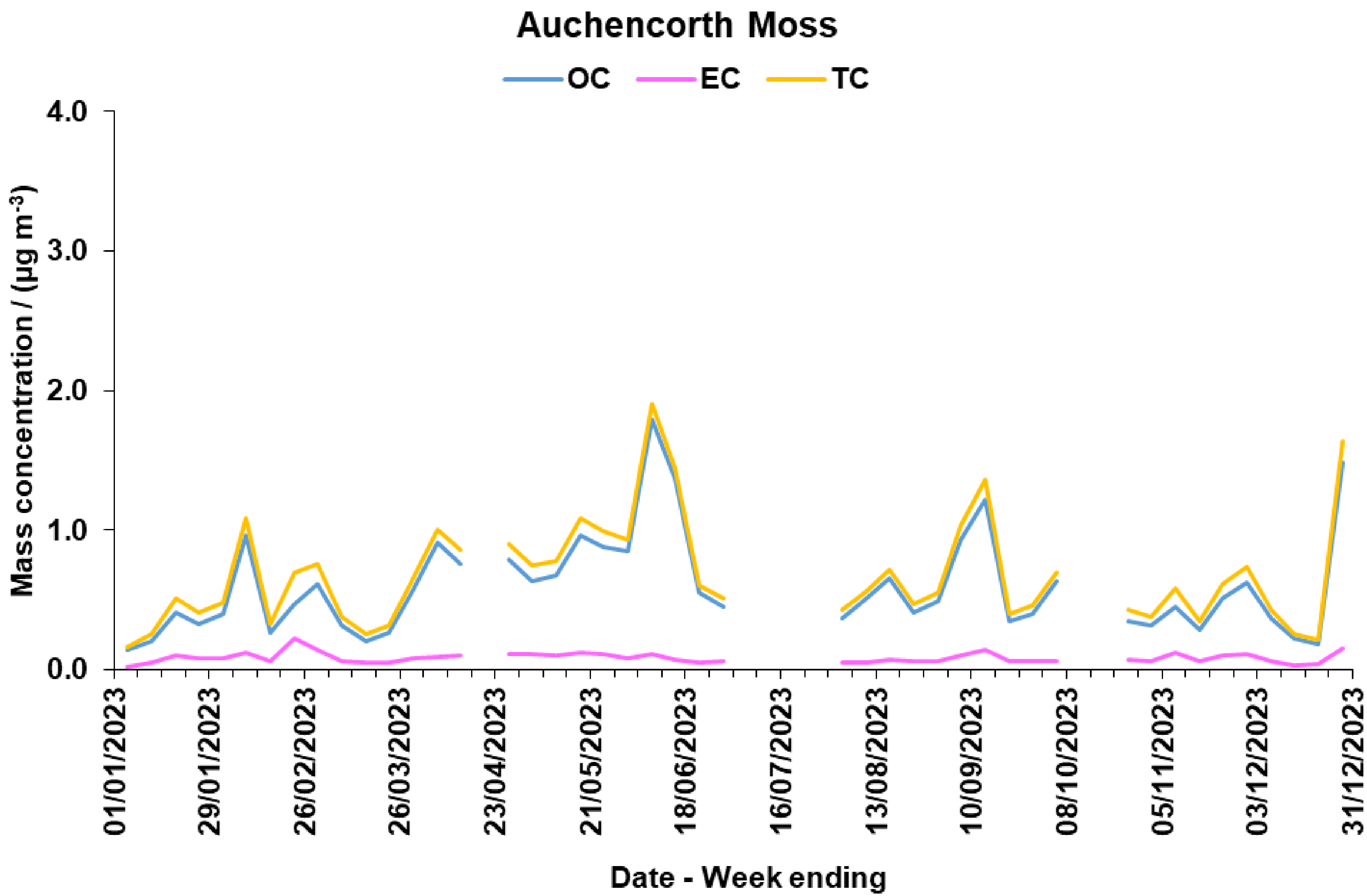


Figure 32 - Weekly OC, EC, and TC mass concentrations in $PM_{2.5}$ measured at Auchencorth Moss during 2023.

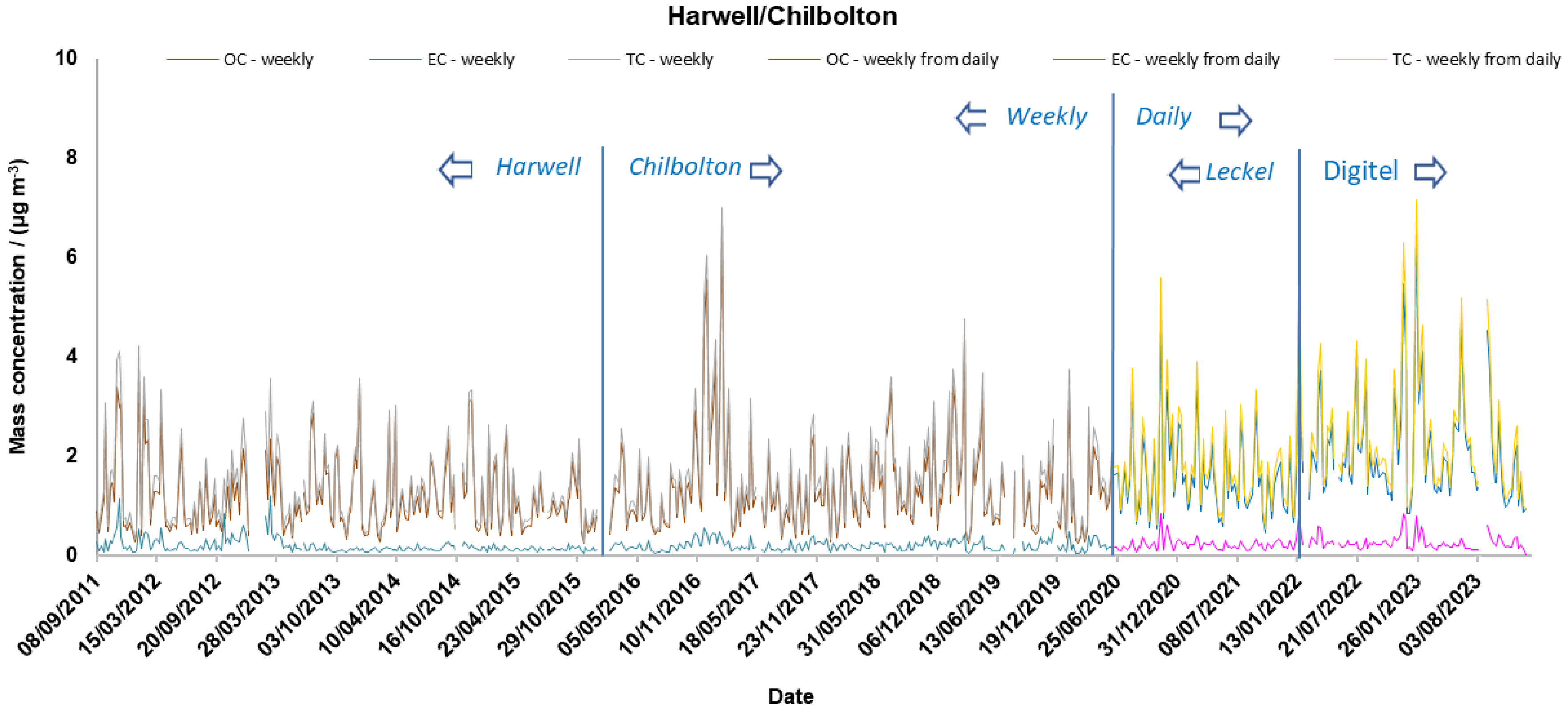


Figure 33 - Time series of the weekly OC, EC, and TC mass concentrations in the $PM_{2.5}$ fraction at Harwell/Chilbolton Observatory since the installation of the sampler up to June 2020 and daily mass concentrations from 11 June 2020. The sampler was replaced by a Digitel sampler in January 2022. The daily mass concentrations measured since June 2020 have been plotted as calculated weekly average for consistency.

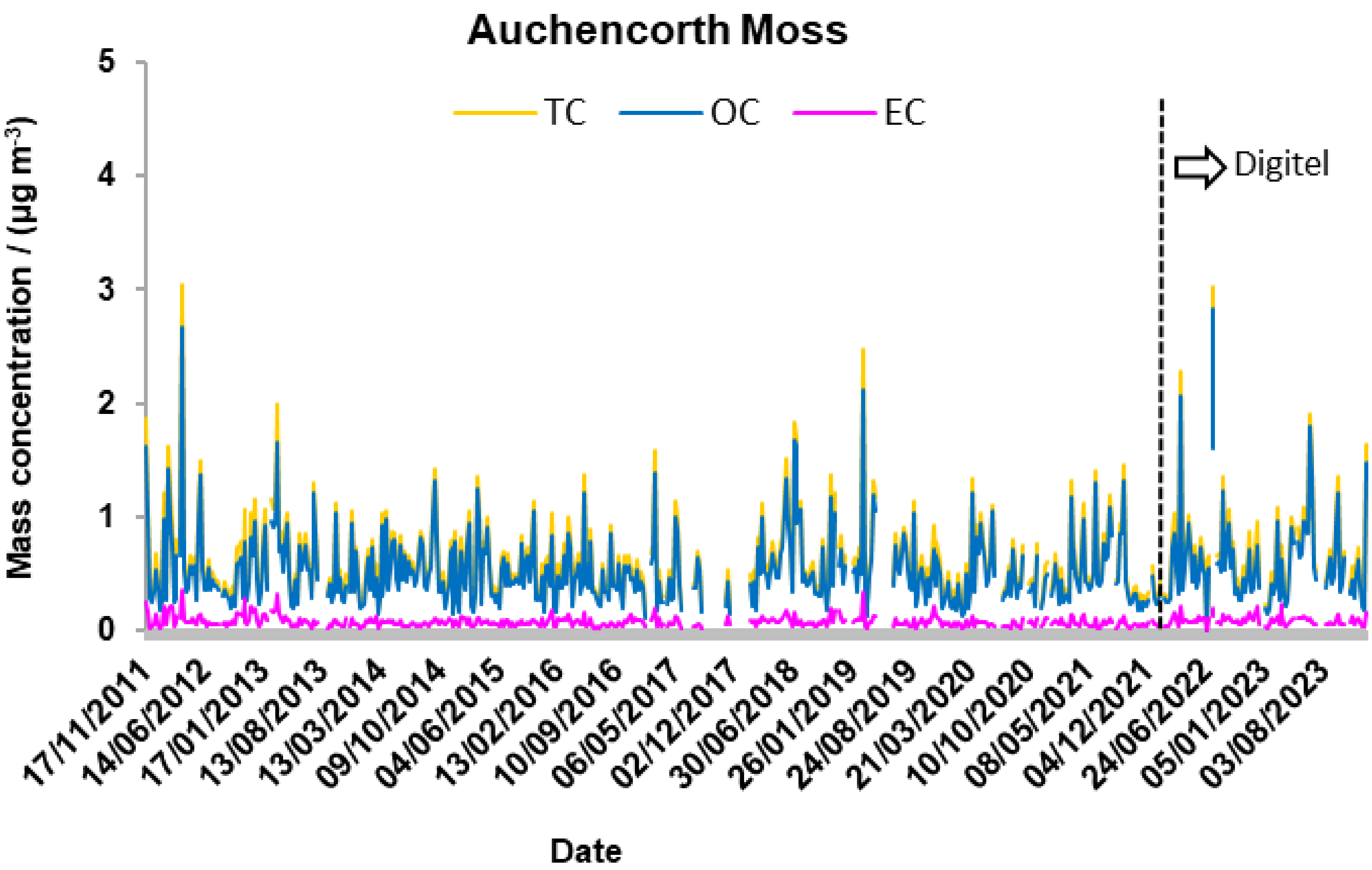


Figure 34 - Time series of weekly OC, EC, and TC in the $PM_{2.5}$ fraction at Auchencorth Moss to the end of 2023.

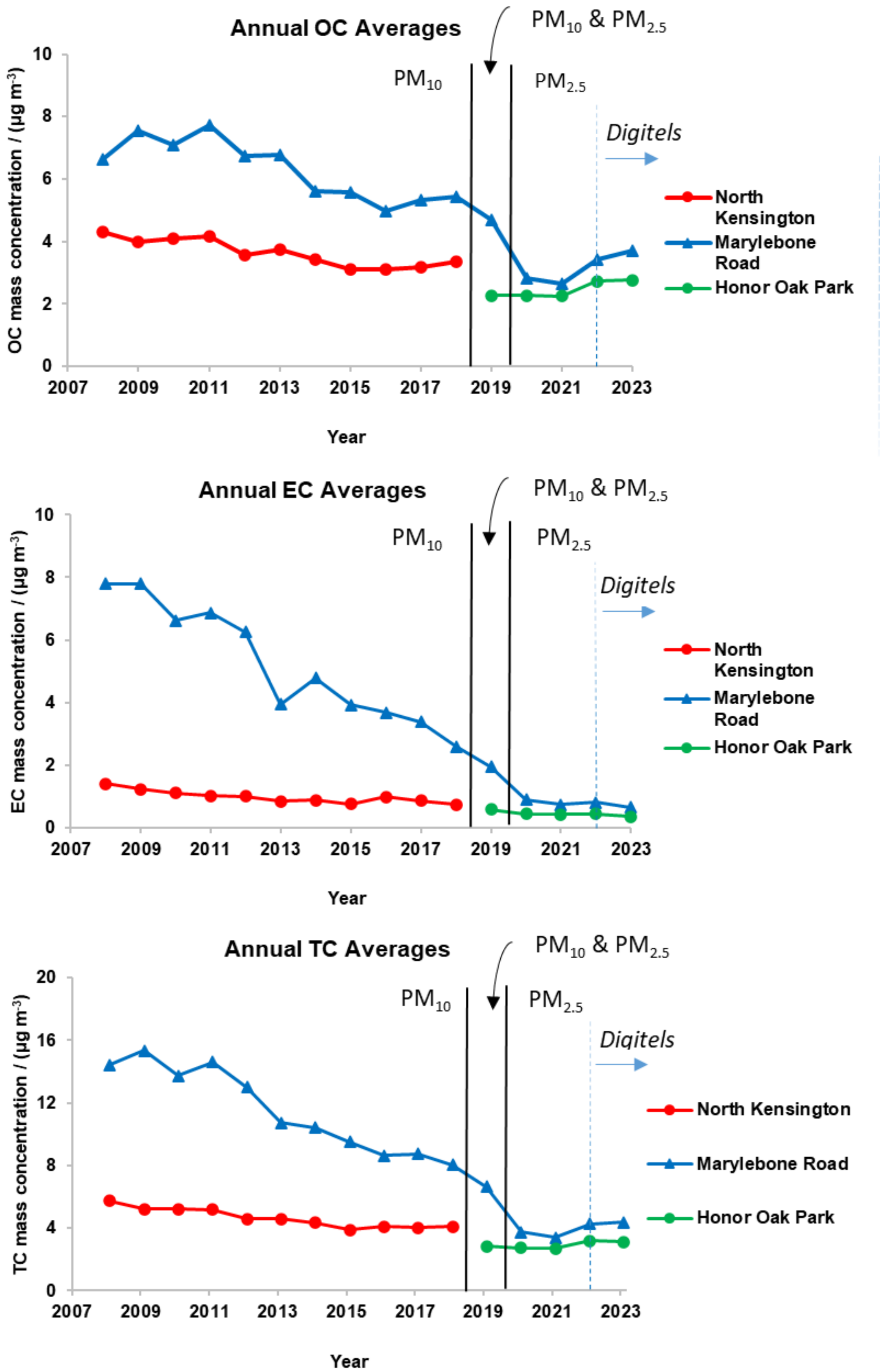


Figure 35 - Annual trends for OC, EC, and TC measurements. PM_{10} sampling heads were changed to $PM_{2.5}$ heads at London Honor Oak Park and London Marylebone Road in February 2019 and October 2019, respectively. Partisol samplers were replaced with Digitel samplers at London Honor Oak Park and London Marylebone Road in 2022.

4.6 BC and UVPM

BC is a measure of the mass concentration of airborne soot-like carbon based on the optical absorption of light at a specific wavelength (880 nm) by particulates collected on a filter. It is often assumed that BC and EC, a measure of soot-like carbon determined by thermo-optical techniques, are the same, however in practice the measured concentration of the EC fraction of TC depends strongly on the method chosen. The term “equivalent black carbon (eBC)” 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 (infrared, IR-2), 880 nm (BC), 660 nm (Red), 590 nm (Yellow), 520 nm (Green), 470 nm (Blue), and 370 nm (UV). In this report, the term BC concentration refers to the mass concentration of particulate matter measured at the 880 nm wavelength also within the infrared range. 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. For this Network the parameter UVPM is calculated by subtracting the BC mass concentration from the UV mass concentration and in principle can be used as an indicator of organic compounds present in e.g. wood and solid fuel emissions.

Table 10 - Annual mean of particulate matter concentrations measured in $PM_{2.5}$ at specific wavelength (indicated in nm in brackets) by AE33 Aethalometers in 2023.

	Mass concentration in $PM_{2.5}$ / (µg m^{-3})							
Site	**UV** (370)	**Blue** (470)	**Green** (520)	**Yellow** (590)	**Red** (660)	**BC** (880)	**IR-2** (950)	**UVPM**
Auchencorth Moss	0.16	0.15	0.14	0.14	0.13	0.13	0.13	0.02
Ballymena Ballykeel	1.09	0.94	0.86	0.82	0.77	0.73	0.73	0.36
Belfast Centre	1.05	1.01	0.94	0.92	0.87	0.83	0.84	0.22
Birmingham A4540 Roadside	1.71	1.72	1.63	1.60	1.54	1.51	1.52	0.19
Birmingham Ladywood	0.72	0.71	0.66	0.65	0.62	0.60	0.60	0.12
Cardiff Centre	1.03	0.97	0.96	0.96	0.93	0.92	0.92	0.11
Chilbolton Observatory	0.48	0.43	0.39	0.37	0.34	0.32	0.32	0.16
Detling	0.54	0.50	0.47	0.45	0.43	0.42	0.42	0.12
Glasgow High Street	0.74	0.75	0.70	0.69	0.66	0.65	0.65	0.09
Glasgow Townhead	0.54	0.54	0.50	0.50	0.48	0.46	0.48	0.07
Kilmakee Leisure Centre	0.80	0.71	0.65	0.63	0.59	0.56	0.57	0.24
London Marylebone Road	1.10	1.06	1.03	0.98	0.95	0.93	0.94	0.16
London North Kensington	0.78	0.72	0.66	0.64	0.59	0.56	0.57	0.21
Strabane 2	1.68	1.30	1.15	1.06	0.99	0.91	0.90	0.77
Average	**0.89**	**0.82**	**0.77**	**0.74**	**0.71**	**0.68**	**0.69**	**0.20**

BC and UVPM concentration data for 2023 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 2023 time series - BC

Figure 36 to Figure 40 show the BC mass concentrations measured in 2023. 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.

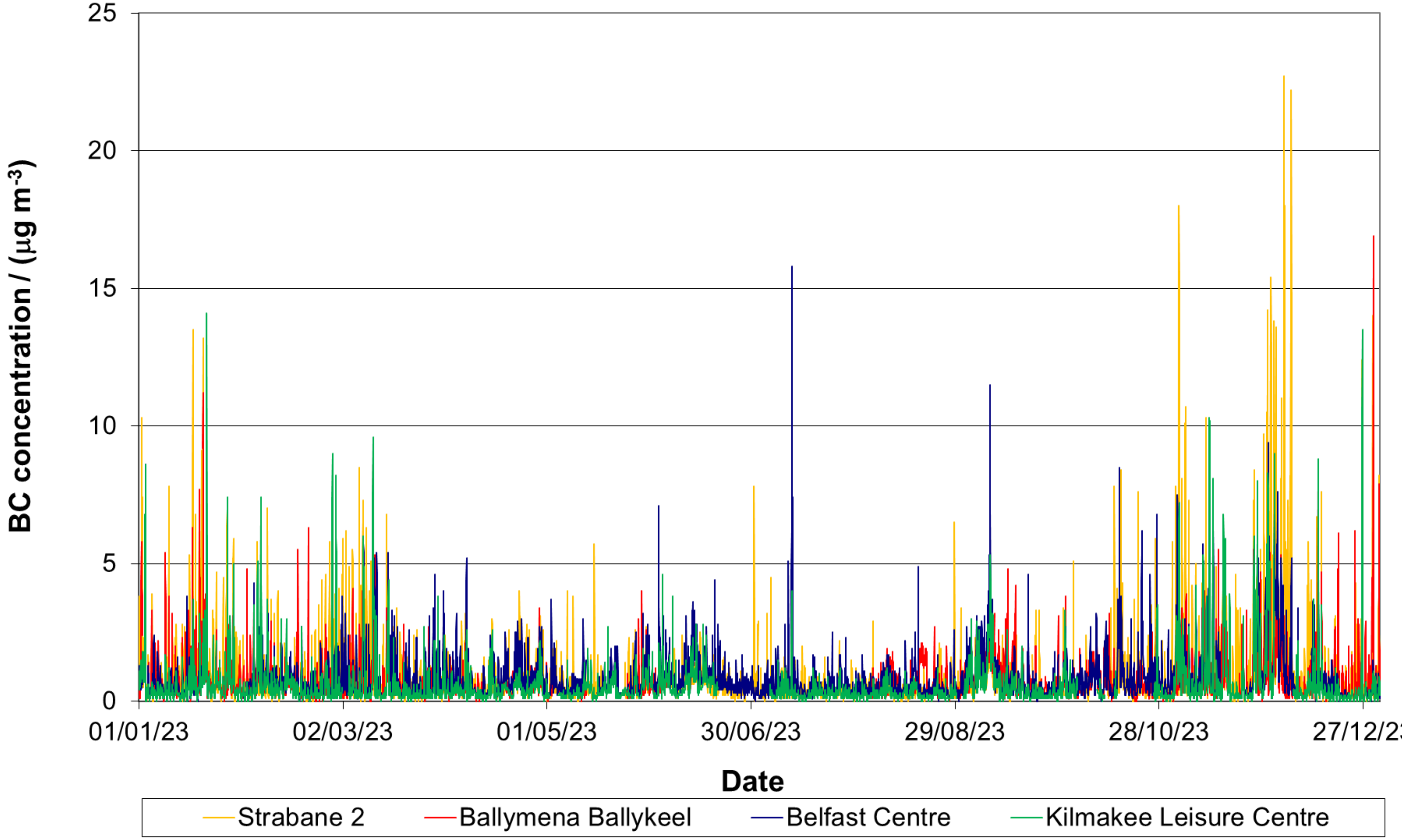


Figure 36 - BC concentrations during 2023 in Northern Ireland.

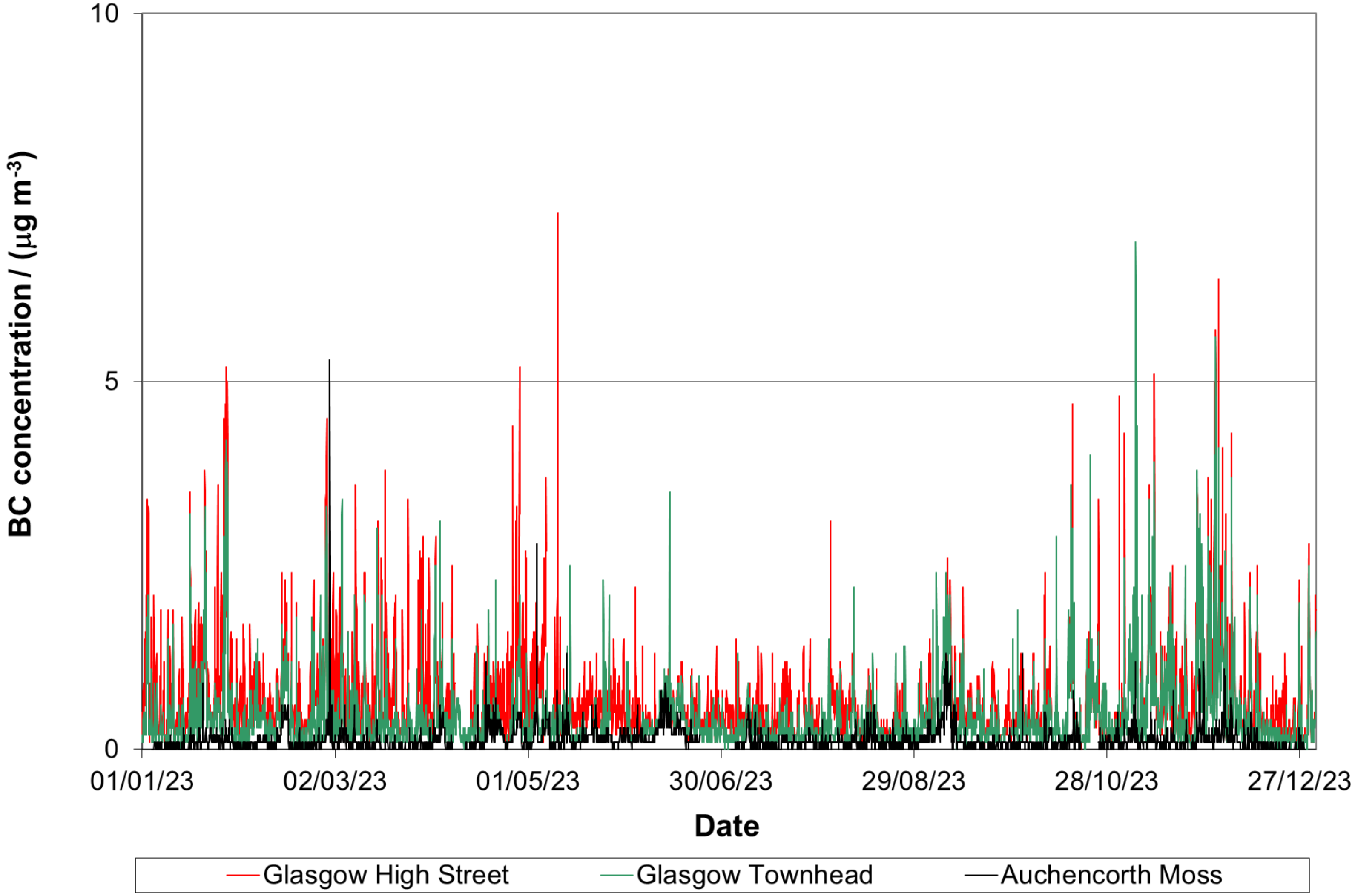


Figure 37 - BC concentrations during 2023 in Scotland.

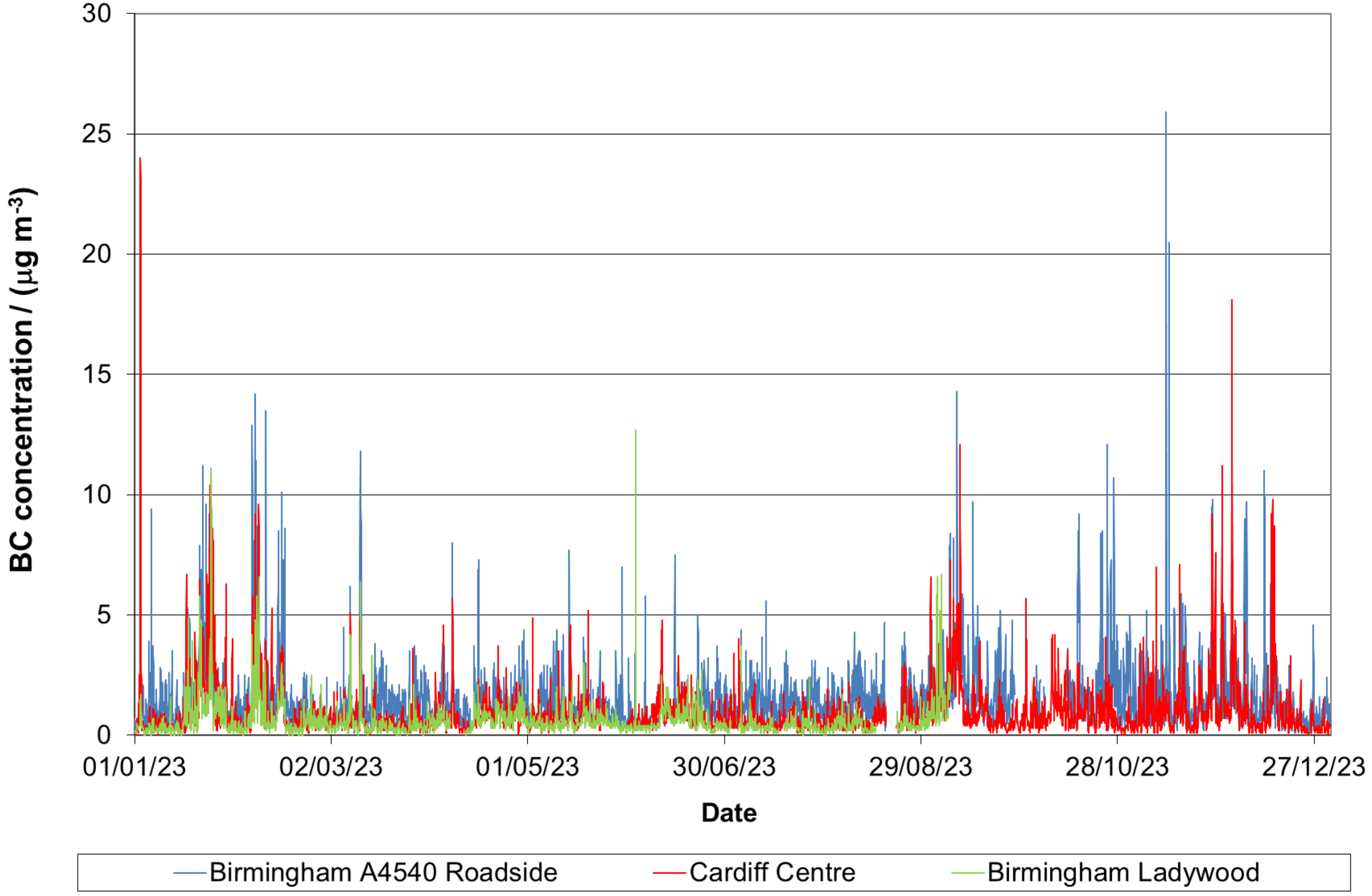


Figure 38 - BC concentrations during 2023 in Wales and the Midlands of England.

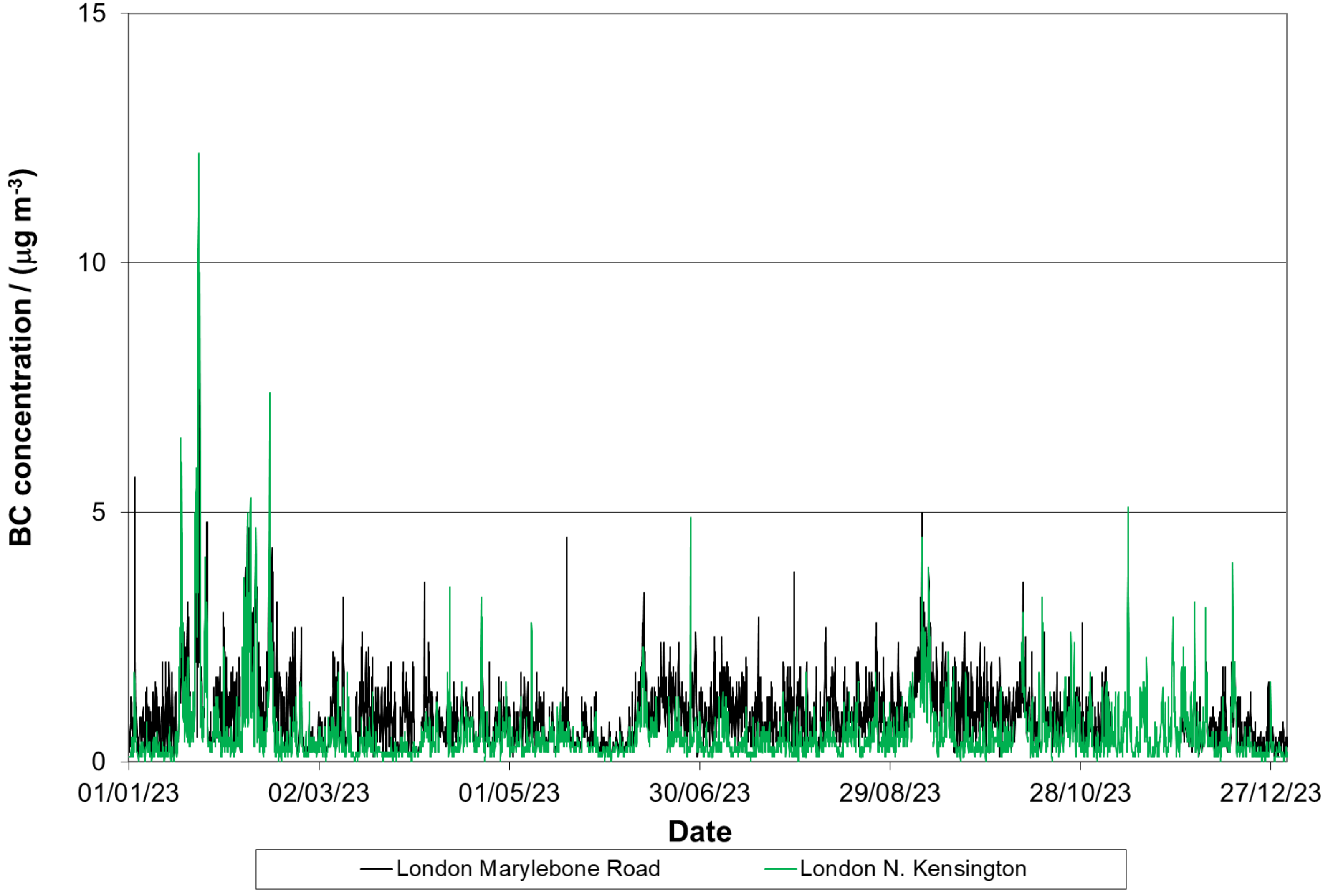


Figure 39 - BC concentrations during 2023 in London.

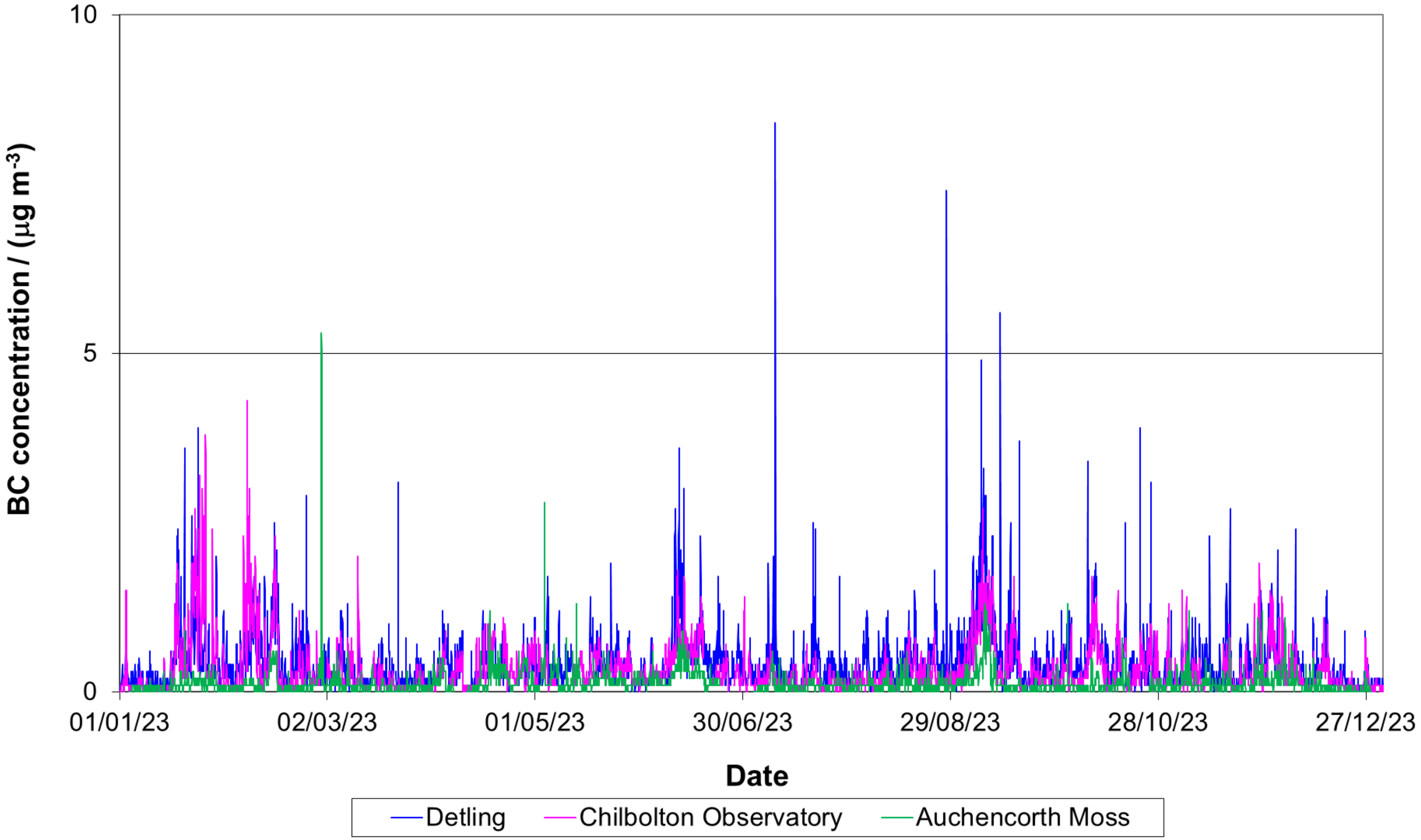


Figure 40 - BC concentrations during 2023 at rural locations.

4.6.2 2023 annual averages - BC

The annual mean concentrations are presented as a bar graph (Figure 41) to aid the comparison of sites.

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

The urban increments for London, Birmingham and Glasgow were all lower in 2023 compared to 2022. The roadside increment for Birmingham was larger than that for London, however it has dropped from 1.07 µg m^{-3} in 2022 to 0.82 µg m^{-3}.

Figure 42 shows how the urban and roadside increments in London have changed over the period 2012 to 2023. 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 42.

Table 11 - Urban and roadside increments in BC concentrations in 2023

	BC increment / (µg m^{-3})	
Conurbation	**Urban**	**Roadside**
London	0.20	0.37
Birmingham	0.26	0.82
Glasgow	0.34	0.20

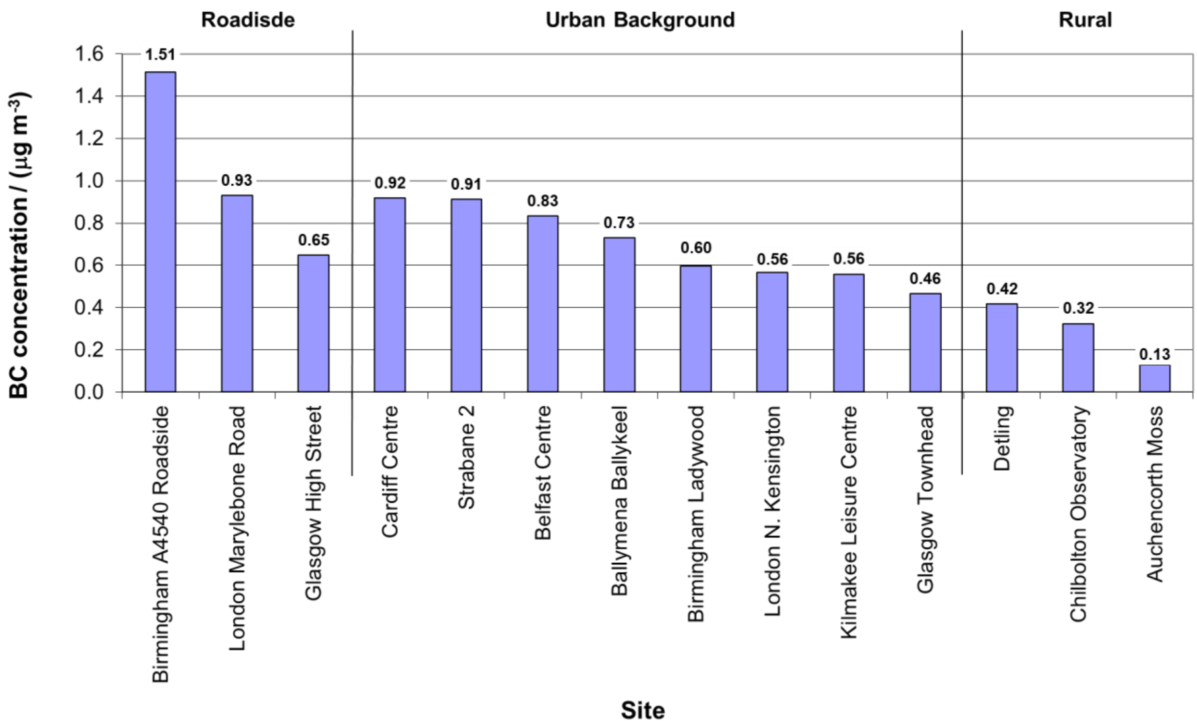


Figure 41 - Annual mean BC concentrations measured in 2023.

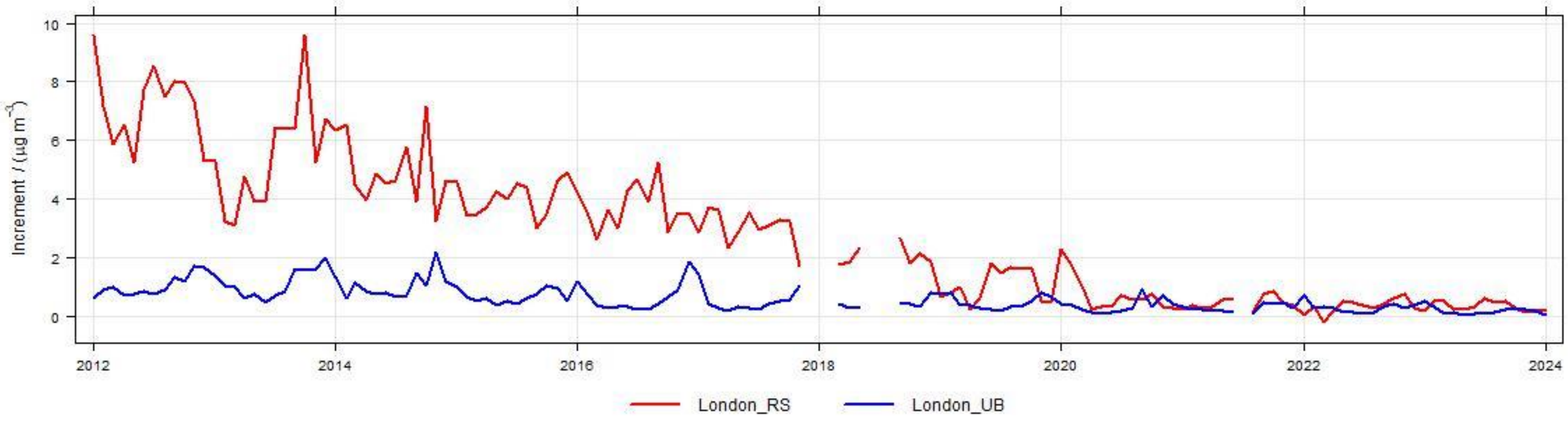


Figure 42 - Urban (UB) and roadside (RS) increments in London for the period 2012 to 2023. The tick marks on the x-axis indicate the start of the year indicated.

4.6.3 2023 annual averages - UVPM

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

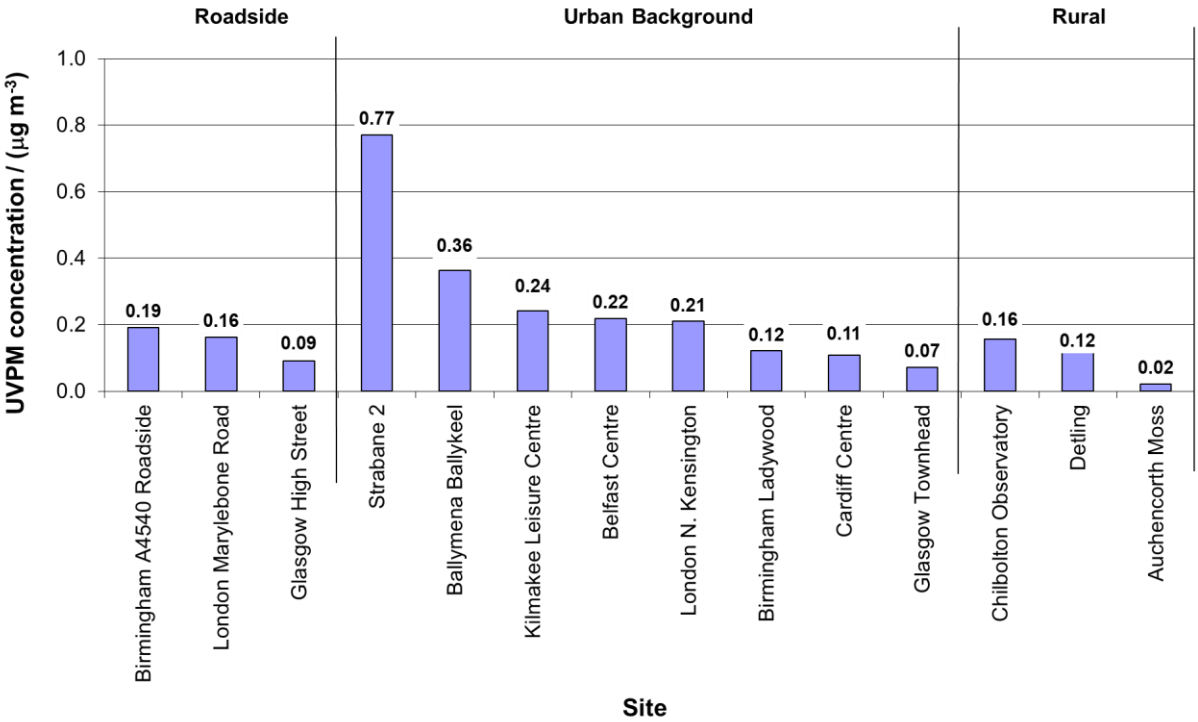


Figure 43 - Annual mean UVPM concentrations for 2023

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

Table 12 - Urban and roadside increments in UVPM concentrations in 2023

	UVPM increment / (µg m^{-3})	
Conurbation	**Urban**	**Roadside**
London	0.07	-0.04
Birmingham	-0.05	0.06
Glasgow	0.05	0.02

The urban and roadside increments at all sites were small (or slightly negative), indicating that domestic emissions or other potential sources of UVPM (such as road traffic) in the three conurbations were negligible., There was no significant difference in increments between 2022 and 2023.

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	0.04	18
Ballymena Ballykeel	0.12	54
Strabane 2	0.51	235

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 fuel other than smokeless fuel in Strabane 2. Changes in the UVPM increment in Northern Ireland over the last ten years are summarised in Figure 44.

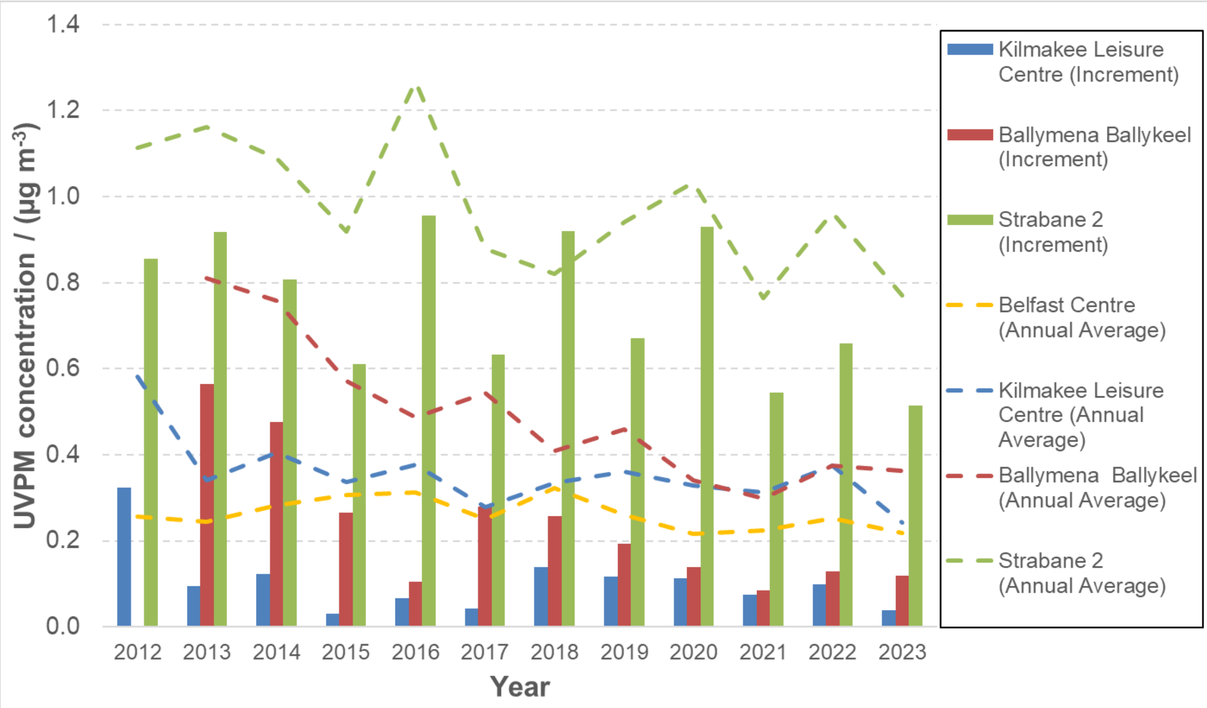


Figure 44 - Annual Mean UVPM concentrations and increments compared to Belfast Centre for 2012-2023.

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 2023 data are presented in Figure 45 to Figure 58.

Data from 2009-2023 are presented in Figure 59 to Figure 63. 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 - 2023, are considered to be less biased when compared to the single year (2023) measurements presented in Figure 45 to Figure 58.

Figure 45 to Figure 63 are generated using the OpenAir Tools run on the R software platform[27,28].

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 apart from London Marylebone Road, where concentrations are mostly stable during daytime. 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 2023

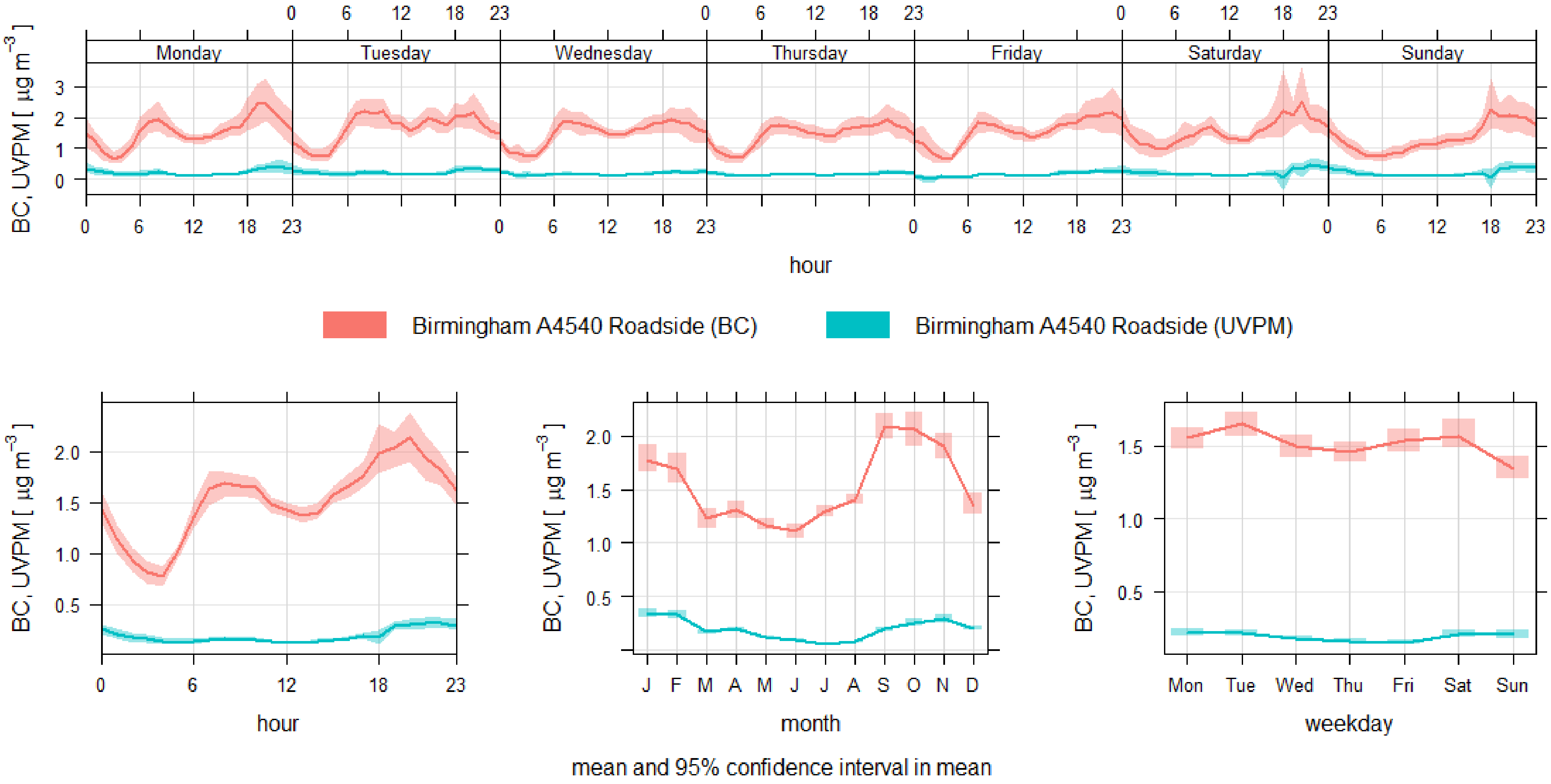


Figure 45 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at Birmingham A4540 Roadside for 2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

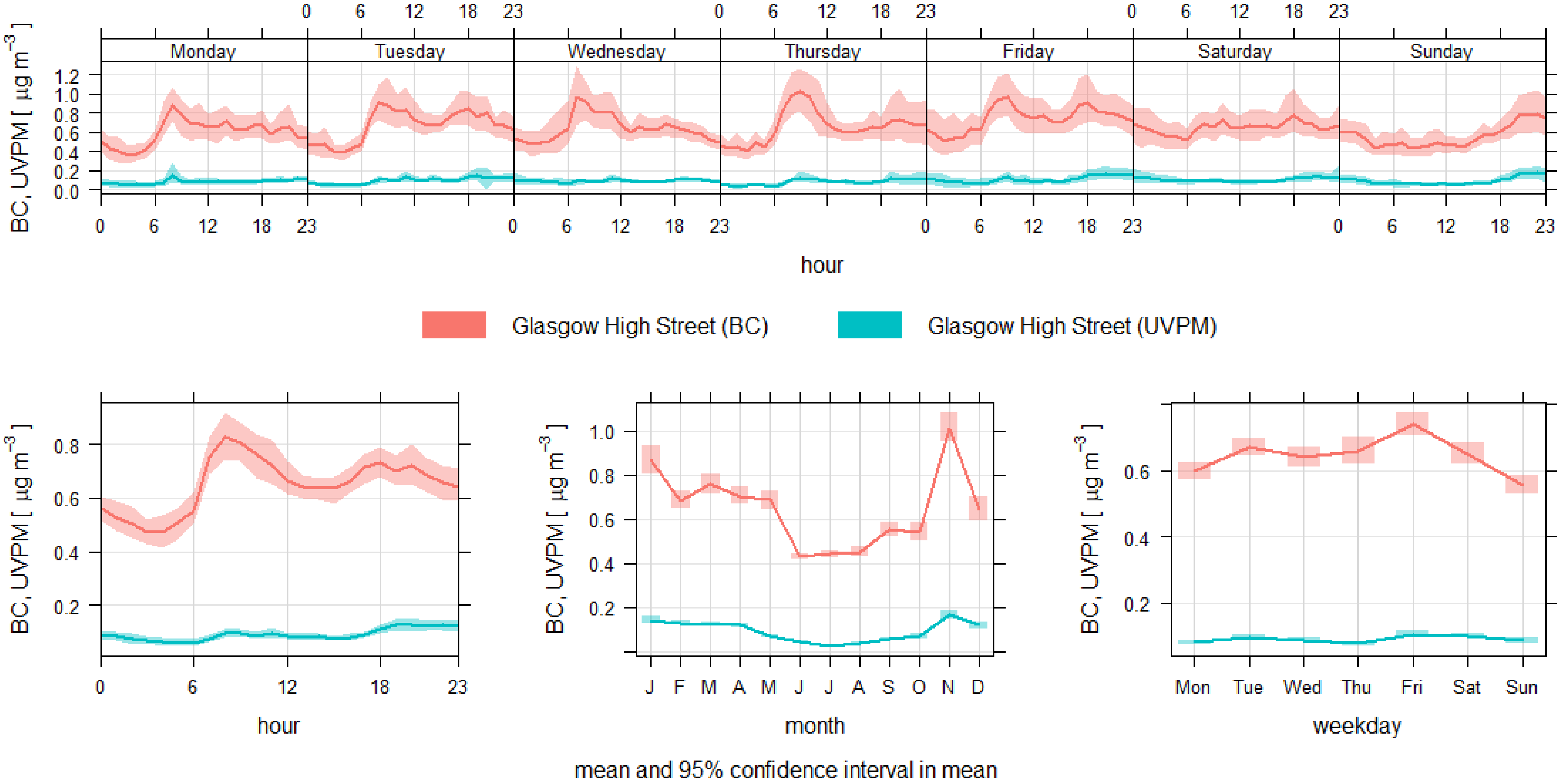


Figure 46 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at Glasgow High Street for 2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

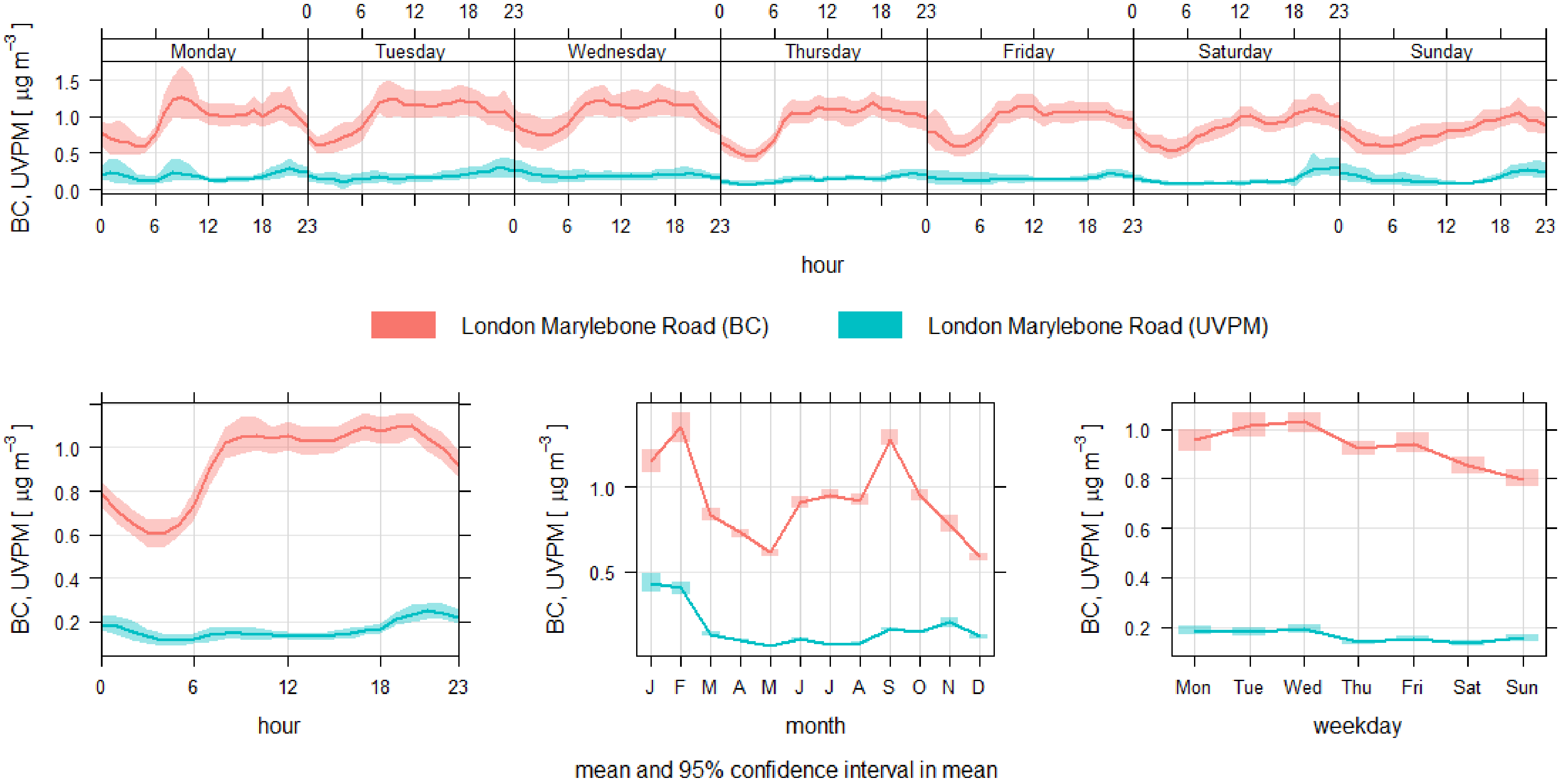


Figure 47 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at London Marylebone Road for 2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

BC and UVPM data at urban background sites for 2023

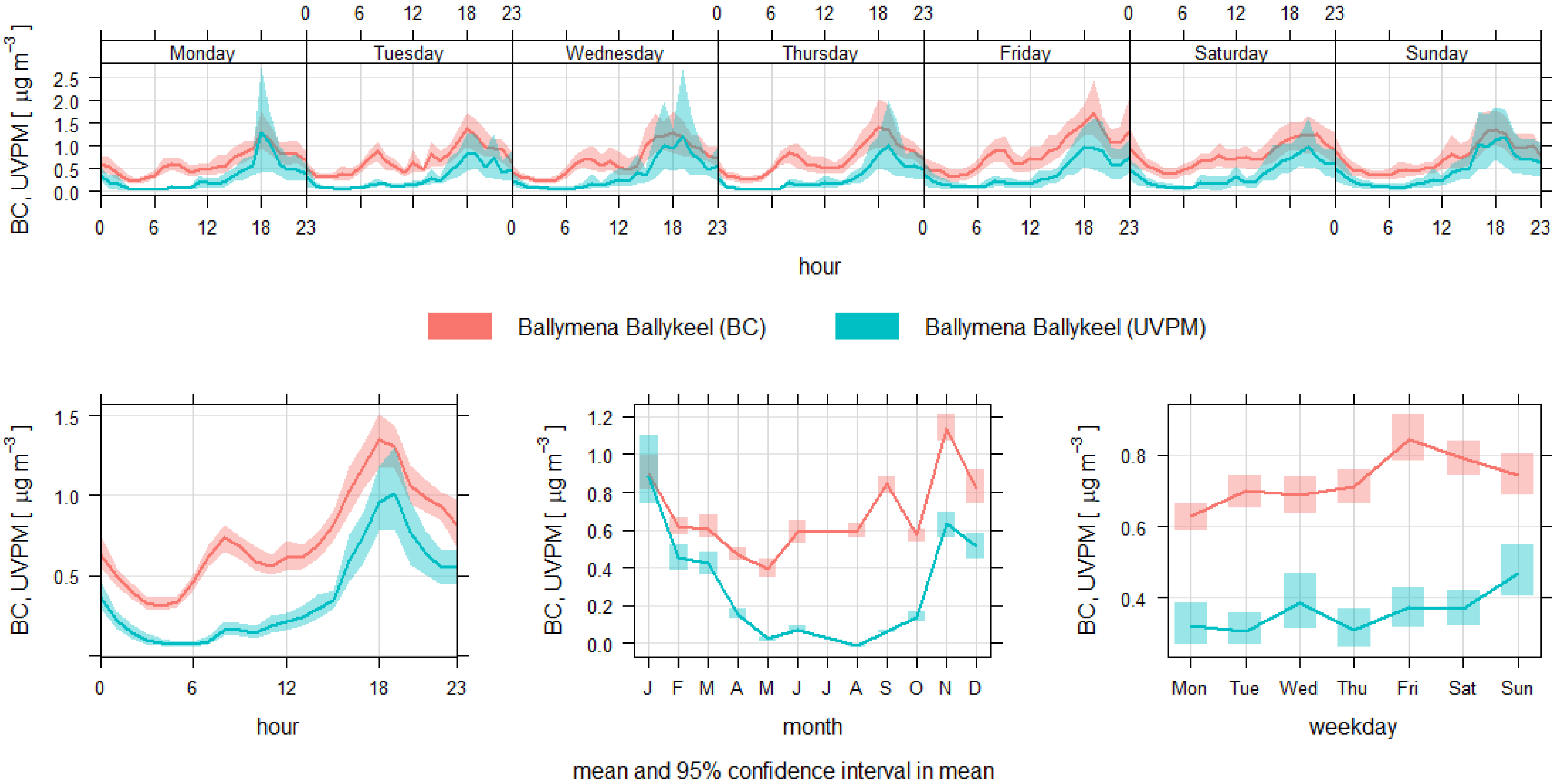


Figure 48 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at Ballymena Ballykeel for 2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

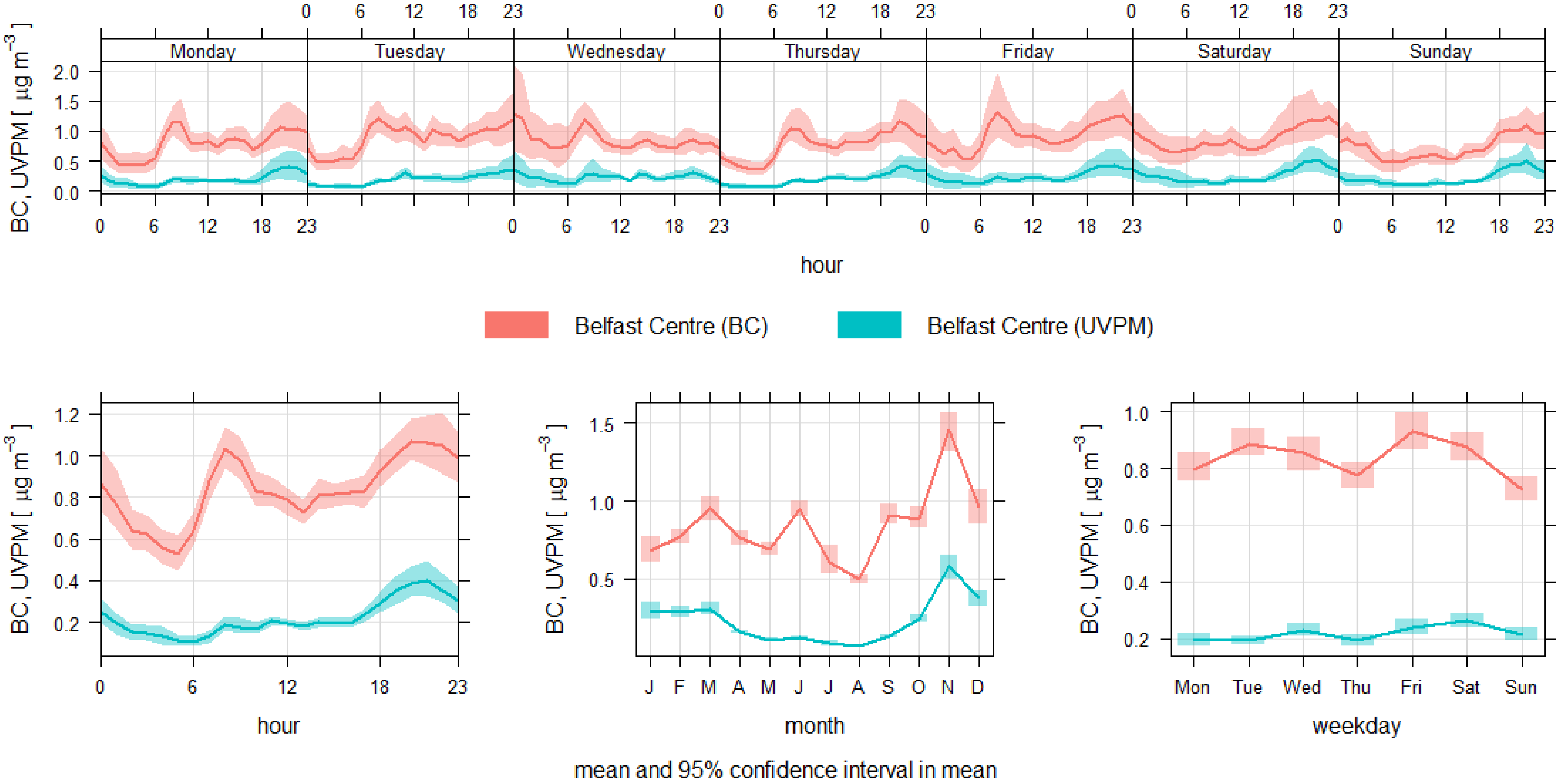


Figure 49 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at Belfast Centre for 2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

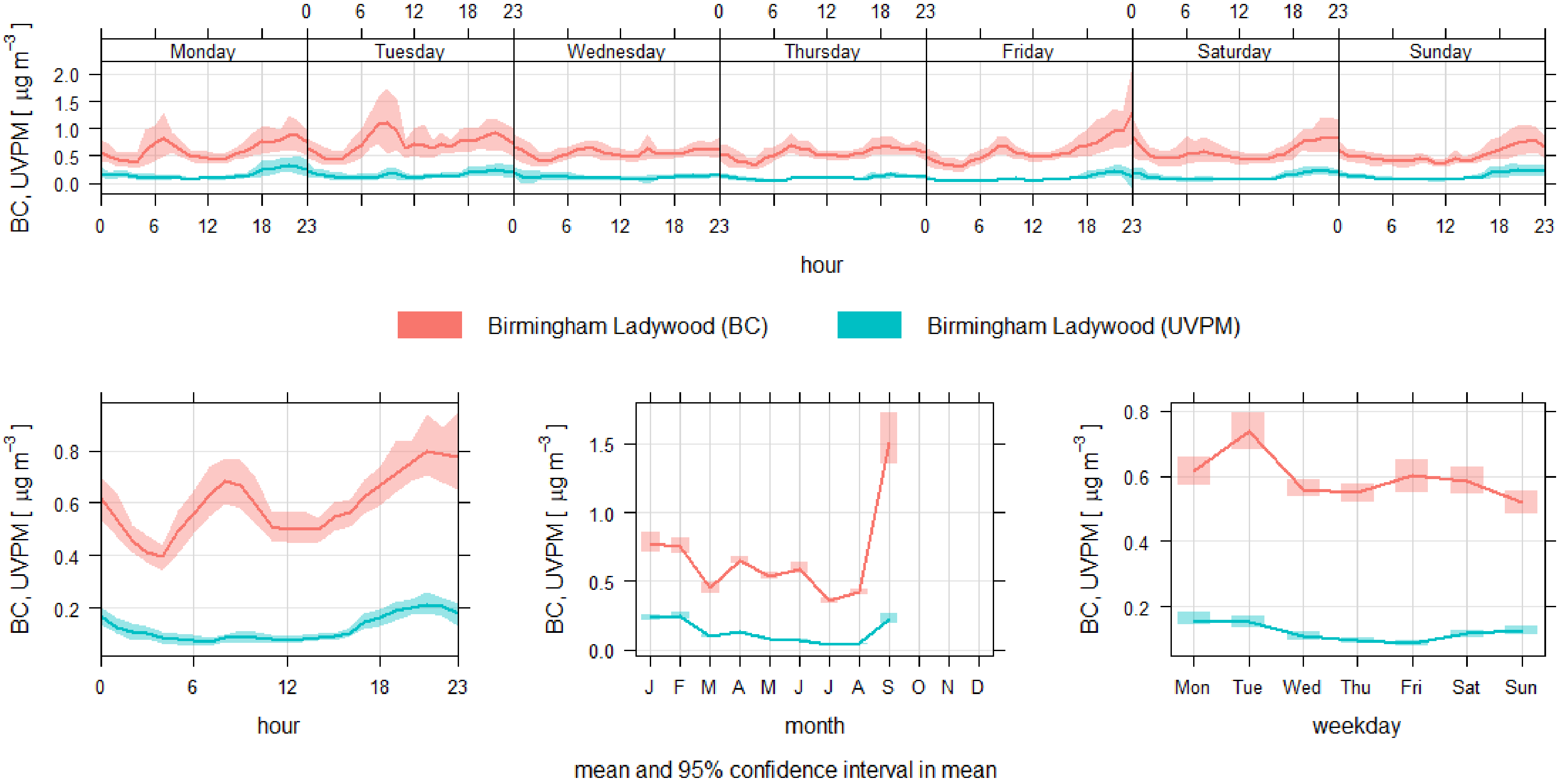


Figure 50 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at Birmingham Ladywood for 2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean. Data from 7 September 2024 to the end of the year have been excluded from these plots as the mass concentrations were not valid, due to wrong filter tape being used in this period. Note that the September result in the monthly plot is automatically produced by the software based on limited data that might not represent the BC and UVPM mass concentrations of this month.

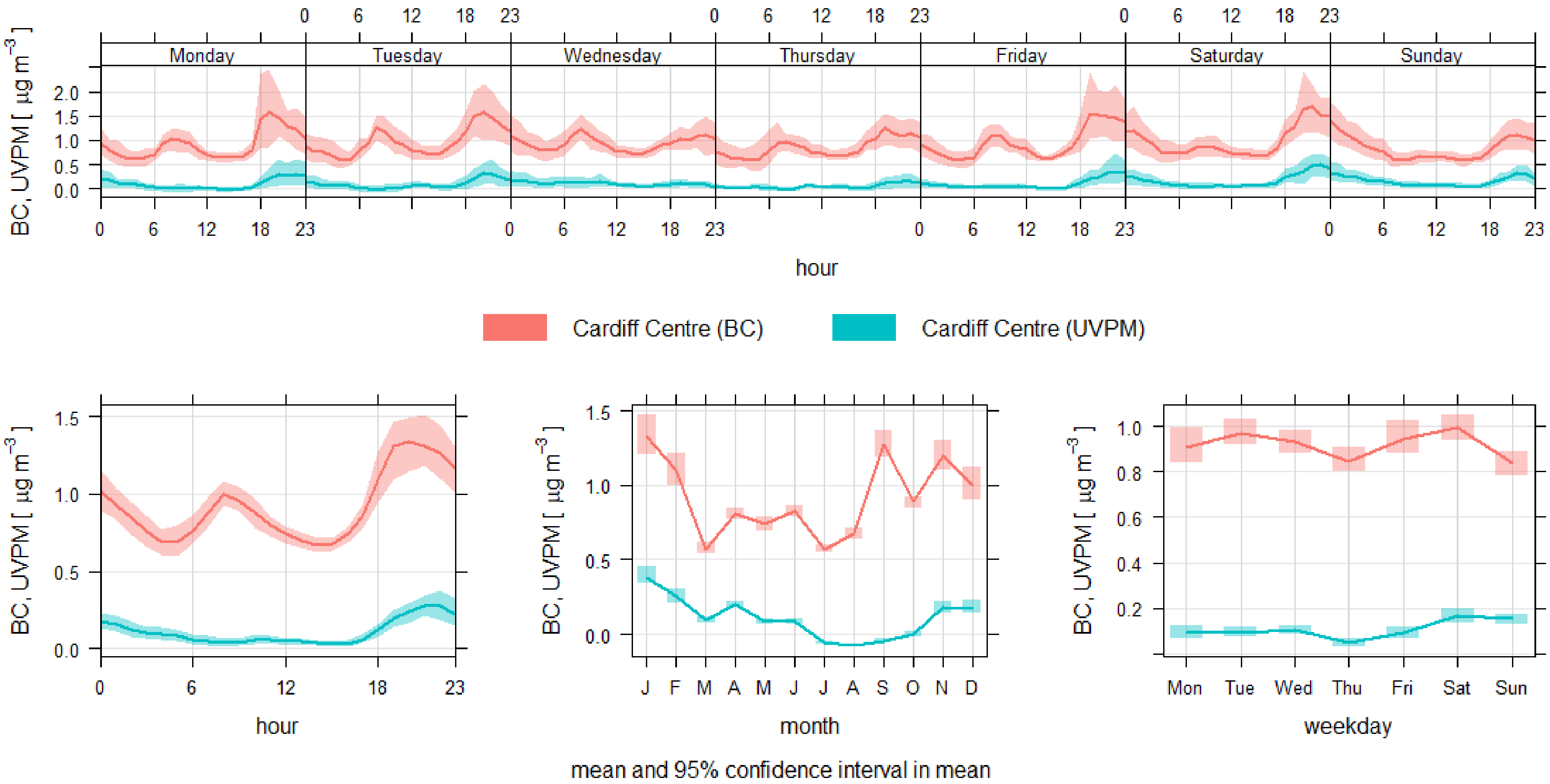


Figure 51 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at Cardiff Centre for 2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

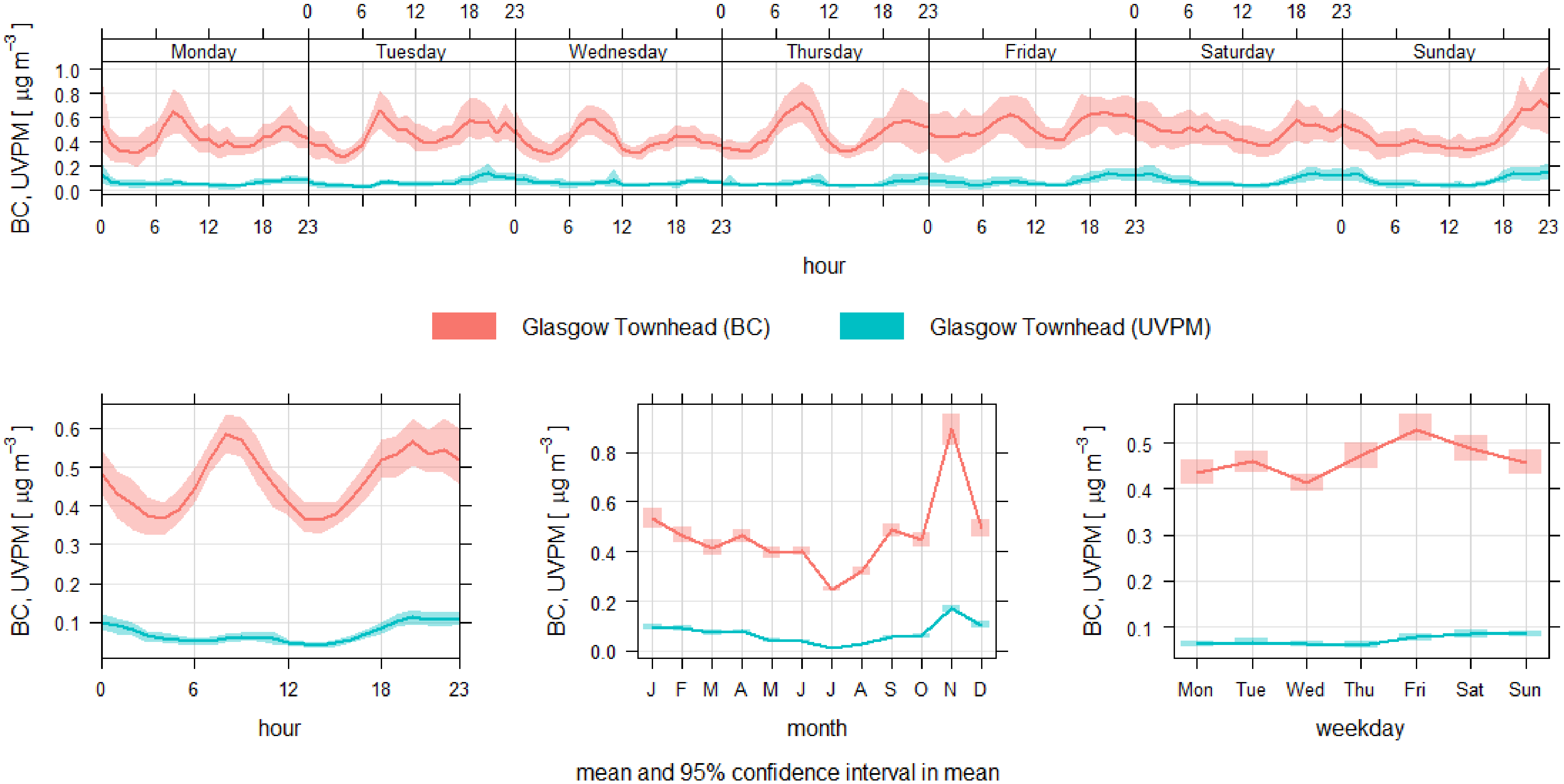


Figure 52 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at Glasgow Townhead for 2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

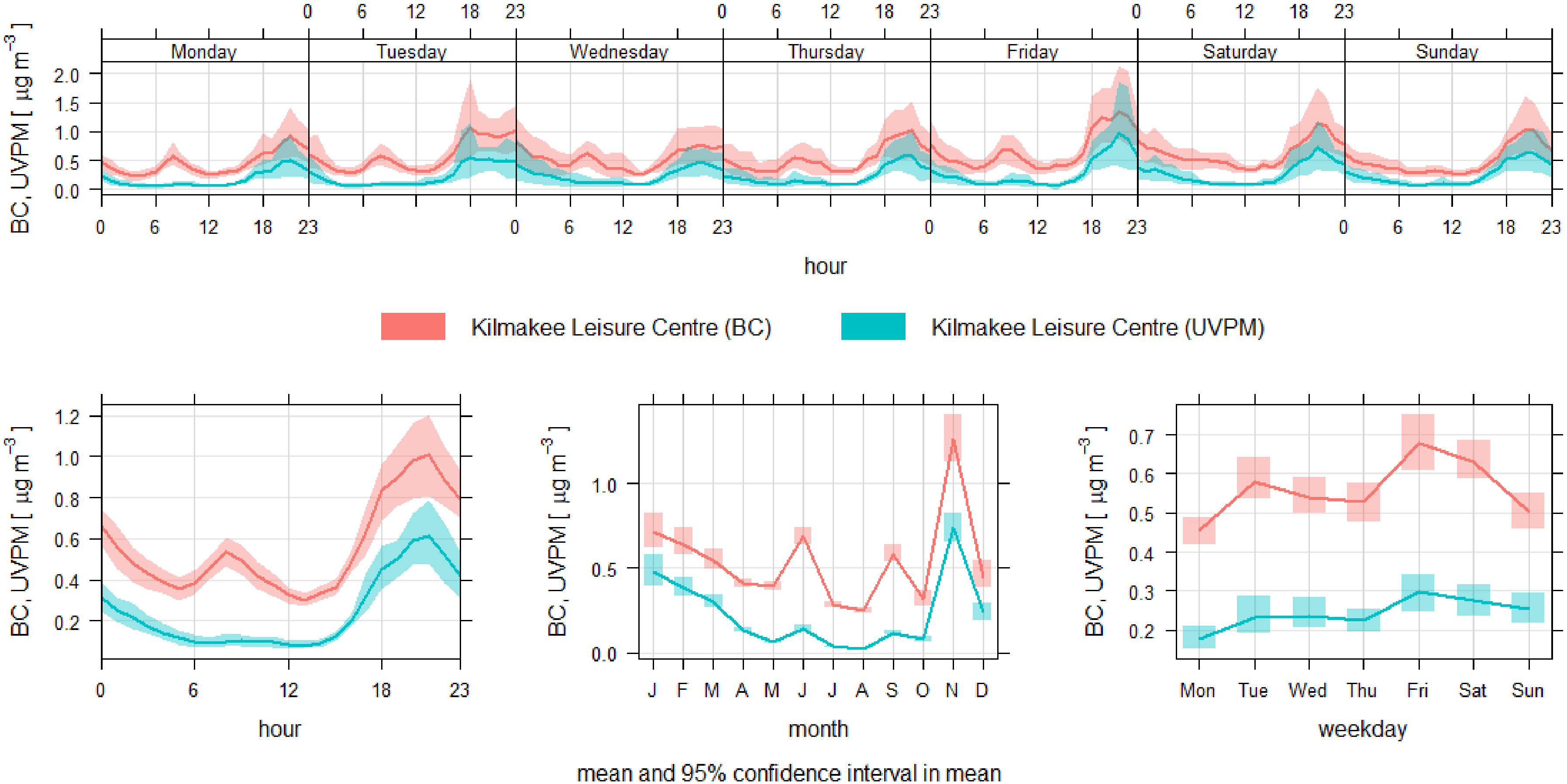


Figure 53 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at Kilmakee Leisure Centre for 2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

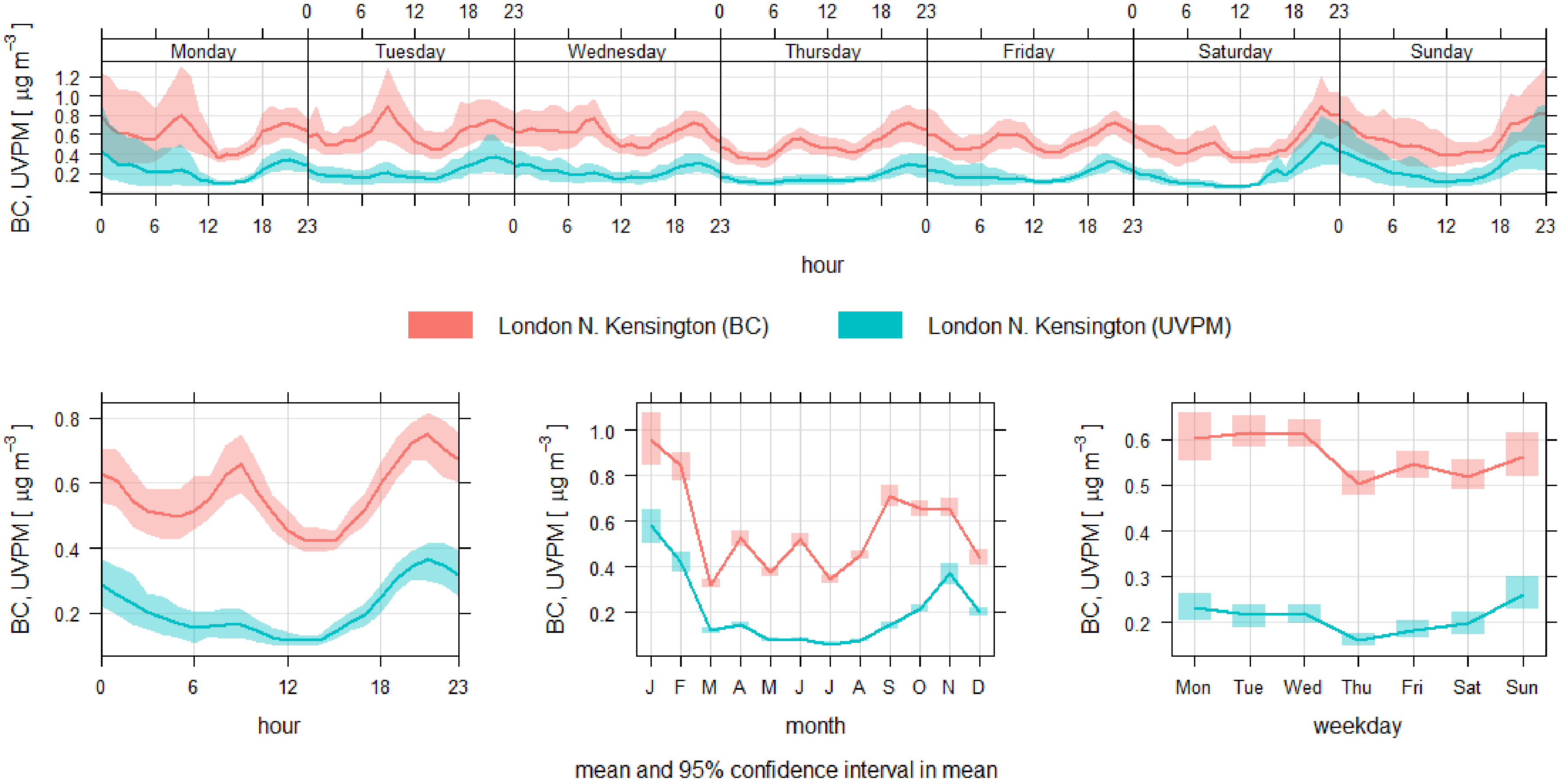


Figure 54 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at London North Kensington for 2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

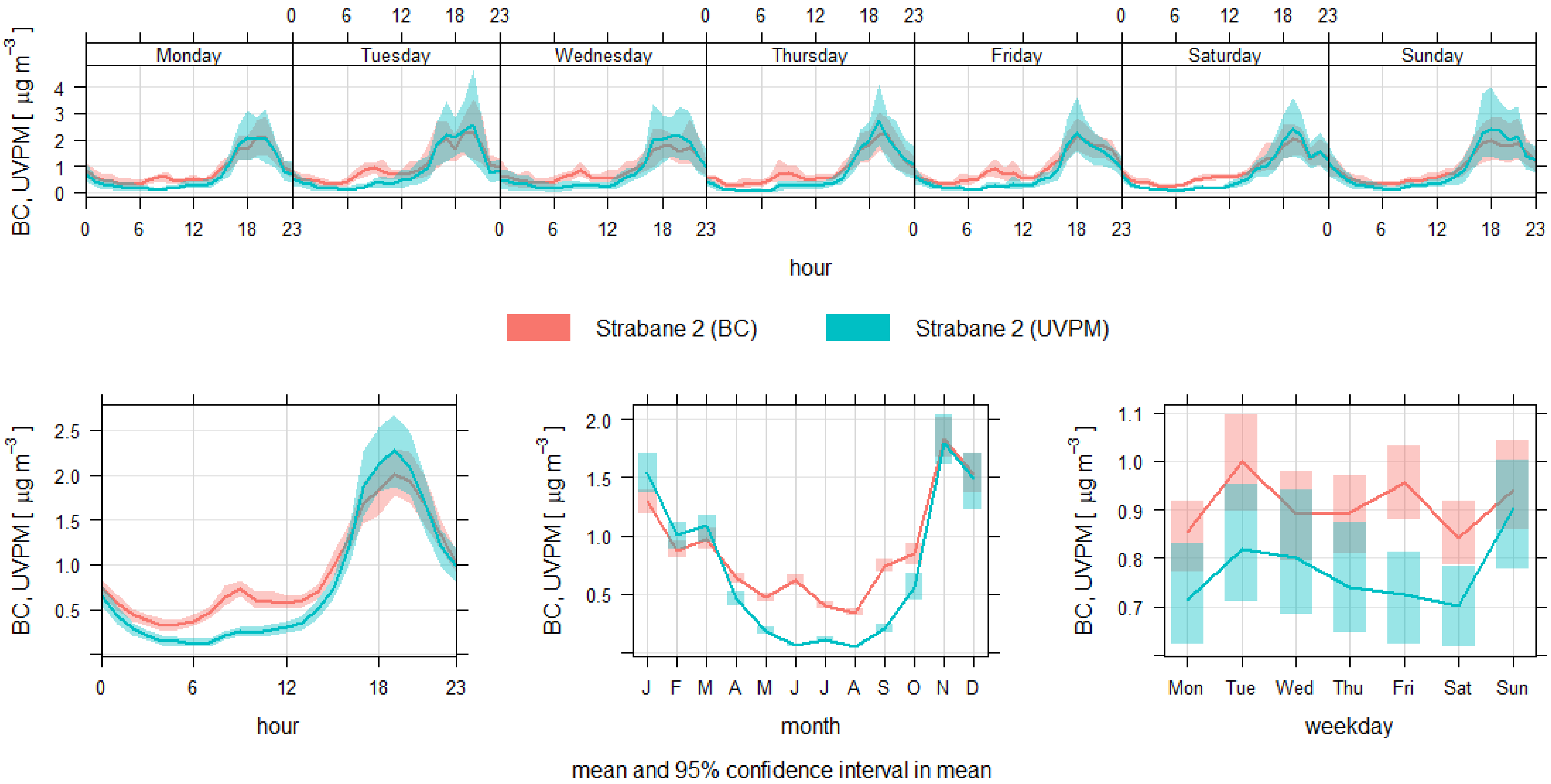


Figure 55 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at Strabane 2 for 2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

BC and UVPM data at rural background sites for 2023

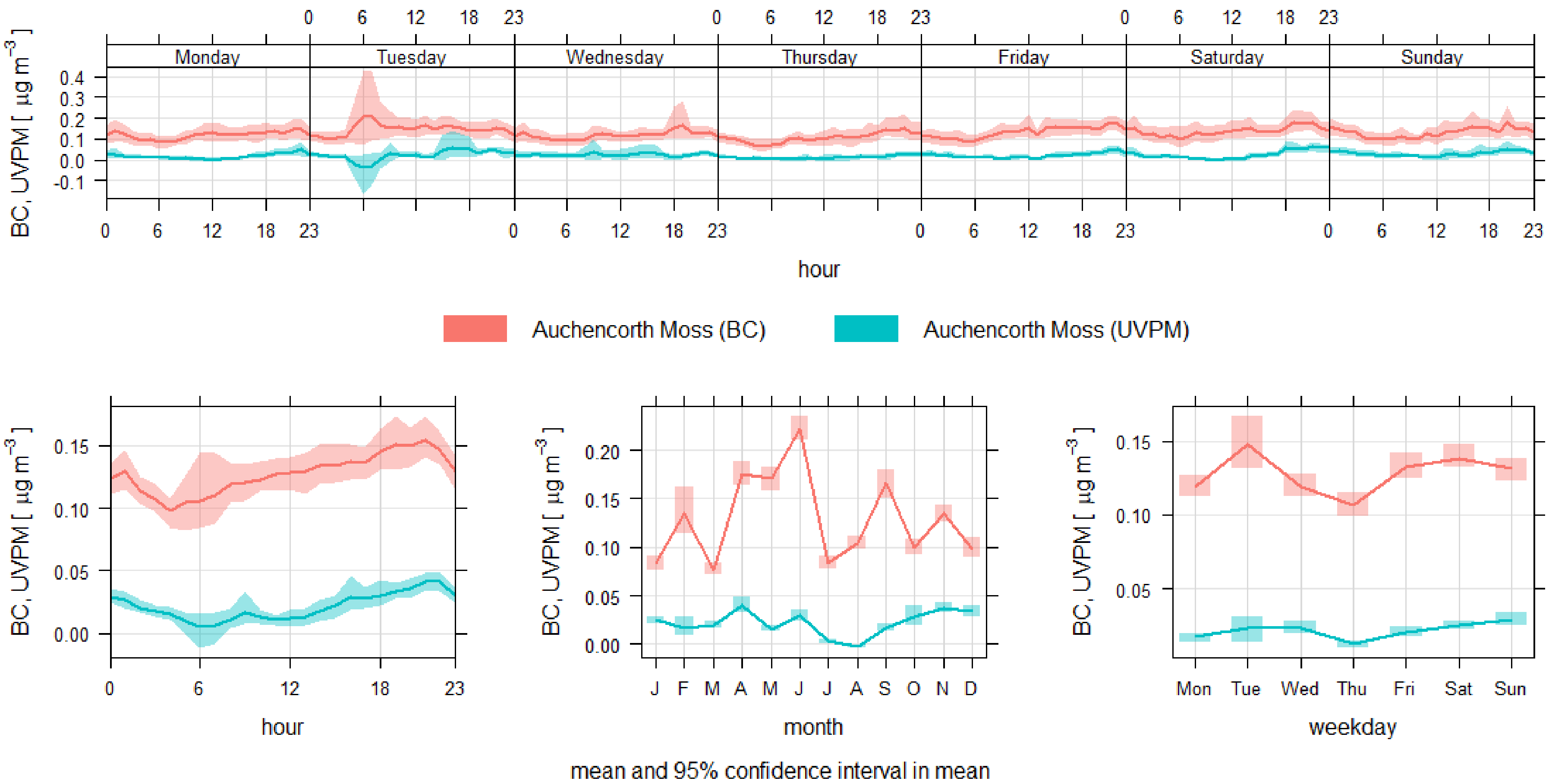


Figure 56 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at Auchencorth Moss for 2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

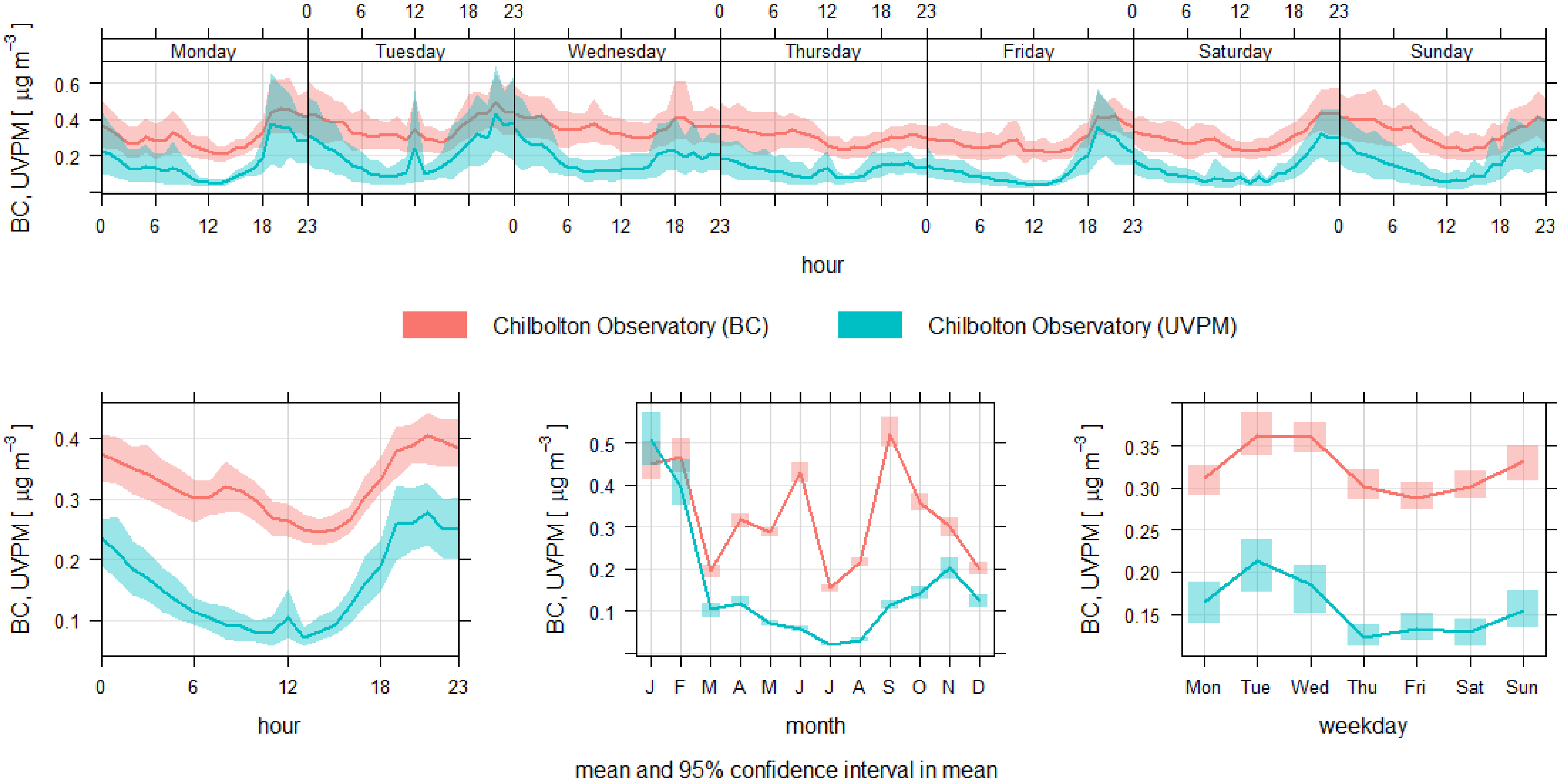


Figure 57 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at Chilbolton Observatory for 2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

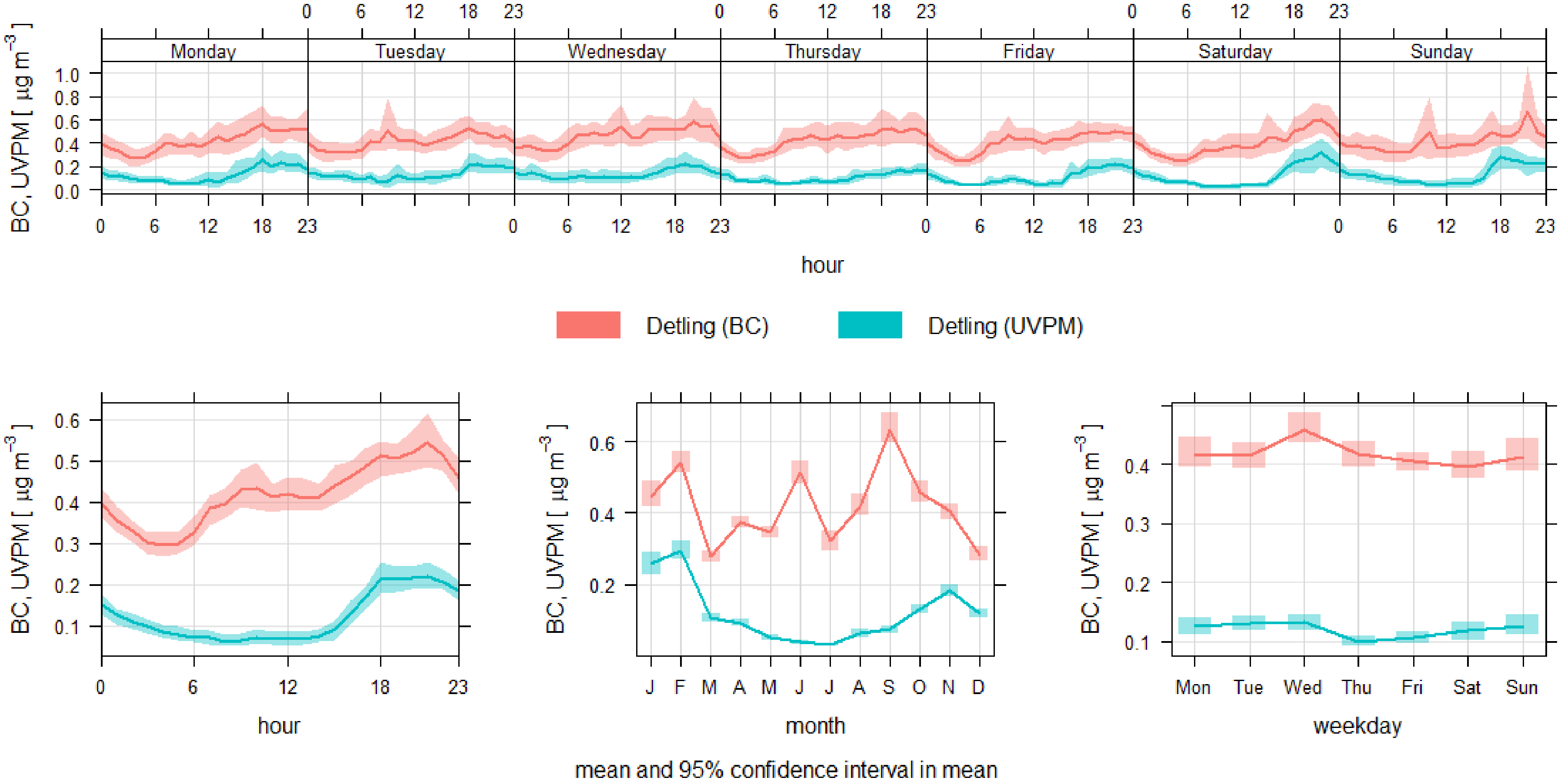


Figure 58 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at Detling for 2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

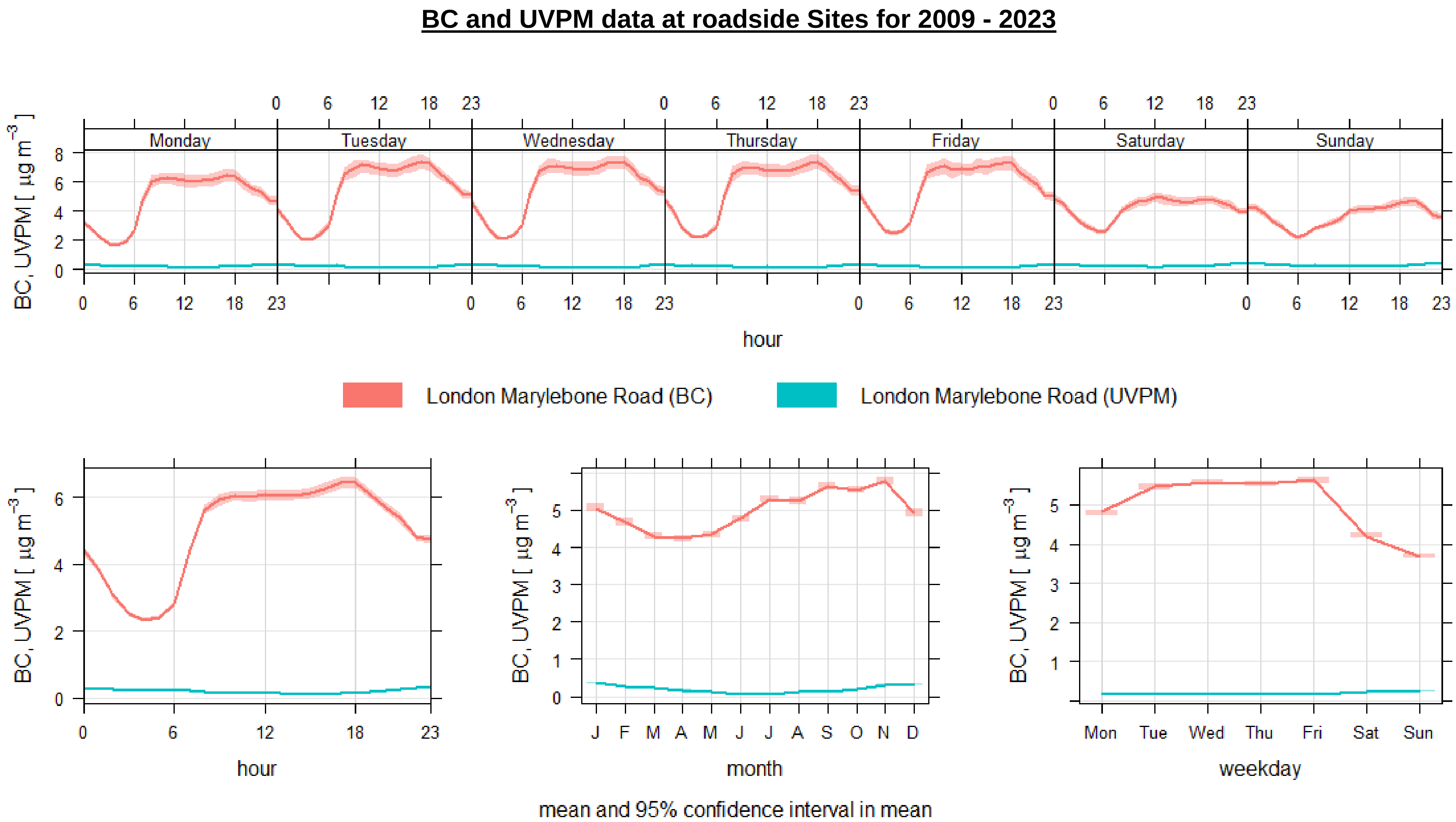


Figure 59 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at London Marylebone Road for 2009-2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

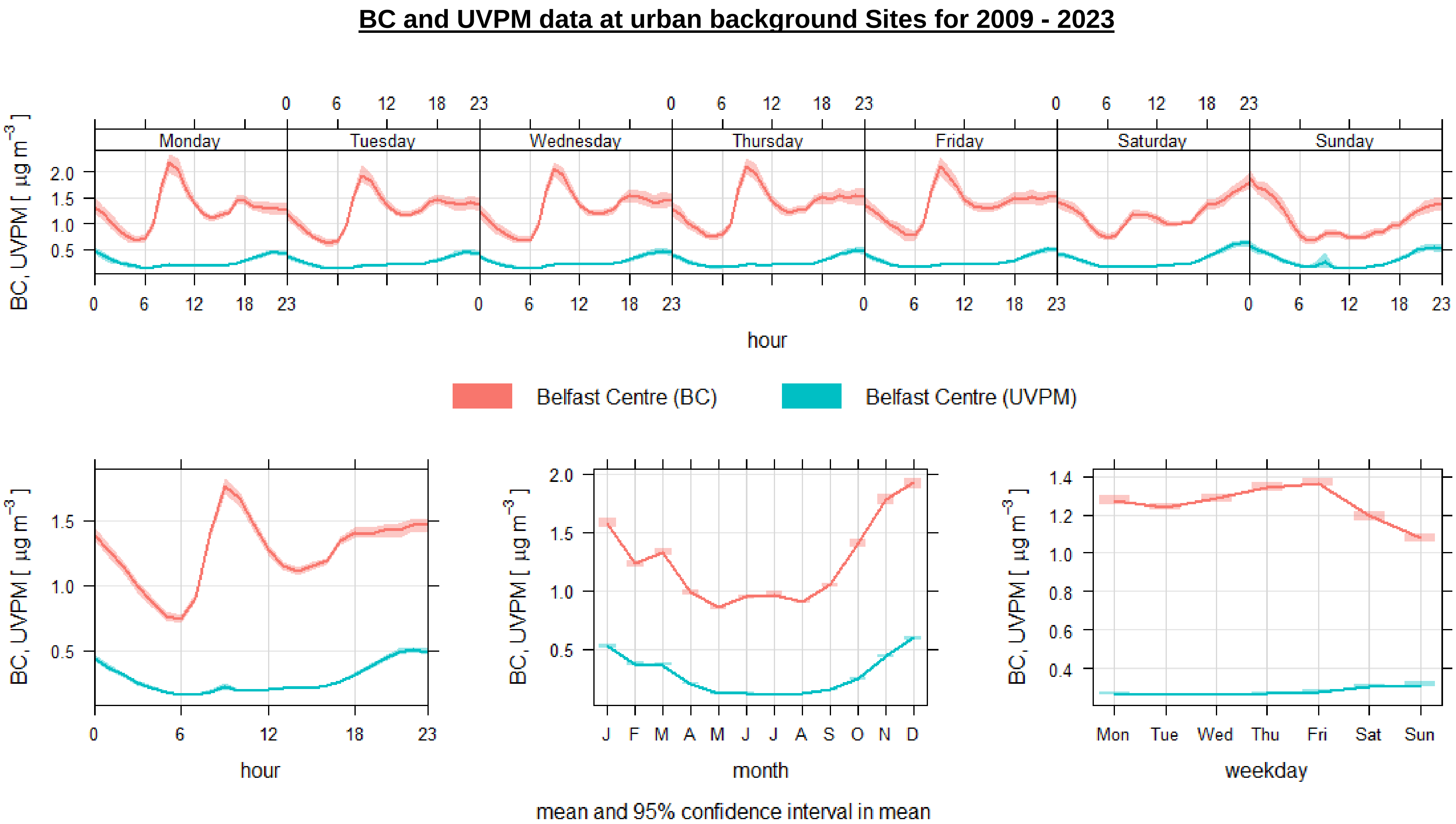


Figure 60 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at Belfast Centre for 2009-2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

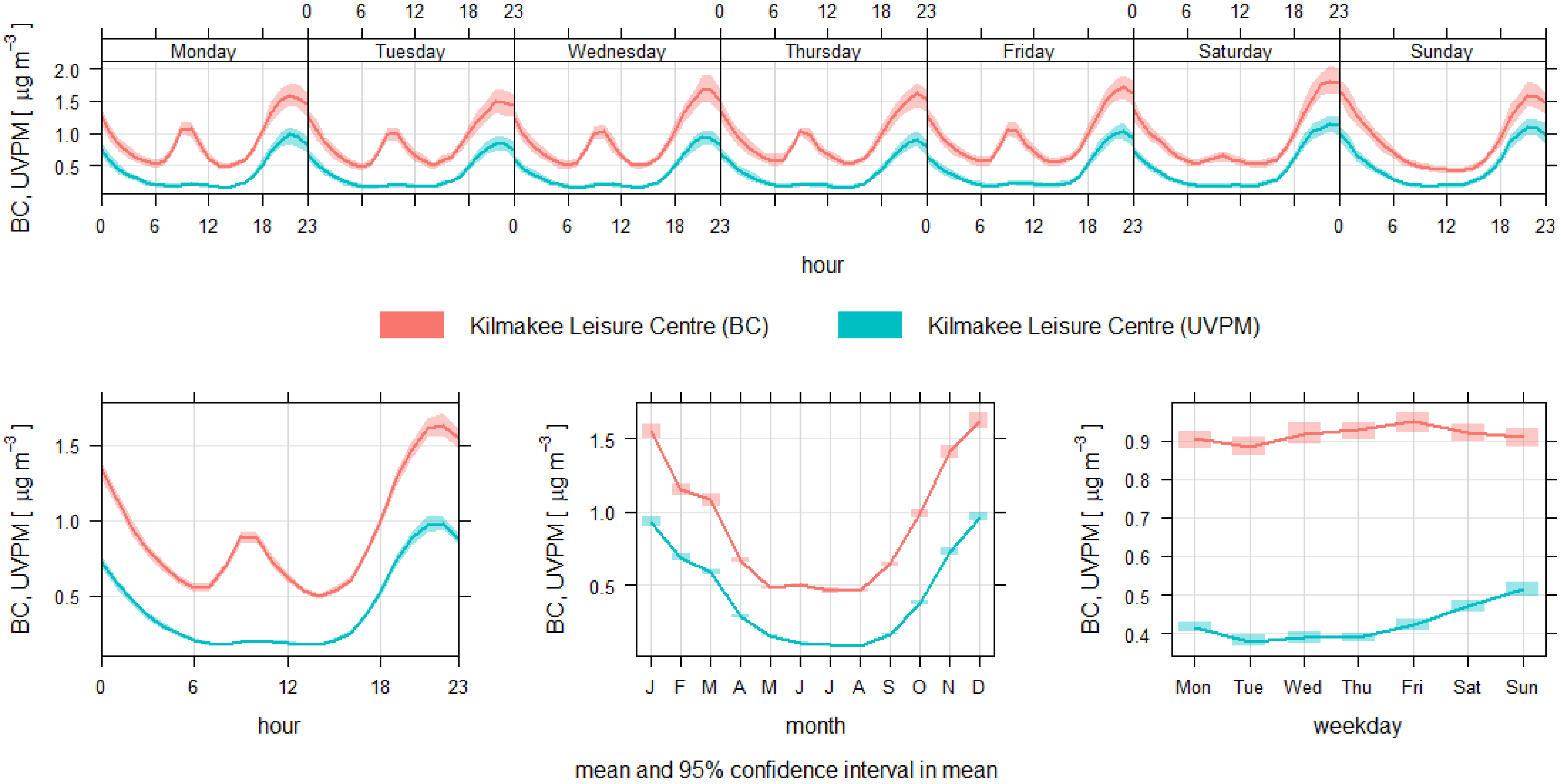


Figure 61 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at Kilmakee Leisure Centre for 2009-2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

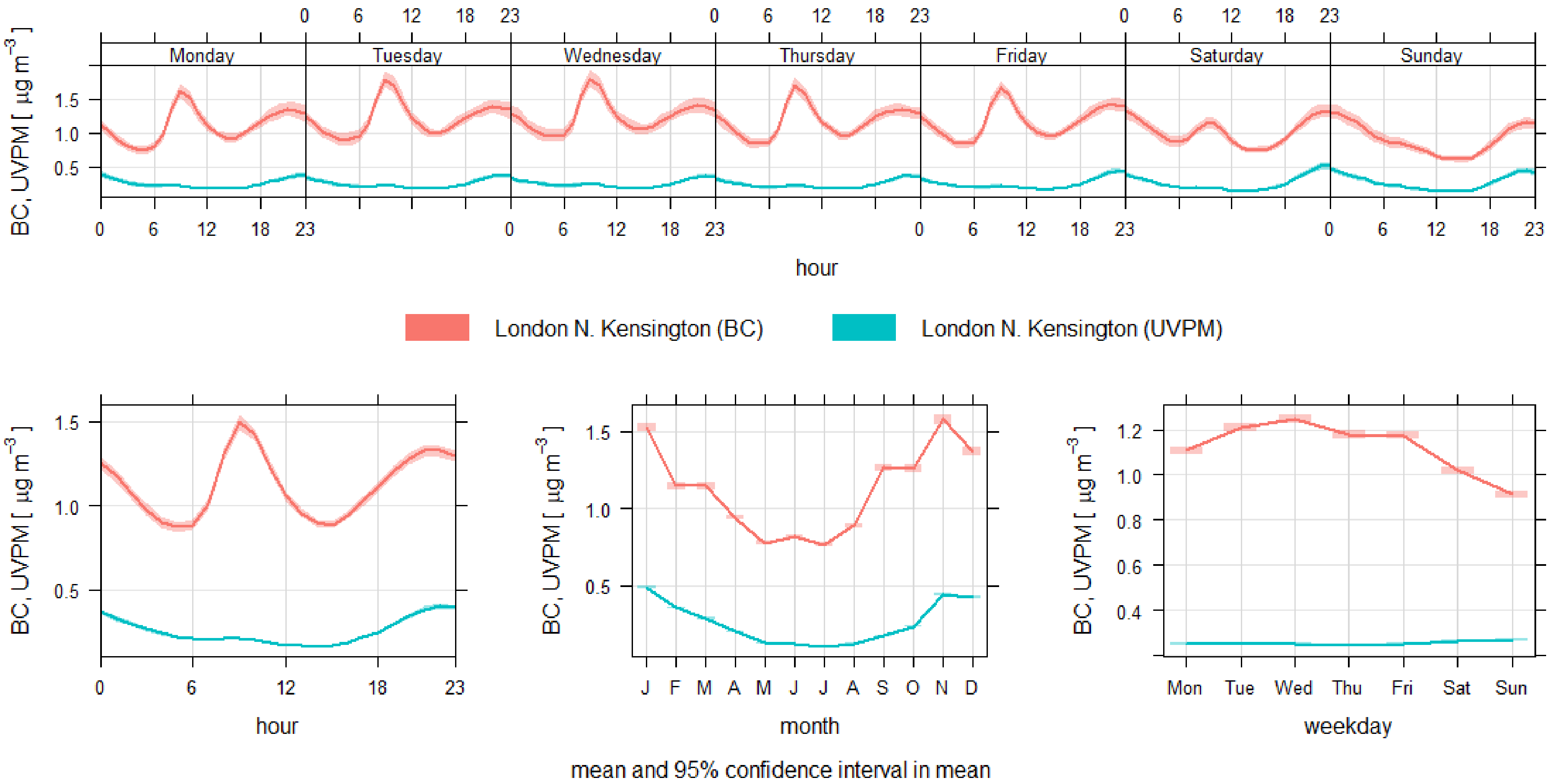


Figure 62 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at London North Kensington for 2009-2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

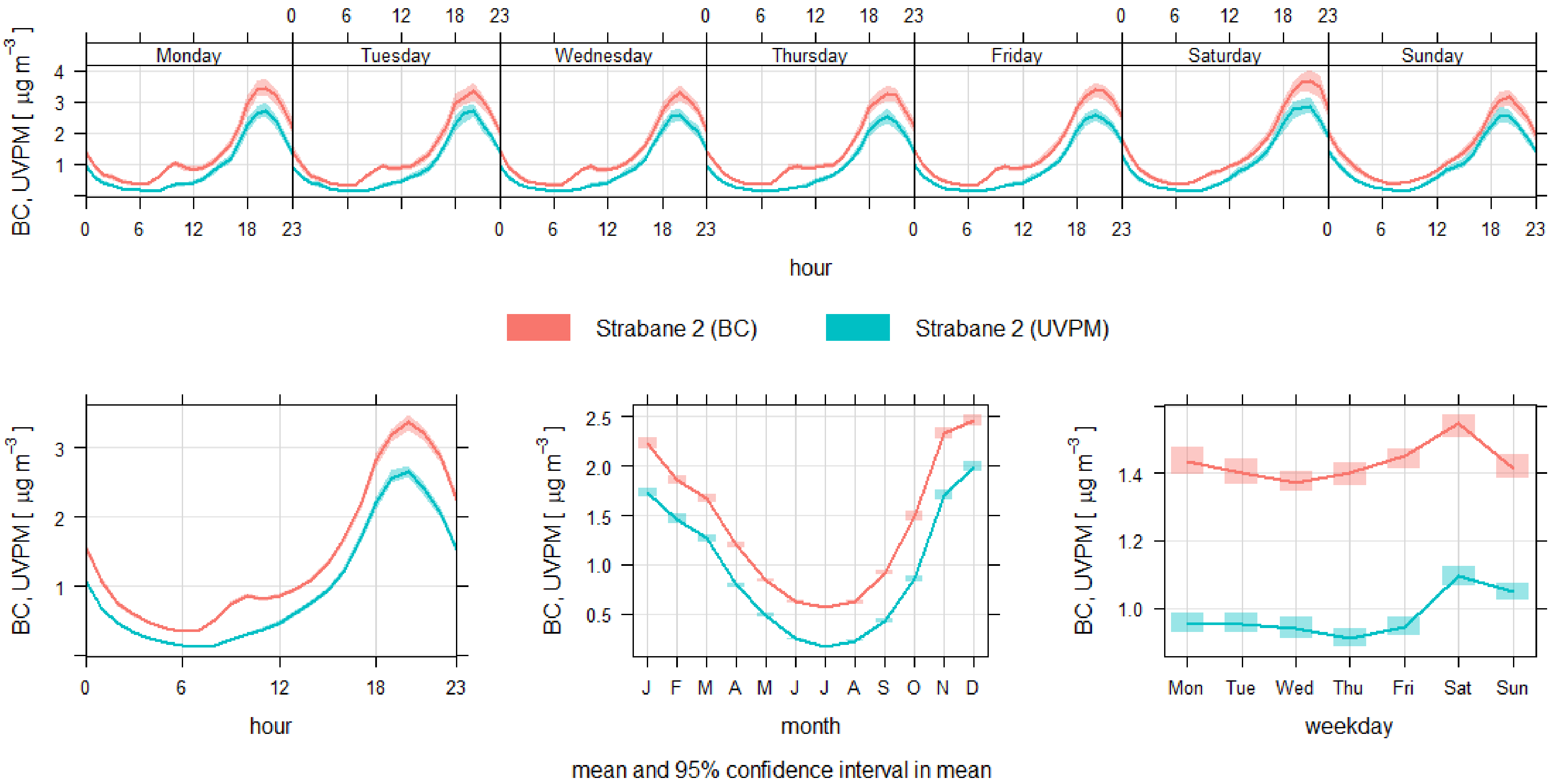


Figure 63 - Diurnal, weekly and monthly variations of BC and UVPM mass concentrations at Strabane 2 for 2009-2023. The solid lines represent the mean black carbon or UVPM mass concentration, and the shaded areas represent the 95% confidence interval in the mean.

4.6.5 Long-term trends

Figure 64 and Figure 65 show the trend in BC concentrations from the longest running sites in the Network, as monthly averages over the full calendar years 2009 to 2023.

The Theil-Sen method in OpenAir[27,28] 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 64 and Figure 65. 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 2023 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 66 and Figure 67 show the long-term trends in UVPM concentration.

The London Marylebone Road UVPM concentration showed an upward trend over the period 2009 to 2023, 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, these results should be treated with caution as only the trends determined for the London N. Kensington and Kilmakee Leisure Centre sites are statistically significant.

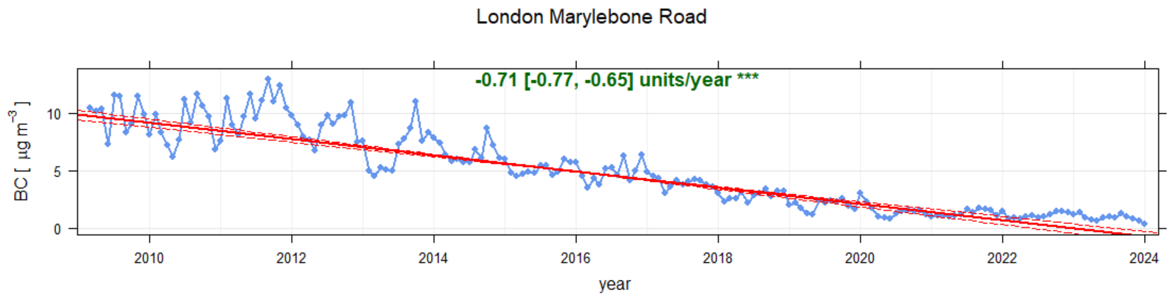


Figure 64 – Long-term trends in BC concentration measured at the London Marylebone Road roadside site, 2009 – 2023.

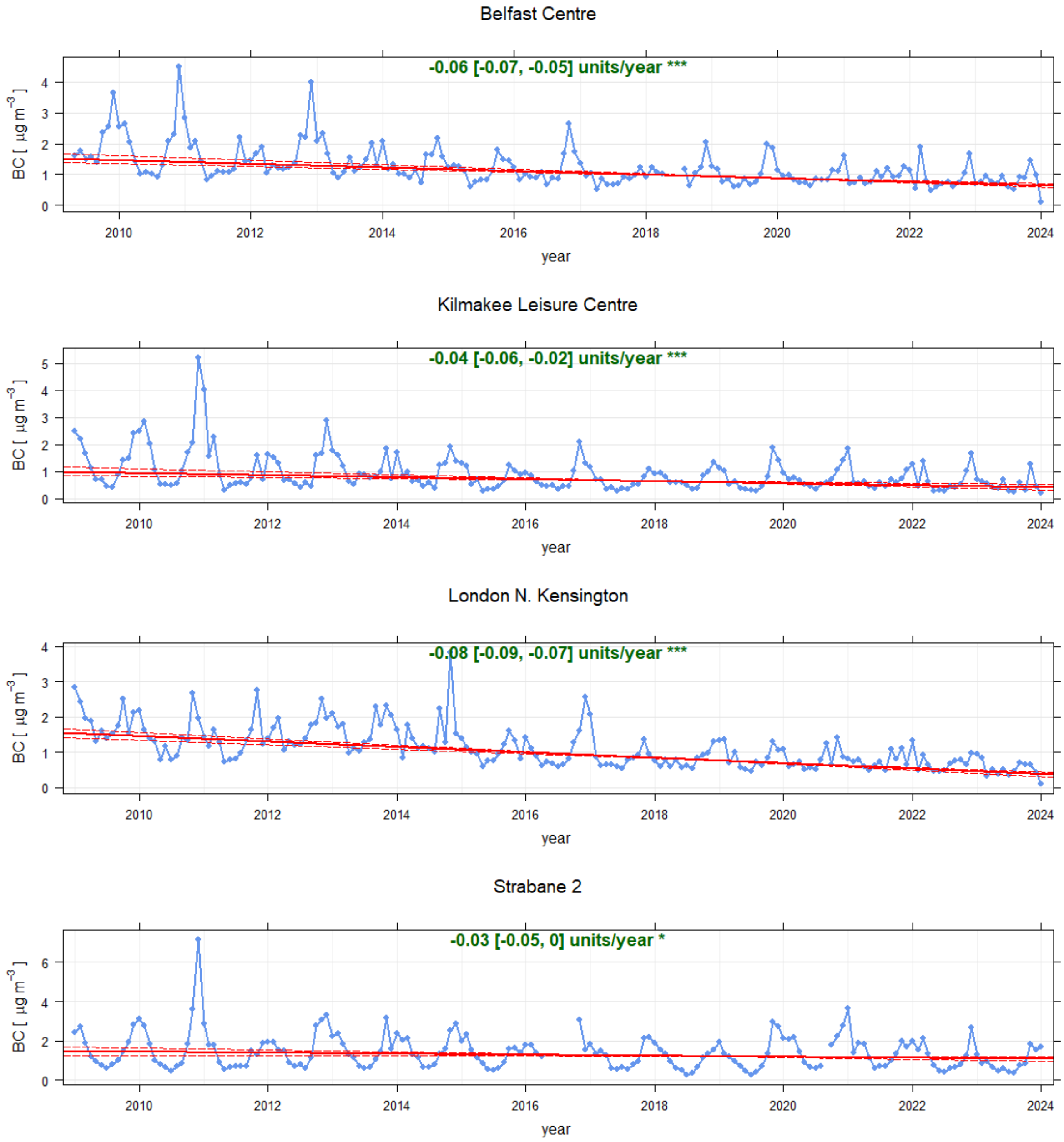


Figure 65 - Long-term trends in BC concentration measured at urban background sites, 2009 – 2023.

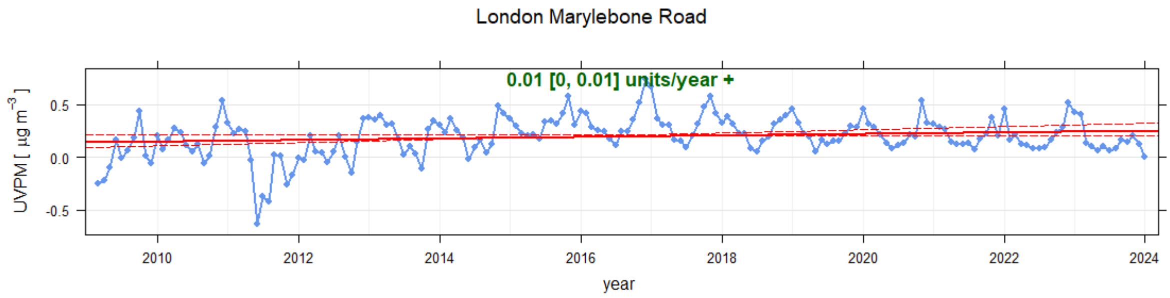


Figure 66 – Long-term trend in UVPM concentrations measured at roadside sites, 2009 – 2023.

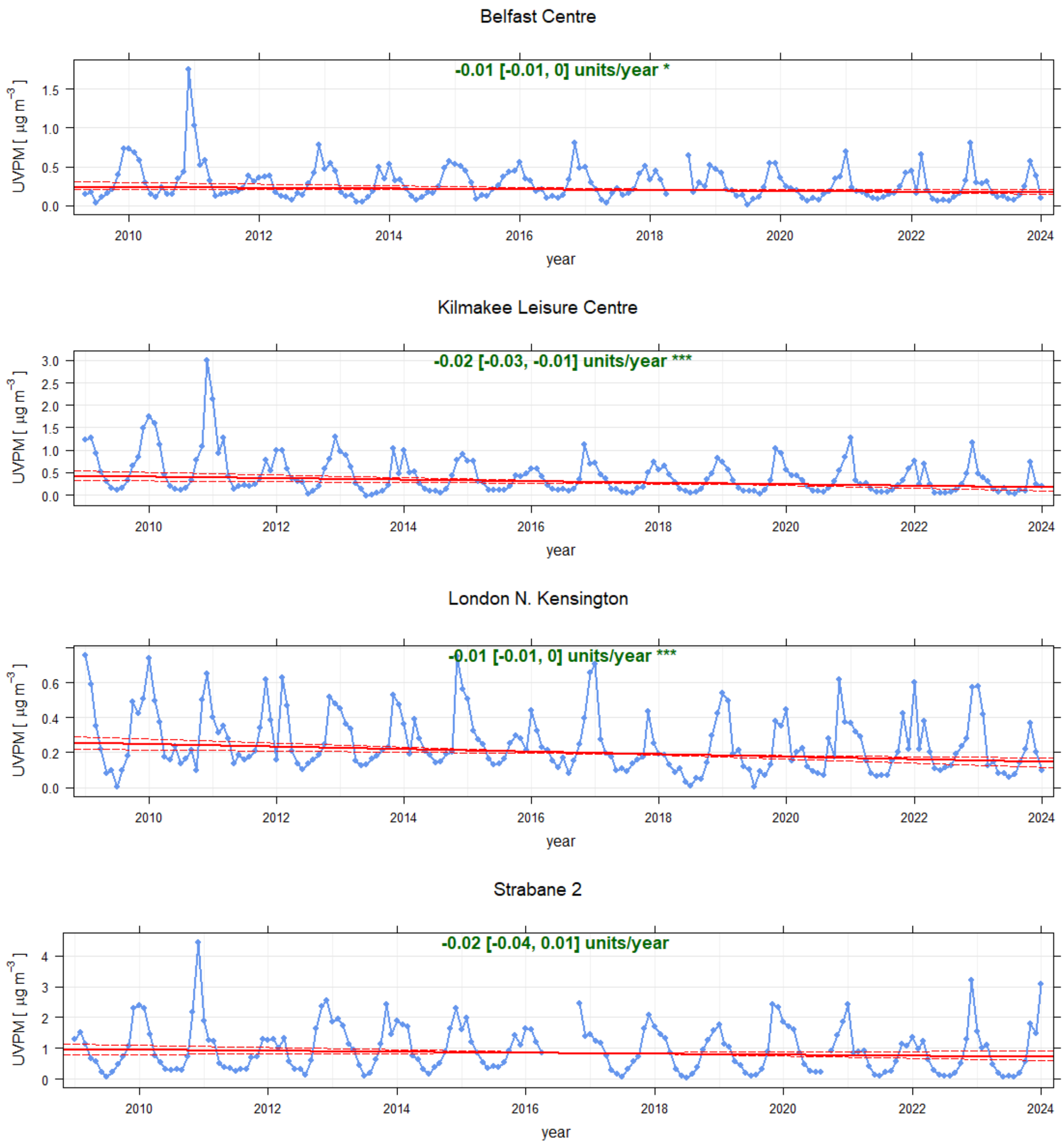


Figure 67 - Long-term trends in UVPM concentrations measured at urban background. sites, 2009 – 2023.

4.6.6 Comparisons with other pollutants

Comparisons are possible between EC and BC concentrations at two sites, and with also 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 68. The regression is calculated according to the Reduced Major Axis (RMA) method[32] (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 method is more 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[33].

There was a good linear correlation (R^2 ~ 0.8) with similar relationship between the EC and BC concentrations measured at the Chilbolton Observatory and London Marylebone Road sites in 2023 (see Table 14).

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

Year	Chilbolton Observatory* Relationship	R^2	London Marylebone Road** 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
2023	1.61x – 0.06	0.874	1.60x – 0.11	0.826

Notes

* 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 and 2023 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 and 2023 data are from the $PM_{2.5}$ Digitel sampler.

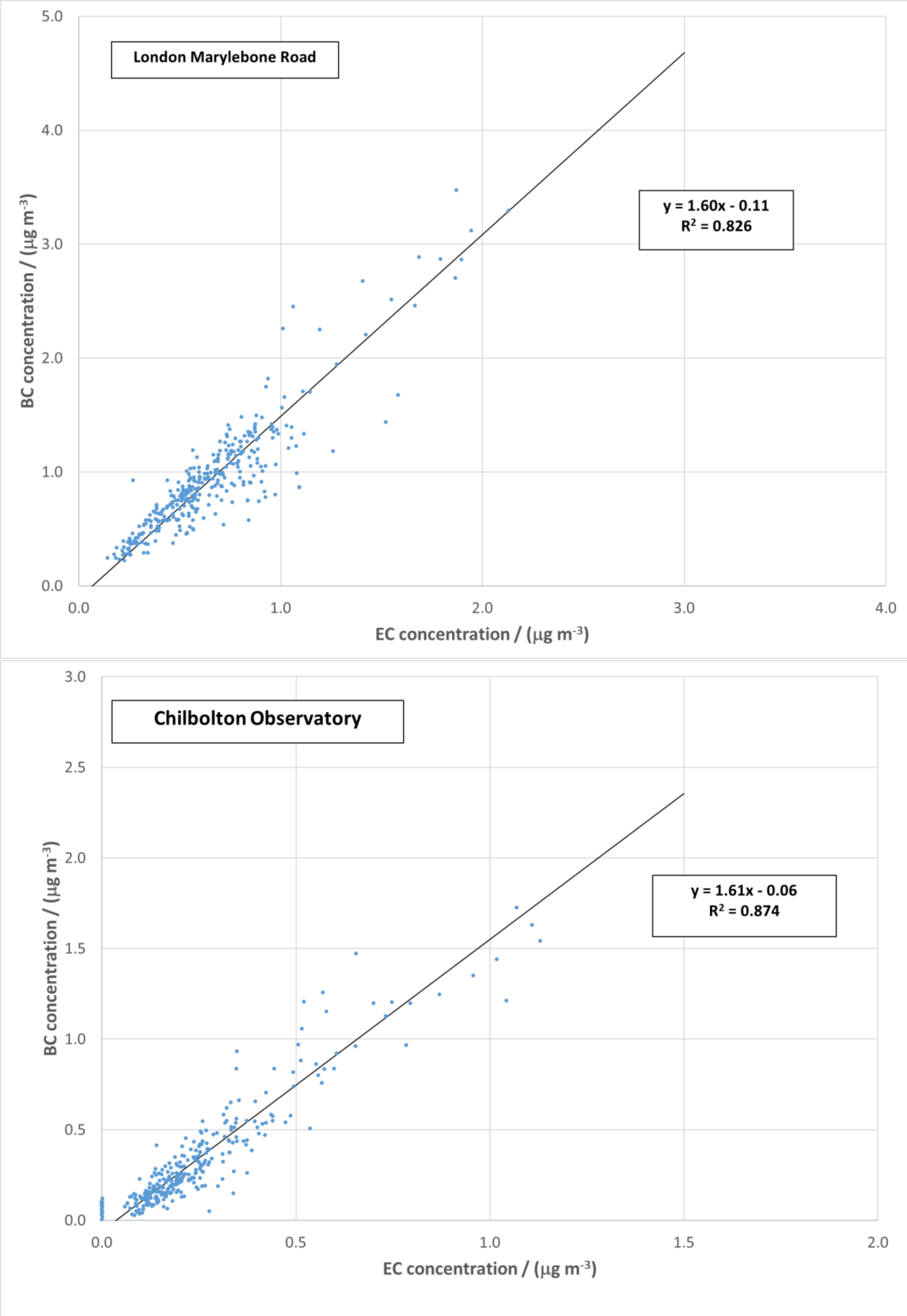


Figure 68 - Comparison between BC and EC at the London Marylebone Road and Chilbolton Observatory sites in 2023.

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 / (µg m^{-3})	PM_{10} / (µg m^{-3})	$PM_{2.5}$ / (µg m^{-3})	BC as % of PM_{10}	BC as % of $PM_{2.5}$
Auchencorth Moss	0.1	6 (FIDAS)	3 (FIDAS)	2	4
Belfast Centre	0.8	13 (FIDAS)	7 (FIDAS)	6	12
Birmingham A4540 Roadside	1.5	15 (FIDAS)	8 FIDAS)	10	19
Birmingham Ladywood	0.6	11 (FIDAS)	7 (FIDAS)	5	9
Cardiff Centre	0.9	16 (BAM)	10(BAM)	6	9
Chilbolton Observatory	0.3	10 (FIDAS)	6 (FIDAS)	3	5
Detling*	0.4	12 (TEOM FDMS)	-	3	-
Glasgow High Street	0.6	10 (FIDAS)	5 (FIDAS)	6	13
Glasgow Townhead	0.5	9 (FIDAS)	5 (FIDAS)	5	9
London Marylebone Road	0.9	18 (BAM)	12 (BAM)	5	8
London North Kensington	0.6	12 (FIDAS)	8 (FIDAS)	5	7
Strabane 2	0.9	12 (REF.EQ)	8 (FIDAS)	8	11

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 had a higher percentage of BC than the other sites. BC therefore represented a noticeable 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, Glasgow High Street 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 $PM_{2.5}$ MONITORING EXPANSION PROGRAMME

5.1 Introduction

Following the Environment Act 2021[11] and the new legally binding $PM_{2.5}$ targets published through The Environmental Targets (Fine Particulate Matter) (England) Regulations 2023[1], Defra has requested an expansion of the PCN&BC Network to provide additional PM speciation data to enhance the measurement evidence base associated with the $PM_{2.5}$ environmental targets. In 2023, the PCN&BC Network team were involved in various activities to prepare for expanding the Network. The current plan for expansion of the PCN&BC Network involves two new multi-instrument rural 'supersites', including SMPSs, ACSMs, and aethalometers; and a further 15 new sites for BC measurements in England.

5.2 Particle size distribution

In 2022, NPL carried out market research on, and subsequently (in August 2023) the EA tendered for, new SMPS equipment. In August 2023, a one-month trial of a GRIMM SMPS (5416/5420/DMA) took place at NPL. This involved assessing the instrument performance against the tender technical requirements (which were successfully met):

- The required data was retrievable and in an appropriate format.
- Data coverage was ≥ 85% for the one-month trial.
- There was training and a training manual for the LSO (NPL) for the use of the trial period. Guidance was clear and detailed enough to enable an experienced operator to follow correctly.
- The ESU Service Engineer (ET) got to site within the agreed time (<3 working days).
- Butanol fill frequency (≥ 14 days).

Following the trial, four GRIMM SMPSs (model 5416/5420/DMA) were purchased by the EA and were delivered by ET in March 2024.

5.3 Aerosol mass and chemical composition

In 2022, ERG carried out market research on new instruments to measure aerosol mass and chemical composition, and subsequently (in early 2023) two Aerodyne time-of-flight (ToF)-ACSMs were purchased by the EA. ERG received and set up the instruments for lab testing at ICL in September 2023. Training of staff on ToF-ACSMs (which are different to the Q-ACSMs currently on the Network) took place, and commissioning and test of both instruments in ERG's labs commenced in November 2023, including testing of the UPS and development of data collection software. Proceeding this, one instrument will be decommissioned and stored until deployment; the other will continue daily operation in the lab to establish common issues and solutions.

5.4 BC and UVPM

Following market research activities by NPL in 2022, ten Magee Scientific AE33 aethalometers were purchased by the EA and tested by ACOEM in early 2023. During August to December 2023, a trial took place at two sites (Blackburn and Derby) to test the suitability of cupboard-type ("PR5") housing for the aethalometers[34]. Following the success of the trial, both sites were ready for operation as of January 2024. A further eight Magee Scientific AE33 Aethalometers were purchased by the EA and tested by ACOEM in December 2023.

6 PEER-REVIEW PUBLICATIONS

Three peer-review papers that used data from the PCN&BC data were published by the network delivery team in 2023:

1. *Ambient air particulate total lung deposited surface area (LDSA) levels in urban Europe*[35]

Particle size distribution data measured at the London sites on this Network, 21 sites across the EU, and one site in the US between 2017 and 2019, were used to examine the phenomenology of urban ambient total lung deposited surface area (LDSA). The study showed that peak concentrations of LDSA at urban background and traffic sites are commonly observed in the morning (06:00–8:00 UTC) and late evening (19:00–22:00 UTC), coinciding with traffic rush-hours, biomass burning, and atmospheric stagnation periods. The only LDSA night-time peaks are observed on weekends. Due to the variability of emission sources and meteorology, the seasonal variability of the LDSA concentration revealed significant differences between the four seasons at all monitoring sites. Meanwhile, the correlations of LDSA with other pollutant metrics suggested that Aitken and accumulation mode particles play a significant role in the total LDSA concentration. Overall, the study provides valuable information of LDSA as a predictor in epidemiological studies and for the first time presenting total LDSA in a variety of European urban environments.

2. *The variability of mass concentrations and source apportionment analysis of equivalent black carbon across urban Europe*[36]

The variability of equivalent black carbon (eBC) mass concentrations and their sources in urban Europe was analysed to provide insights into the use of eBC as an advanced parameter for air quality standards. This study compiled eBC mass concentration datasets covering from 2006-2022 from 50 measurement stations, including three sites on this Network. The results highlighted the need for the harmonization of eBC measurements to allow for direct comparisons between eBC mass concentrations measured across urban Europe. The eBC mass concentrations exhibited a decreasing trend across site types as follows: traffic > urban background > suburban background > rural background. The eBC mass concentrations exhibited significant spatiotemporal heterogeneity, including marked differences in eBC mass concentration and variable contributions of pollution sources to bulk eBC between different cities. Seasonal patterns in eBC concentrations were also evident, with higher winter concentrations observed in a large proportion of cities, especially at urban background and suburban background sites. The contribution of eBC from fossil fuel combustion, mostly traffic (eBCT) was higher than that of residential and commercial sources (eBCRC) at all sites. Nevertheless, eBCRC still had a substantial contribution to total eBC mass concentrations at a majority of the sites. eBC trend analysis revealed decreasing trends for eBCT over the last decade, while eBCRC remained relatively constant or even increased slightly in some cities.

3. Characterising a mobile reference station (MoRS) to quantify personal exposure to air quality[37]

A novel mobile air quality monitoring system 'Mobile Reference Station' (MoRS) was designed and built for the simultaneous measurement of a broad aerosol size distribution (10 nm–35 μm), concentrations of nitrogen dioxide and ozone, environmental parameters (noise, relatively humidity and temperature) as well as collecting filter samples for laboratory analysis. Field testing of MoRS, including against the SMPS at London Marylebone Road showed excellent inter-comparability against reference instrumentation and good agreement with reference instruments in the ultrafine aerosol range, although there was an overestimation of fine particle aerosols. The MoRS was deployed on mainline train and London Underground journeys, and the paper presents data from these measurement campaigns.

Other peer-review papers that used data from the PCN&BC Network published in 2023, include:

1. *Phenomenology of ultrafine particle concentrations and size distribution across urban Europe*[38], which showed evidence of increasing urban background concentrations of ultrafine particles from north to south-east Europe and proposed that road traffic emissions are the main source of ultrafine particles in urban Europe.

2. *Limited impact of diesel particle filters on road traffic emissions of ultrafine particles*[39], which studied roadside measurements of particle size distributions from 2010 to 2021. The work showed that the introduction of diesel particle filters steadily reduced black carbon concentrations over this period, but had little effect on nucleation mode particles, and only a small decrease in the concentration of ultrafine particles was reported.

7 REFERENCES

[1] The Environmental Targets (Fine Particulate Matter) (England) Regulations 2023 (UK SI 2023/96). Available at: https://www.legislation.gov.uk/uksi/2023/96/contents/made

[2] Defra UK-AIR website: https://uk-air.defra.gov.uk/

[3] The Air Quality Standards Regulations 2010 (UK SI 2010/1001). Available at https://www.legislation.gov.uk/uksi/2010/1001/contents/made

[4] The Air Quality Standards Regulations (Northern Ireland) 2010 (NI SI 2010/188). Available at https://www.legislation.gov.uk/nisr/2010/188/contents/made

[5] The Air Quality Standards (Scotland) Regulations 2010 (S SI 2010/204). Available at https://www.legislation.gov.uk/ssi/2010/204/contents/made

[6] The Air Quality Standards (Wales) Regulations 2010 (W SI 2010/1433, W. 126). Available at https://www.legislation.gov.uk/wsi/2010/1433/contents/made

[7] Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe (2008) *Official Journal* **L152**, 11/06/2008, 1 – 44 (EN). https://eur-lex.europa.eu/eli/dir/2008/50/oj

[8] Commission Directive (EU) 2015/1480 of 28 August 2015 amending several annexes to Directives 2004/107/EC and 2008/50/EC of the European Parliament and of the Council laying down the rules concerning reference methods, data validation and location of sampling points for the assessment of ambient air quality, *Official Journal* **L226**, 29/08/2015, 4 – 11 (EN). https://eur-lex.europa.eu/eli/dir/2015/1480/oj

[9] UK Department for Environment, Food, and Rural Affairs (2019), *Clean Air Strategy*. Available at: https://www.gov.uk/government/publications/clean-air-strategy-2019

[10] UK Department for Environment, Food, and Rural Affairs (2023), *Environmental Improvement Plan*. Available at: https://www.gov.uk/government/publications/environmental-improvement-plan

[11] Environment Act 2021 c. 30. Available at https://www.legislation.gov.uk/ukpga/2021/30/contents

[12] Technical Specification CEN/TS 16976:2016, *Ambient air - Determination of the particle number concentration of atmospheric aerosol.*

[13] European Standard EN 16976:2024, *Ambient air - Determination of the particle number concentration of atmospheric aerosol.*

[14] Technical Specification CEN/TS 17434:2020, *Ambient air - Determination of the particle number size distribution of atmospheric aerosol using a Mobility Particle Size Spectrometer (MPSS).*

[15] FURGER, M., RAI, P., SLOWIK, J.G., CAO, J., VISSER, S., BALTENSPERGER, U., PRÉVÔT, A.S.H. Automated alternating sampling of PM_{10} and $PM_{2.5}$ with an online XRF spectrometer. *Atmospheric Environment: X*, 2020, **5**, 100065. https://doi.org/10.1016/j.aeaoa.2020.100065.

[16] TREMPER, A.H., FONT, A., PRIESTMAN, M., HAMAD, S.H., CHUNG, T.C., PRIBADI, A., BROWN, R. J.C., GODDARD, S.L., GRASSINEAU, N., PETTERSON, K., KELLY, F.J., GREEN, D.C. Field and laboratory evaluation of a high time resolution x-ray fluorescence instrument for determining the elemental composition of ambient aerosols. *Atmospheric Measurement Techniques,* **11(6)**, 3541–3557. https://doi.org/10.5194/amt-11-3541-2018.

[17] European Standard EN 16909:2017, *Ambient air- Measurement of elemental carbon (EC) and organic carbon (OC) collected on filters.*

[18] DRINOVEC, L., MOČNIK, G., ZOTTER, P., PRÉVÔT, A. S. H., RUCKSTUHL, C., COZ, E., RUPAKHETI, M, SCIARE, J., MÜLLER, Y, WIEDENHOSER, A. and HANSEN, A. D. A. The "dual-spot" Aethalometer: An improved measurement of aerosol black carbon with real-time loading compensation. *Atmospheric Measurement Techniques*, 2015, **8(5)**, 1965–1979. https://doi.org/10.5194/amt-8-1965-2015.

[19] Defra UK-AIR website Black Carbon Network page:
https://uk-air.defra.gov.uk/networks/network-info?view=ukbsn

[20] International standard ISO 9001:2015, *Quality management systems — Requirements.*

[21] International standard ISO/IEC 17025:2017, *General requirements for the competence of testing and calibration laboratories.*

[22] FRENEY, E., FAVEZ, O., GROS, V. Development of a measurement standardization and data submission protocol for aerosol particle mass spectroscopy based on Aerosol Chemical Speciation Monitor (ACSM) products. *ACTRIS, 2016.*
https://www.actris.eu/sites/default/files/Documents/ACTRIS-2/Deliverables/WP3_D3.3_M16.pdf

[23] European standard EN 12341:2023, *Ambient air — Standard gravimetric measurement method for the determination of the PM_{10} or $PM_{2,5}$ mass concentration of suspended particulate matter.*

[24] QUINCEY, P. G., SARANTARIDIS, D., TUCH, T., YLI-OJANPERÄ, J., HÖGSTRÖM, R., LÜÖND, F., NOWAK, A., JORDAN-GERKENS, A., RICCOBONO, F., IIDA, K., SAKURAI, H. and OWEN, M. EURAMET Comparison 1282: Comparison of condensation particle counters. Final Report. *NPL Report AS 94,* 2014.
http://eprintspublications.npl.co.uk/id/eprint/6453

[25] CRENN, V. *et al*. ACTRIS ACSM intercomparison – Part 1: Reproducibility of concentration and fragment results from 13 individual Quadrupole Aerosol Chemical Speciation Monitors (Q-ACSM) and consistency with co-located instruments. *Atmos. Meas. Tech.,* 2015, **8**, 5063–5087. https://doi.org/10.5194/amt-8-5063-2015

[26] European Partnership of Metrology project STANBC website: www.stanbc.com

[27] The OpenAir project website: www.openair-project.org

[28] CARSLAW, D.C. and ROPKINS, K. OpenAir - An R package for air quality data analysis. Environmental Modelling & Software, 2012, 27-28, 52-61.
https://doi.org/10.1016/j.envsoft.2011.09.008

[29] Regulation (EC) No 715/2007 of the European Parliament and of the Council of 20 June 2007 on type approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) and on access to vehicle repair and maintenance information (Text with EEA relevance) *Official Journal* **L 171**, 29.6.2007, p. 1–16 (EN). http://data.europa.eu/eli/reg/2007/715/oj

[30] Commission Regulation (EU) No 459/2012 of 29 May 2012 amending Regulation (EC) No 715/2007 of the European Parliament and of the Council and Commission Regulation (EC) No 692/2008 as regards emissions from light passenger and commercial vehicles (Euro 6) Text with EEA relevance. *Official Journal* **L 142**, 1.6.2012, p. 16–24 (EN). http://data.europa.eu/eli/reg/2012/459/oj

[31] Commission Regulation (EU) 2017/1151 of 1 June 2017 supplementing Regulation (EC) No 715/2007 of the European Parliament and of the Council on type-approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) and on access to vehicle repair and maintenance information, amending Directive 2007/46/EC of the European Parliament and of the Council, Commission Regulation (EC) No 692/2008 and Commission Regulation (EU) No 1230/2012 and repealing Commission Regulation (EC) No 692/2008 (Text with EEA relevance)*Official Journal* **L 175,** 07/07/2017, p. 1–643 (EN). http://data.europa.eu/eli/reg/2016/646/oj

[32] AYERS, G. P. Comment on regression analysis of air quality data. Technical Note. *Atmospheric Environment*, 2001, **35**, 2423-2425. https://doi.org/10.1016/S1352-2310(00)00527-6

[33] CIUPEK, K., QUINCEY, P., GREEN, D.C., BUTTERFIELD, D., and FULLER, G.W. Challenges and policy implications of long-term changes in mass absorption cross-section derived from equivalent black carbon and elemental carbon measurements in London and south-east England in 2014–2019, *Environmental Science: Processes & Impacts*, 2021, **23**, 1949-1960, https://doi.org/10.1039/D1EM00200G

[34] CIUPEK, K., WALKER, D., NPL Report: Black carbon trial campaign 2023; *National Physical Laboratory*, 2024, ENV 56. https://doi.org/10.47120/npl.ENV56

[35] LIU, X. *et al.*, Ambient air particulate total lung deposited surface area (LDSA) levels in urban Europe. *Science of The Total Environment*, 2023, **898**, 165466. https://doi.org/10.1016/j.scitotenv.2023.165466

[36] SAVADKOOHI, M. *et al.*, The variability of mass concentrations and source apportionment analysis of equivalent black carbon across urban Europe. *Environment International*, 2023, **178**, 108081.https://doi.org/10.1016/j.envint.2023.108081

[37] HEDGES, M., PRIESTMAN, M., CHADEAU-HYAM, M., SINHARAY, R., KELLY, F. K., and GREEN, D. C., Characterising a mobile reference station (MoRS) to quantify personal exposure to air quality, *Atmospheric Environment*, 2023, **315**, 120160. https://doi.org/10.1016/j.atmosenv.2023.120160

[38] TRECHERA, P. *et al.*, Phenomenology of ultrafine particle concentrations and size distribution across urban Europe. *Environment International*, 2023, **172**, 10. https://doi.org/10.1016/j.envint.2023.107744

---

[39] DAMAYANTI, S., HARRISON, R. M., POPE, F., BEDDOWS, D. C. S., Limited impact of diesel particle filters on road traffic emissions of ultrafine particles, *Environment International,* 2023, **174**, 107888. https://doi.org/10.1016/j.envint.2023.107888

NPL REPORT ENV 56

BLACK CARBON MEASUREMENTS IN THE UNITED KINGDOM – TRIAL CAMPAIGN 2023

KRZYSZTOF CIUPEK
DOUGLAS WALKER

AUGUST 2024

Black carbon measurements in the United Kingdom - Trial campaign 2023

K. Ciupek and D. Walker
Atmospheric and Environmental Science Department, NPL

ISSN 2059-6030

https://doi.org/10.47120/npl.ENV56

National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

Approved on behalf of NPLML by
Craig Barnfield, Group Leader – Air Quality & Aerosol Metrology Group

CONTENTS

1 BLACK CARBON TRIAL CAMPAIGN

A trial campaign was conducted at two sites with black carbon (BC) network aethalometers (Aerosol Magee Scientific, model AE33) to assess the suitability of a small cupboard (“PR5”) type housing, which differs from the usual walk-in cabins used to accommodate these instruments.

This report is a summary of data for August – November 2023 collected at two new sites: Blackburn Audley Park and Derby Stockbrook Park.

2 INSTALLATION

At both 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 was constructed from stainless steel.

Figures 1 and 2 show the two sites, Blackburn Audley Park (site ID B7B) installed 22/08/2023, and Derby Stockbrook Park (site ID D7B) installed 08/09/2023; both are urban background measurement sites.

Figure 1 – PR5 housing at Blackburn Audley Park site.

Figure 2 – PR5 housing at Derby Stockbrook Park site.

3 DATA CAPTURE

Table 1 shows the data capture percentages for the period Q3-Q4:

22/08/2023 – 20/11/2023 for Blackburn Audley Park (site ID B7B) – Urban Background
08/09/2023 – 20/11/2023 for Derby Stockbrook Park (site ID D7B) – Urban Background

These results are based on validated AE33 aethalometer data.
For aethalometer: Red = <80 %; amber = 80-90 %; green = >90 %.

Table 1 – Data capture for BC measurements

Site	Q3-Q4*
Blackburn Audley Park (B7B)	100 %
Derby Stockbrook Park (D7B)	99 %

*Q3-Q4: time coverage from installation date (22/08/2023 for Blackburn Audley Park and 08/09/2023 for Derby Stockbrook Park) until 20/11/2023.

4 BC MASS CONCENTRATIONS

4.1 INTRODUCTION

The data presented in this report has been analysed following the same quality assurance and quality control (QA/QC) procedures used for all other datasets related to the BC network.

Table 2 shows mean values from all channels. Annual averages from the BC network in 2022 are also provided for Birmingham and London traffic sites as a comparison[1].

The results from the 880 nm channel give the quantitative concentration of “black” carbon (freshly emitted soot), and those from 370 nm channel indicate the presence of aromatic organic compounds that are found in wood smoke, biomass-burning smoke, and tobacco smoke. The ultraviolet particulate matter (UVPM) is calculated as the difference between UV and BC channels.

Table 2 – Mean mass concentration of particulate matter measured at specific wavelengths (in nm, indicated on brackets) by AE33 Aethalometers in Q3-Q4. As a comparison, annual mean values from Birmingham and London traffic sites are provided together with BC network 2022 average values measured at specific wavelengths at all sites across the UK.

	PM mass concentration / (μg m^{-3})							
Site	**UV**	**Blue**	**Green**	**Yellow**	**Red**	**BC**	**IR-2**	**UVPM**
	(370)	(470)	(520)	(590)	(660)	(880)	(950)	
Blackburn Audley Park	1.12	1.08	1.03	1.00	0.97	0.94	0.95	0.18
Derby Stockbrook Park	1.14	1.06	1.00	0.96	0.93	0.90	0.90	0.24
2022 BC Network (BCN)								
Birmingham A4540 Roadside	2.03	2.06	1.95	1.91	1.84	1.81	1.82	0.22
London Marylebone Road	1.31	1.27	1.23	1.17	1.13	1.10	1.10	0.21
BCN Annual Average (2022)	1.10	1.01	0.95	0.92	0.87	0.84	0.84	0.25

4.2 TIME SERIES

Figure 3 shows the BC concentrations measured from the installation dates to 20 November 2023. The time resolution of the measurement is hourly. Elevated BC concentrations were observed during the initial days of September, whereas the prominent peak observed on 5 November can be attributed to Guy Fawkes fireworks.

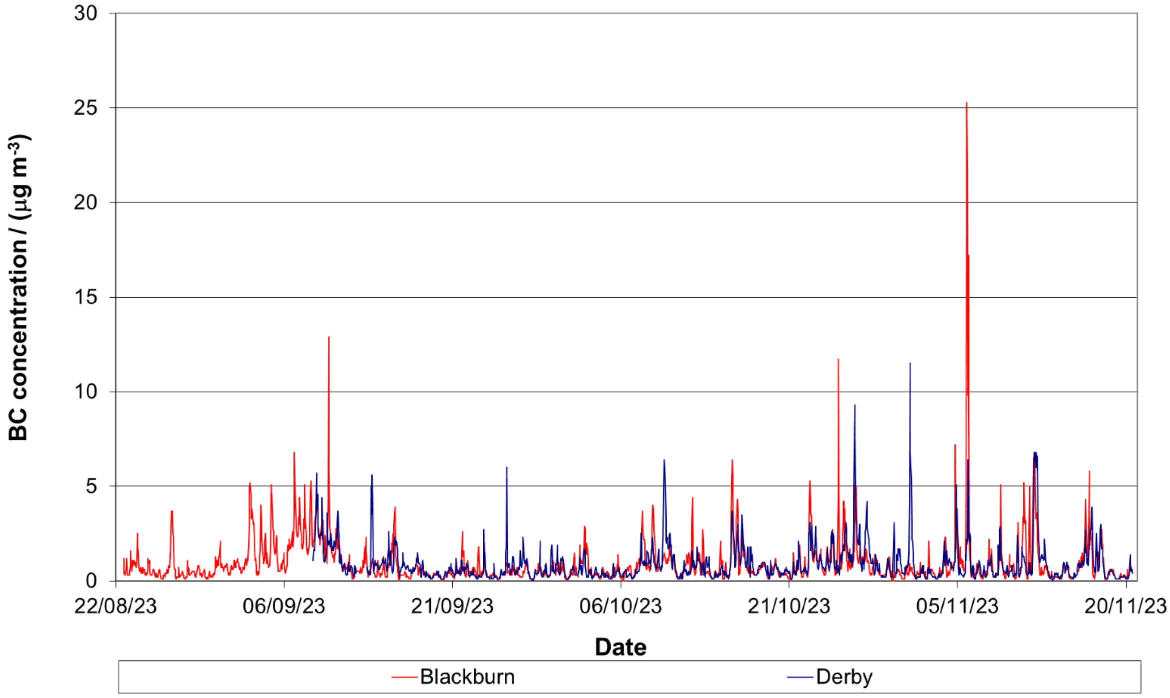


Figure 3 – Hourly BC concentrations between 22/08/2023 and 20/11/2023.

4.3 DIURNAL AND WEEKLY PROFILES – BC AND UVPM

This section presents analysis of the temporal variation of BC and UVPM concentrations. For all the charts, the continuous line is the mean value and the shaded area around the line represents the uncertainty in the mean y-value. This uncertainty is due to the spread of results over that averaging period calculated through bootstrap sampling, expressed with a level of confidence of 95 %.

The temporal variation plots (Figure 4 and Figure 5), which account for daily, hourly, and weekday patterns, show that the BC concentrations consistently surpass those of UVPM. Additionally, there are distinct spikes in BC concentrations, with the first notable surge occurring during early morning and a secondary spike appearing in the late evening. This temporal pattern indicates potential sources or activities that contribute to these elevated BC levels during these specific hours. Moreover, at the weekends, there is an increase in BC and UVPM concentrations, potentially due to secondary heating and/or recreational wood burning, which is particularly pronounced at the Derby Stockbrook Park monitoring site.

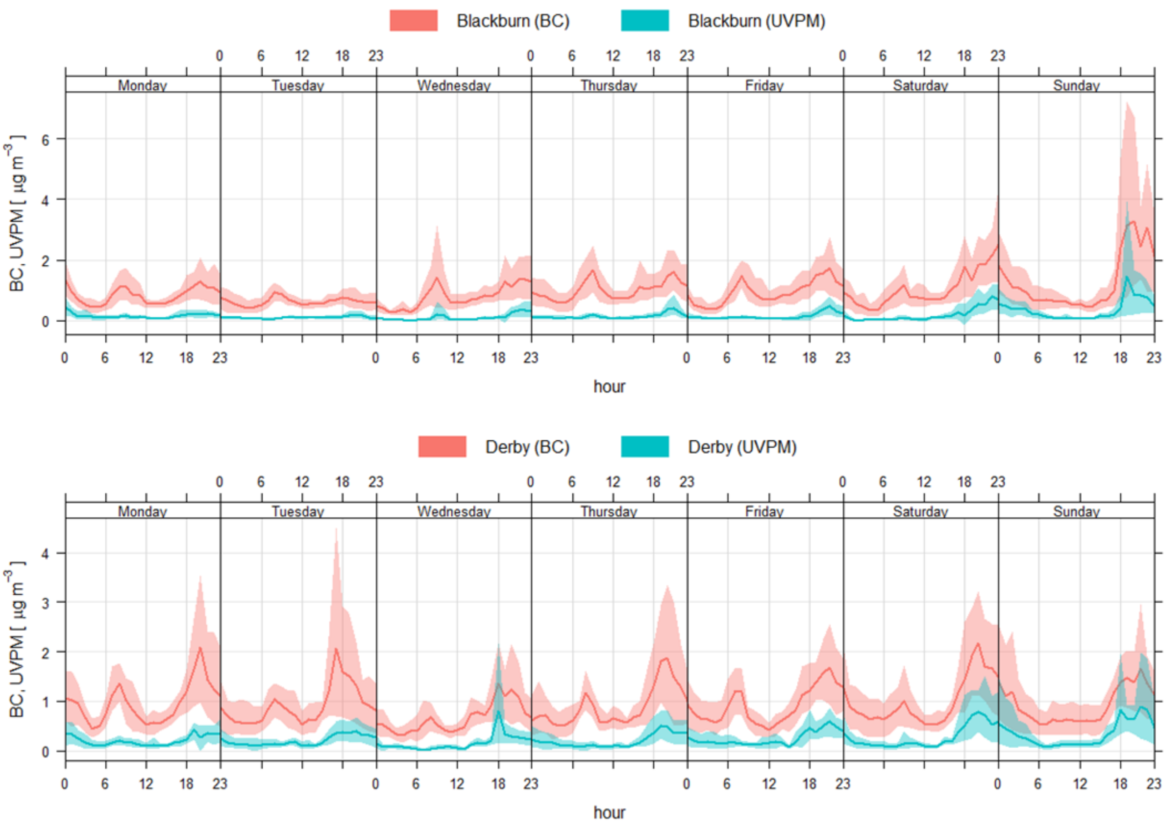


Figure 4 – Weekly variations of BC and UVPM concentrations at Blackburn Audley Park (top) and Derby Stockbrook Park (bottom).

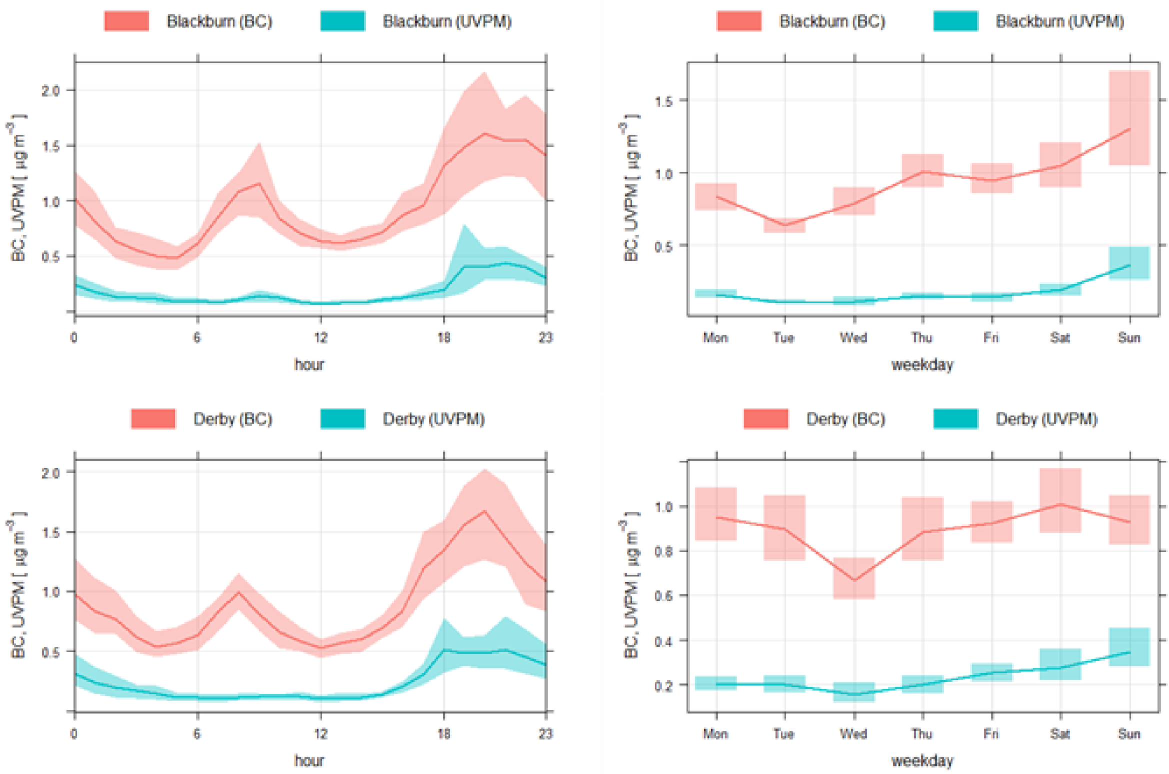


Figure 5 - Hourly (left) and weekday (right) variations of BC and UVPM concentrations at Blackburn Audley Park (top) and Derby Stockbrook Park (bottom).

5 TEMPERATURE AND HUMIDITY MEASUREMENTS

5.1 INTRODUCTION

The quality of data obtained from aethalometers can be influenced by several environmental parameters, including temperature and humidity. High temperatures can affect the stability of the aethalometer's internal components and sensors, potentially leading to inaccuracies in data. Conversely, low temperatures can reduce the instrument's efficiency, affecting its sensitivity and response time. Elevated humidity levels can lead to the condensation of water vapour on the aethalometer's optics or filters, potentially biasing measurements. On the other hand, very dry conditions can affect the dispersion of aerosol particles and the instrument's performance.

Sudden variations in temperature and humidity have a discernible influence on the noise and stability of aethalometer data. Such fluctuations are frequently a consequence of environmental factors, with the air conditioning (AC) unit installed within the cabin often being the main contributor. These rapid changes in temperature and humidity driven by the AC system, can introduce instability and noise into the aethalometer's measurements, potentially affecting data quality.

Throughout the duration of this campaign, the deployment of certified temperature (T) and relative humidity (RH) sensors at both monitoring sites have been implemented as follows:

- At the Blackburn Audley Park site, three probes were installed. The first probe (T/RH-ambient) was positioned outside the PR5 housing to measure the ambient air conditions. The second sensor (T/RH-enclosure) was placed within the cabin to monitor the enclosed environment's specific conditions. The third sensor (T/RH-sample) was situated at the sampling line in close proximity to the inlet of the aethalometer, facilitating the real-time monitoring of air conditions directly before the data acquisition. The system offers the advantage of 1 min resolution time, matching that of the aethalometer. Meteorological data (temperature and relative humidity) was also provided from a weather station located at Blackpool Airport, with an hourly average time resolution. In the middle of October, a stand-alone sensor (B7B-T/RH) was installed within the cabin as a backup for the previously described three-probe system.
- At the Derby Stockbrook Park site, a single sensor (D7B-temp/RH) was installed within the cabin to measure local environmental conditions. Meteorological data was also provided from a weather station located at Birmingham Airport, at an hourly average time resolution.

5.2 TEMPERATURE AND HUMIDITY PROBE DATA

Figure 6 presents two plots displaying the measurements of RH and T recorded at the nearest airports to Blackburn Audley Park and Derby Stockbrook Park, which are Blackpool Airport and Birmingham Airport, respectively.

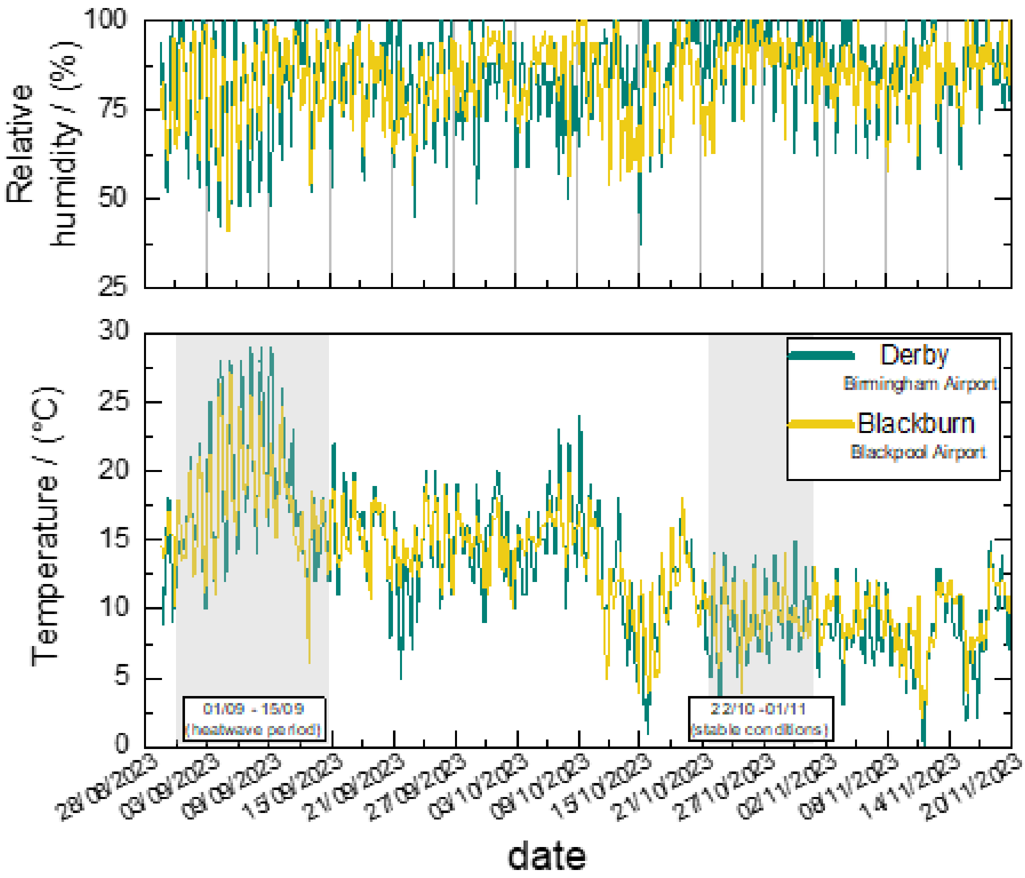


Figure 6 – Relative humidity and temperature measurements from Birmingham and Blackpool airports as ambient references for Derby Stockbrook Park and Blackburn Audley Park sites, respectively. In grey are two analysis periods, selected to study their impact on instrumental noise and black carbon data quality. They are described as the heatwave (01/09/23 – 15/09/23) and stable conditions (22/10/23 – 01/11/23).

Figure 6 provides a general overview of the meteorological conditions in the proximity of the respective monitoring sites. Two distinct periods have been deliberately selected for the focused analysis, the heatwave period from 1 to 15 September and the stable atmospheric condition period from 22 October to 1 November. These specific time frames have been chosen to conduct an in-depth investigation into the influence of temperature and humidity on instrumental noise and the quality of measured black carbon concentrations.

5.2 HEATWAVE PERIOD 01/09/23 – 15/09/23

Figure 7 illustrates the fluctuations in temperature observed during the heatwave period at the beginning of September. Throughout this timeframe, the ambient temperature shows significant variation, ranging predominantly between approximately 15°C to 30°C. Notably, during the days characterised by heightened external temperatures, both the temperature within the PR5 housing enclosure and the temperature measured at the sampling line (T-sample sensor placed in close proximity to the inlet of the Aethalometer), display changes within a narrower range, fluctuating from 15°C to 21°C.

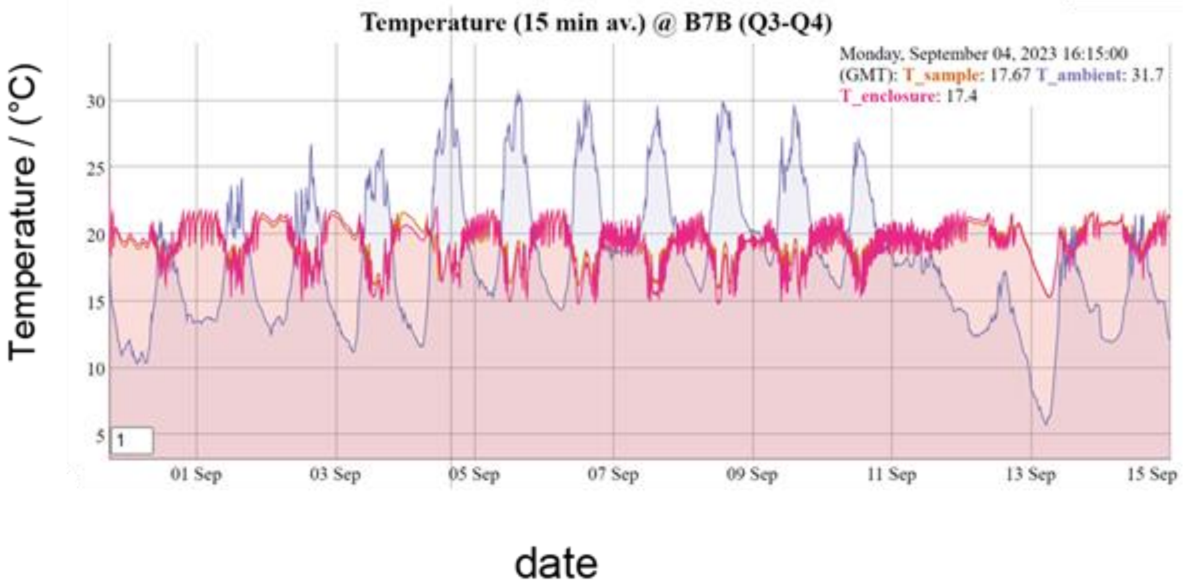


Figure 7 – 15 min averaged temperature measurements at Blackburn Audley Park site during the heatwave period (01/09/23 – 15/09/23). The highest ambient temperature, 31.7°C was recorded on 4 September in the afternoon.

RH measurements conducted by the three-sensor system at the Blackburn Audley Park site are presented in Figure 8. As a comparison, the 1 h averaged results from Blackpool airport are also included, showing a good agreement with the ambient air monitoring sensor (T/RH-ambient).

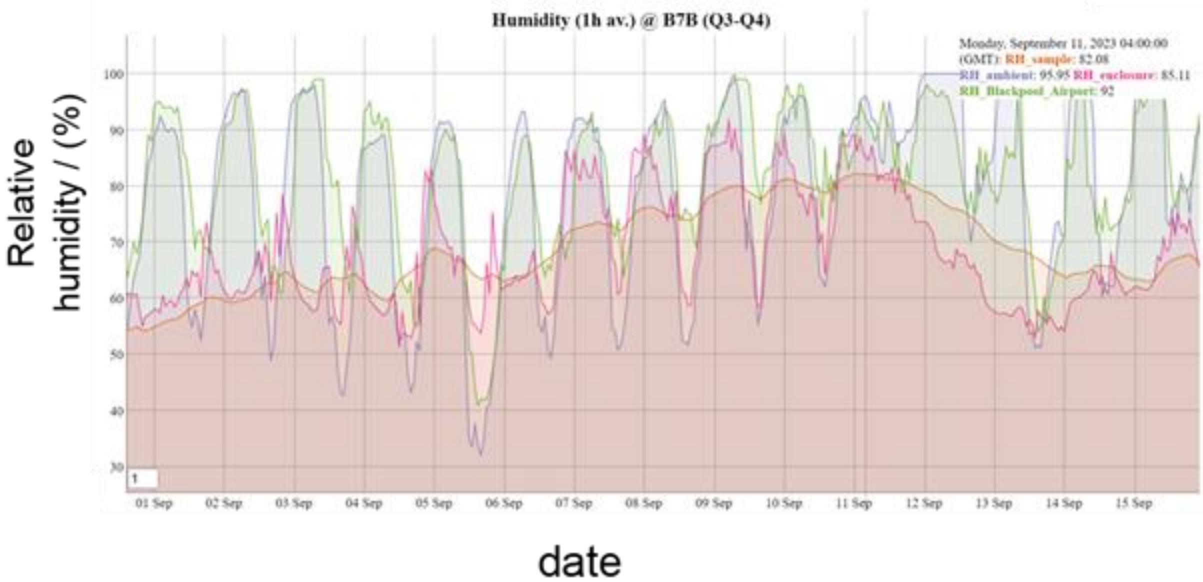


Figure 8 – Hourly averaged relative humidity measurements at Blackburn Audley Park site and at Blackpool Airport during the heatwave period (01/09/23 – 15/09/23).

Notably, Figure 8 demonstrates fluctuations in ambient relative humidity, ranging from approximately 40 % to 95 %. In contrast, the variations in humidity measurements within the enclosure are usually smaller than those observed outside the PR5 housing, with the exception of period between 5 September and 11 September. During that period, the RH within the cabin are similar to ambient conditions. Moreover, it can be observed that the RH-sample sensor readings (sensor installed at the sampling line near the Aethalometer inlet) shows a gradual rise in RH from approximately 60 % on 4 September to 82 % by 11 September. This steady increase in RH indicates possible condensation of water vapour during the heatwave period when the sampled ambient air enters the environment controlled by the AC unit, which is at a much lower temperature.

The impact of these conditions on BC measurements is presented in Figure 9. The blue data line represents validated measurements used to calculate 1 h averages. The green lines represent raw data from Aethalometer AE33 which in most cases are equal to validate results (thus the green line is not entirely visible on the plot). However, for the period between 8 to 11 September exceptionally low values of BC were excluded from the calculations, introducing a positive bias when computing the 1 h concentrations. Such negative BC values were not observed with the AE22 Aethalometer model previously used within the UK Black Carbon Network, thus a threshold value of -0.5 mg m^{-3} was employed to exclude unrealistic results from the overall measurement dataset. This approach may not be ideal for the new model AE33 where the time resolution is 1 min (instead of 5 min for the AE22 model).

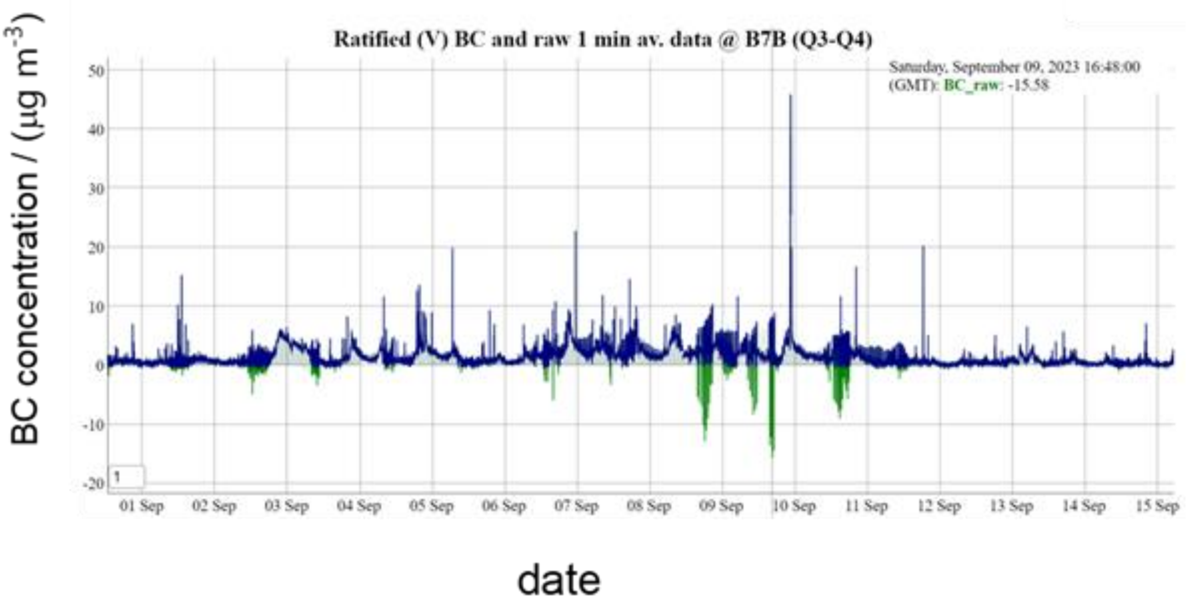


Figure 9 – One minute BC concentrations at Blackburn Audley Park site during the heatwave period (01/09/23 – 15/09/23). The blue line of data represents validated measurements. The green line of data represents raw data from the Aethalometer AE33.

An evident correlation emerges when considering the increasing RH observed in the sampling line, as presented in Figure 7, which could potentially account for the increased instrumental noise in Figure 9. This rise in RH is most likely due to ambient air temperature fluctuations and the operating AC system within the PR5 housing, leading to humidity condensation within the sampling line.

A similar analysis was conducted for the Derby Stockbrook Park sites during the same period. Figure 10 displays the temperature data recorded by a small sensor (D7B-temp) installed within the PR5 housing at the Derby Stockbrook Park site, compared to ambient temperature data obtained from Birmingham Airport weather station. It can be observed that the enclosure temperatures are notably higher than those reported at the airport. The observed pattern of temperature changes and the consistently higher range of temperatures recorded within the cabinet potentially indicates two scenarios: either a positive bias of the sensor resulting in invalid data or an issue with the proper operation of the AC system within the enclosure. Unfortunately, due to the limited memory capacity of the sensor system, verification to determine if this issue persists after the heatwave period could not be conducted. Moreover, access to the site was limited because of health and safety limitations arising from the cabinet doors opening directly onto the road. The whole housing was rotated at the end of November.

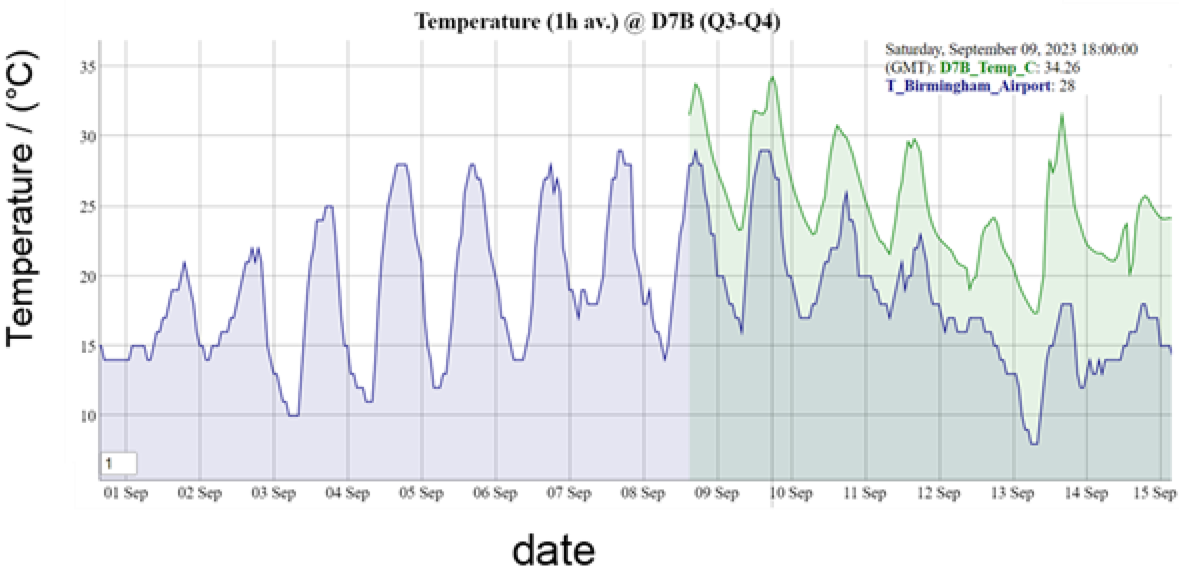


Figure 10 – Comparison of temperature data between a sensor inside the PR5 housing at the Derby Stockbrook Park site (D7B-temp) and ambient temperature recorded at Birmingham Airport weather station. Enclosure temperatures notably exceed those reported at the airport, suggesting a potential sensor bias or malfunction in the air conditioning system at Derby Stockbrook Park site. Note: installation date at Derby Stockbrook Park site is 8 September.

The RH results at the Derby Stockbrook Park site and the 1 h averaged results from Birmingham Airport are presented in Figure 11. The readings appear within a reasonable range, indicating that the issue observed with temperature readings, may be attributed to either a malfunctioning or inefficient AC unit within the PR5 housing.

As a comparison to Blackburn Audley Park site (see Figure 9), Figure 12 shows 1 min BC concentrations at the Derby Stockbrook Park site. It can be observed that at the Derby Stockbrook Park site, the potential influence of humidity and temperature fluctuations is less evident (raw data in green are equal to validated data represented as blue lines). However, it is important to note that the Aethalometer installation at this site occurred on 8 September, which was during the middle of the heatwave period. Thus, any potential enhanced instrumental noise levels may not be evident on the same scale as at the Blackburn Audley Park site, which operated for the whole heatwave period.

Unfortunately, the cause of a noticeable data gap on 12 – 13 September is uncertain; possibilities include a power cut or maintenance activities at the site.

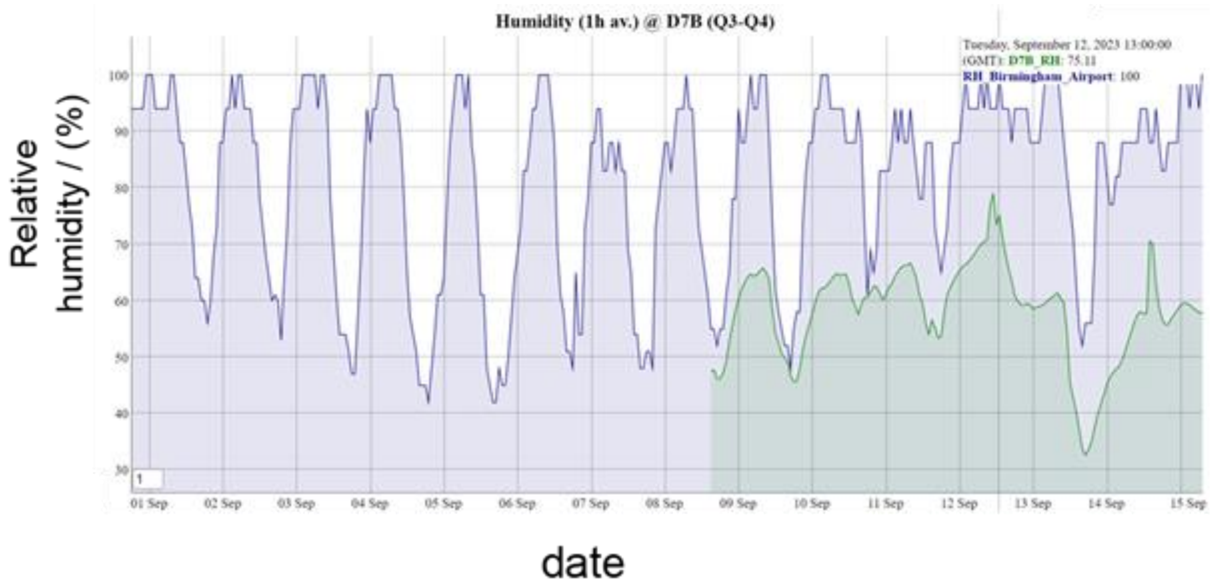


Figure 11 – Comparison of relative humidity data between a sensor inside the PR5 housing at the Derby Stockbrook Park site (D7B-temp) and the ambient relative humidity recorded at Birmingham Airport weather station. Note: installation at the Derby Stockbrook Park site is 8 September.

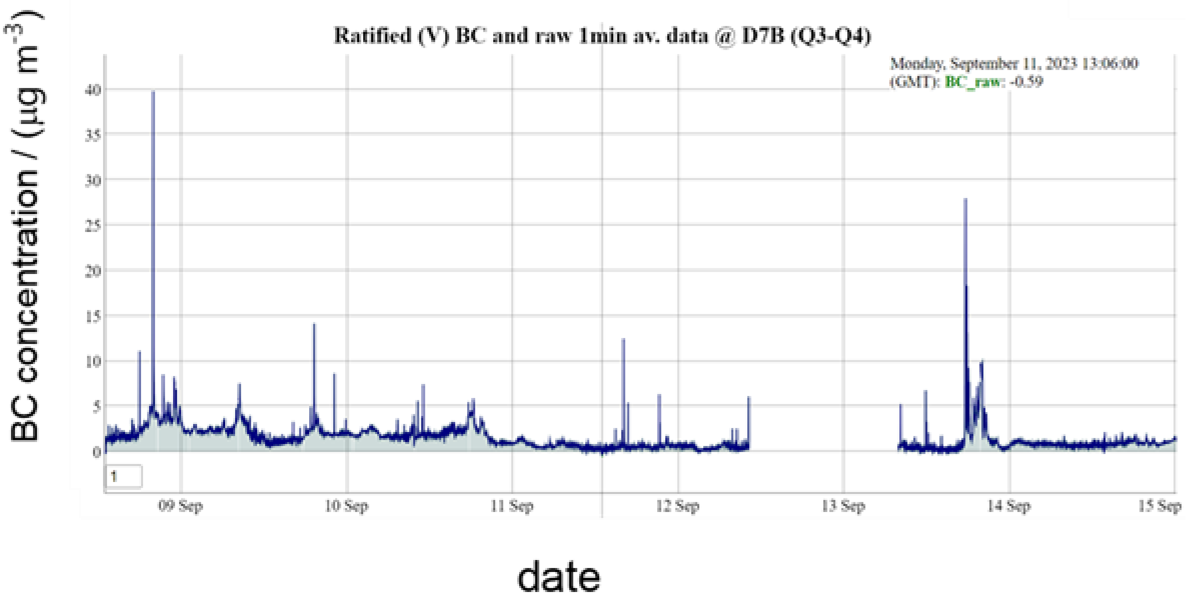


Figure 12 – One minute BC concentrations at Derby Stockbrook Park site during the heatwave period (01/09/23 – 15/09/23). The blue line of data represents validated measurements. The green line represents raw data from Aethalometer AE33 with the lowest measurement of BC on 11 September (-0.6 µg m^{-3}).

5.3 STABLE ATMOSPHERIC CONDITIONS 22/10/23 – 01/11/23

An analogous analysis to that in Section 5.2 was conducted for the timeframe spanning from 22 October to 1 November at both monitoring sites, characterised by stable atmospheric conditions. During this period, the prevailing temperatures were close to 9°C, indicating relatively cooler environmental conditions. Additionally, there was a consistent trend of notably high RH levels across both sites, contributing to a generally stable and moisture-rich atmosphere. This timeframe offered an opportunity to examine and compare the environmental parameters, particularly temperature and humidity, and their potential impact on the data quality connected with the instrumental noise at the respective monitoring sites.

Figure 13 illustrates 15 min averaged temperature measurements obtained from a three-sensor system and an additional small sensor (B7B-temp) placed within the PR5 housing, serving as a backup for the main three-sensor setup. A striking observation emerges from this comparison as both sets of temperature data showcase a high level of agreement. The readings from the backup sensor inside the housing closely align with those recorded by the three-sensor system, indicating a consistency and reliability between the measurements. Throughout this period, the temperature variations within the cabin fluctuated between 14°C to 22°C.

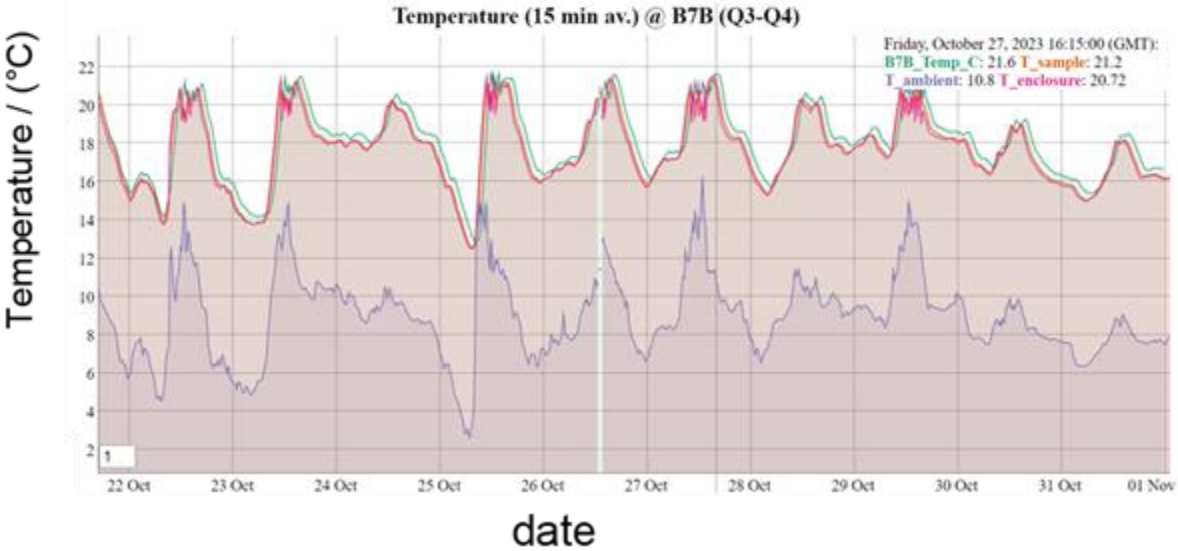


Figure 13 – Temperature 15 minutes averaged measurements at Blackburn Audley Park site during the stable condition period (22/10/23 – 01/11/23).

RH measurements during stable atmospheric condition period at the Blackburn Audley park site are presented in Figure 14. As a comparison, the 1 h averaged results from Blackpool Airport are also included showing a good agreement with the sensor monitoring ambient air (RH-ambient) at the site. Additionally, coherence between small sensor measurements (B7B-RH) and a RH enclosure readings once again confirms agreement between the different monitoring setups, both within and outside the housing.

During this period, the sampled RH measurements remain stable at around 55 %. This stability suggests a consistent and predictable humidity level within the sampling line. Additionally, contrasting with the previously described heatwave conditions in September, no significant fluctuations or substantial changes in RH were observed inside the PR5 housing.

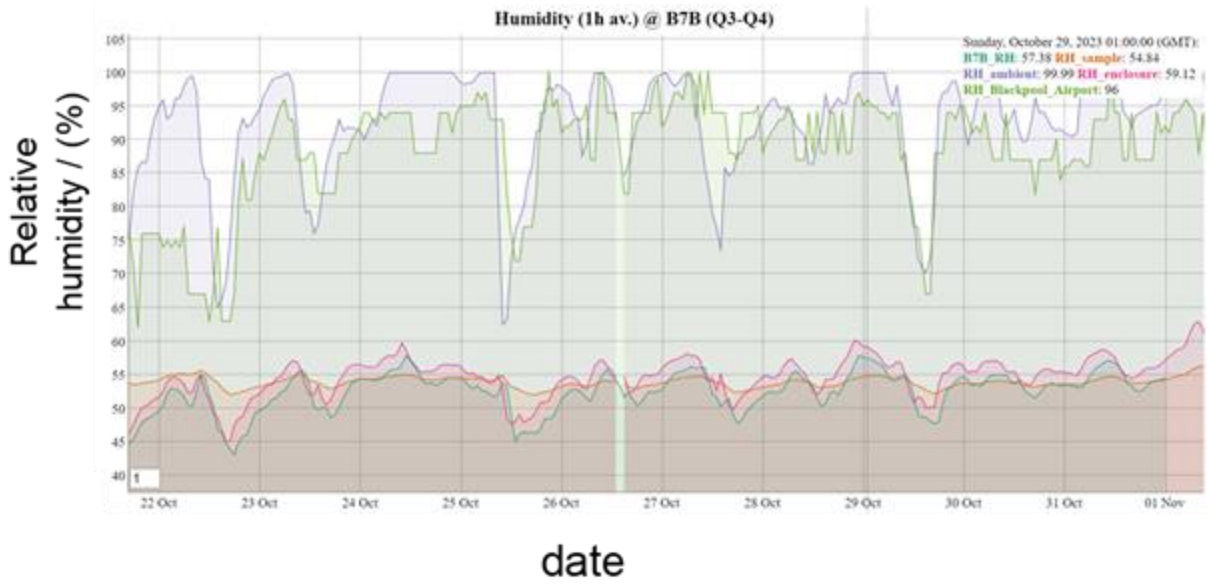


Figure 14 – Hourly averaged relative humidity measurements at Blackburn Audley Park site and at Blackpool Airport during the stable condition period (22/10/23 – 01/11/23).

Figure 15 and Figure 16 present BC concentration measurements at the Blackburn Audley Park and Derby Stockbrook Park sites, respectively, spanning a phase characterised by stable atmospheric conditions. Unlike the heatwave period (Figure 9), no elevated instrumental noise levels were observed during this period of stable conditions. The data displayed in these figures exhibit a notably good quality, evident from the absence of significant negative BC concentration measured by Aethalometer AE33. Thus, minimal differences were observed between the raw (green lines) and validated (blue lines) 1 min BC data, highlighting the consistency and reliability of the measurements during this stable atmospheric phase.

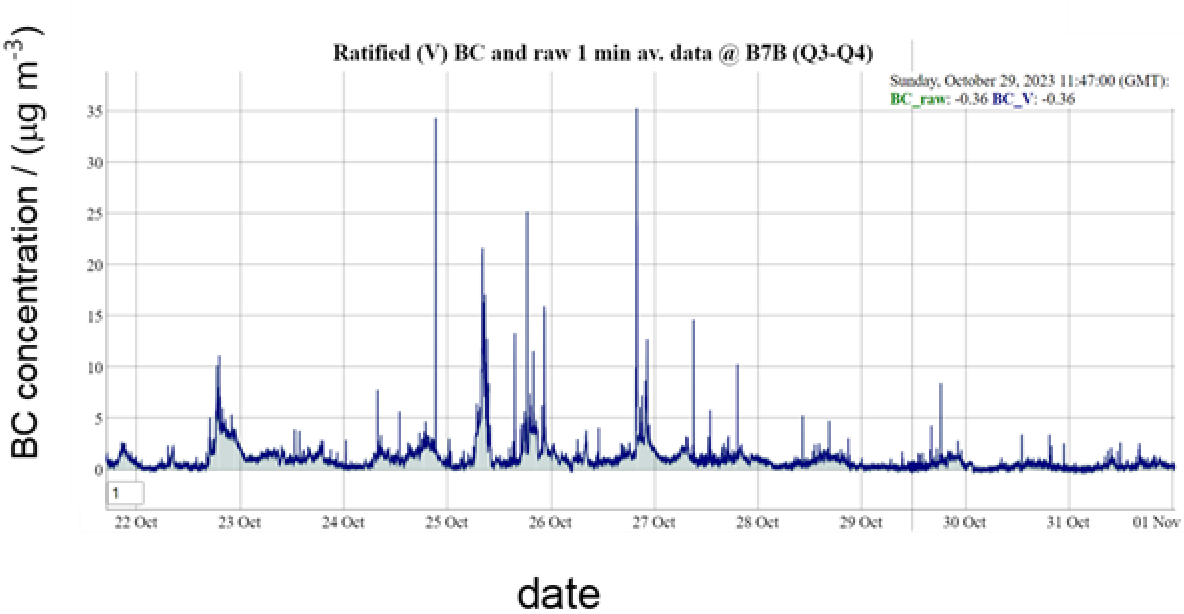


Figure 15 – One minute BC concentrations at Backburn site during the stable condtions period (22/10/23 – 01/11/23). The blue line data represents validated measurements. The green line represents raw data from the Aethalometer AE33.

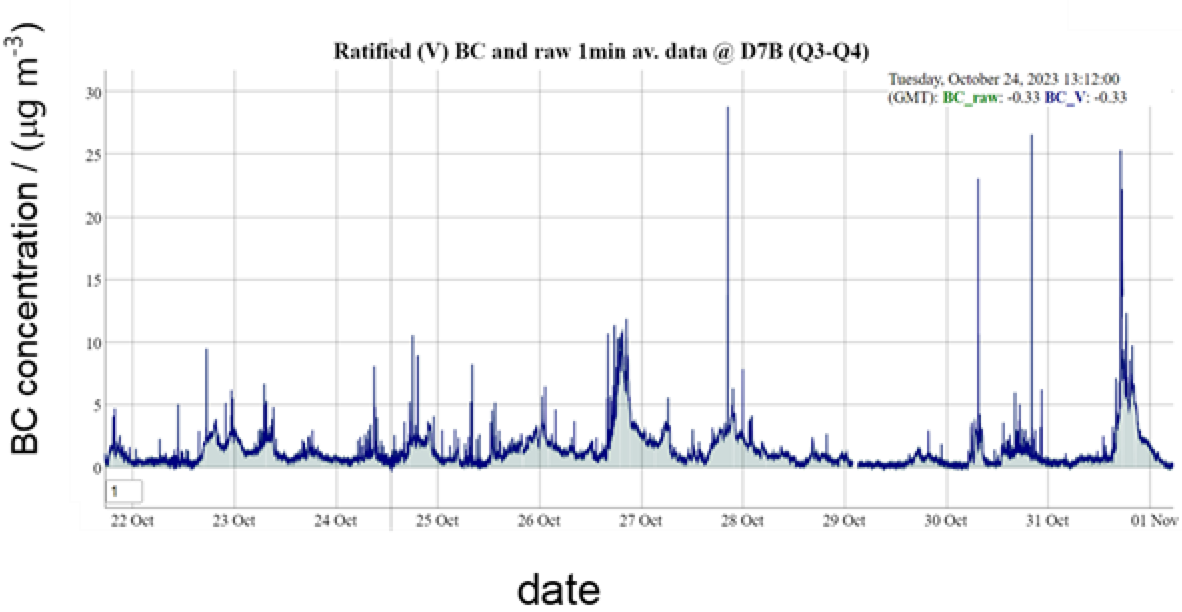


Figure 16 – One minute BC concentrations at Derby Stockbrook Park site during the stable conditions period (22/10/23 - 01/11/23). The blue line data represents validated measurements. The green line represents raw data from Aethalometer AE33.

6 CONCLUSIONS

The primary objective of this analysis was to study BC concentration data measured at Blackburn Audley Park and Derby Stockbrook Park, using aethalometers installed in compact PR5 housing rather than conventional walk-in cabins; with a focus on the potential impact of temperature and humidity variation on instrumental noise and data quality. Two distinct periods were selected based on differing temperature and humidity conditions: a heatwave in September and stable atmospheric conditions in late October.
The findings revealed noticeably increased instrumental noise affecting the data quality during the heatwave period of 01/09/23 – 15/09/23. This was especially observed at the Blackburn Audley Park site, where increased temperature and RH likely led to moisture accumulation inside the sampling line or the aethalometer's chamber case where the optical system and filter tap was installed. At the Derby Stockbrook Park site, where the instrument was installed on 8 September, and thus was not exposed to the same duration of the heatwave as AE33 at Blackburn Audley Park, no elevated instrumental noise levels were observed. It was also evident that the AC unit at Derby Stockbrook Park site is potentially inefficient or non-operational. This is based on available September data from the temperature and humidity sensor installed inside the PR5 housing at this site. Further investigation of the temperature range within the cabin could be potentially verified by the AC service unit, or by analysing temperature data from the ozone and FIDAS instruments (not operated by NPL).

Overall averaged BC concentrations at Blackburn Audley Park and Derby Stockbrook Park sites from date of installation to 20 November were within a typical range for urban background sites in the UK (see Table 2) with ~100 % data capture. However, the effect of enhanced instrumental noise levels during summer period might result in higher uncertainties when analysing seasonal (or short-term) changes of BC concentrations. Thus, a revision of the threshold values for data validity is recommended due to the heightened sensitivity of the AE33 model's 1 min measurements compared to the previous AE22 model's 5 min readings. Additionally, to minimise condensation of vapour within the sampling line at all Network sites, it is advised to isolate these lines with the use of insulation tubing, for example. It is also suggested to revise options to insulate the instrument itself, particularly the filter compartment, by using a plastic cover or bag.

Based on the results presented in this study, both sites are feasible to be incorporated into the Network. Extra caution should be taken when validating measurements conducted during heatwaves due to potential impact of temperature and humidity on the AE33 instruments noise. Given the increased occurrences of extreme weather, continuous monitoring of temperature and humidity may become necessary not only for the ambient air, but also for the enclosure of the cabin/PR5 housing and sampling lines near the instrument's inlet.

7 REFERENCE

[1] CIUPEK, K. *et al*., Airborne Particle Concentrations, Particle Numbers and Black Carbon in the United Kingdom – Annual Report 2022. *National Physical Laboratory*, 2023. NPL Report ENV 50. http://doi.org/10.47120/npl.ENV50