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2010 Annual Report for the UK Black Carbon Network

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EXECUTIVE SUMMARY

This report covers the operation of the UK Black Carbon Network and the data collected by the Network in 2010. The Aethalometer instrument used on the Network makes measurements of Black Carbon (BC) and UV component.

The National Physical Laboratory (NPL) was awarded the contract to restructure and run the UK Black Smoke Network by the Department for Environment, Food and Rural Affairs (Defra) in September 2006. By 2007 the network was making measurements at 21 sites. In 2008 the black smoke samplers were replaced by model AE22 Aethalometers. The Network was reduced to 20 sites in October when Bradford was closed after Defra reviewed it's monitoring requirements.

The 2010 data capture for Aethalometer measurements was 98%. This is a remarkably high figure for an automatic monitoring network and shows the effectiveness of daily on-line surveillance of the equipment.

Measured annual average Black Carbon concentrations on the Network ranged from 0.8 (1.0) $\mu g.m^{-3}$ at Folkestone to 8.8 (10.0) $\mu g.m^{-3}$ at Marylebone Road. Harwell reported an average concentration of 0.5 (0.4) $\mu g.m^{-3}$. The network mean for Black Carbon concentration was 1.9 (2.1) $\mu g.m^{-3}$. The figures in brackets are the corresponding concentrations for 2009.

Measured annual average UV component concentrations ranged from 0.2 (0.0) $\mu g.m^{-3}$ measured at Marylebone Road to 1.3 (0.9) $\mu g.m^{-3}$ measured at Strabane. However, if the negative values measured at Marylebone Road are removed, its annual average concentration is comparable to the other sites. All sites close to the roadside showed significant negative spikes in this parameter.

As with Black Smoke in previous years, Black Carbon concentrations show reasonable agreement between sites located in similar regions of the country showing that there is a regional component to the Black Carbon concentration. The highest concentrations were measured at Marylebone Road, followed by urban centre sites and urban background sites giving comparable measurements, with the lowest measurements being made at the Harwell (rural) and Folkestone (suburban) sites.

Daily averages of the measurements show that the highest concentrations of Black Carbon are found at the beginning of the week with the weekends generally having lower values. The hourly averages of Black Carbon broadly show a commuter traffic based signature with the exception of Strabane and Dunmurry, both in Northern Ireland, which show elevated levels from 15:00hrs to 23:00hrs, which is probably due to local domestic heating.

From the diurnal plots it can be seen that the main driver behind the UV component concentrations is domestic fuel use, with elevated concentrations in the evenings at the urban background sites. Sites in Northern Ireland show the largest evening effect due to the higher use of oil and solid fuel for domestic heating. From the daily averages it can be seen that the UV component concentration is fairly consistent over the week with some rise at the weekend.

Comparisons between Black Carbon concentrations and Elemental Carbon concentrations showed good agreement between the measurements at all the sites where these measurements are collocated (North Kensington, Marylebone Road and Harwell).

Comparisons between particulate mass concentrations and Black Carbon concentrations showed that Black Carbon makes up a significant proportion of the particulate mass concentration at roadside sites. At Marylebone Road the Black Carbon concentration makes up 28% of the PM_{10} concentration and 39% of the $PM_{2.5}$ concentration. A similar comparison was made for the UV component with only Strabane and Dunmurry show a mass contribution greater than 3% from the UV Component.

Comparisons between the UV component and Benzo[a]pyrene concentrations at the Dunmurry site showed good temporal agreement between the two species due to similar emission sources.

By converting Black Smoke Index into Black Carbon concentrations it can be shown that there is no discontinuity in results between the two methods and that there is no obvious short-term trend in the Black Carbon concentrations since 2004. It should be noted that the 2010 Black Carbon concentrations are generally lower than the 2009 concentrations, while the 2010 UV component concentrations are generally higher than the 2009 concentrations.

CONTENTS

1.0 INTRODUCTION

1.1 GENERAL

The National Physical Laboratory (NPL) was awarded the contract to restructure and run the UK Black Smoke Network by the Department for Environment, Food and Rural Affairs (Defra) in September 2006. During 2007 the number of sites in the network expanded from 14 sites to 21 sites, as samplers were installed into mainly Automatic Urban and Rural Network (AURN) sites. By March 2007 all of the 21 sites were operational.

In 2008 the black smoke samplers were replaced by model AE22 Aethalometers. The Network was reduced to 20 sites in October when Bradford was closed after Defra reviewed it's monitoring requirements.

1.2 BLACK CARBON

Black Carbon (BC) is a measure of airborne soot-like carbon (in $\mu g.m^{-3}$) based on the optical absorption of specific wavelengths by particulates collected on a filter. Ideally it is a similar metric to Elemental Carbon (EC), a measure of soot-like carbon determined by thermo-optical (chemical) techniques, though in practice the EC fraction of total carbon depends strongly on the method chosen. BC should have a close relationship to the Black Smoke measure monitored by the network and its predecessors for many decades before the installation of the Aethalometers[1], though again this can be affected by the instruments and circumstances.

BC is typically formed through the incomplete combustion of fossil fuels, biofuel, and biomass, and is emitted in both anthropogenic and naturally occurring soot. It consists of pure carbon in several forms. Black carbon warms the planet by absorbing heat in the atmosphere and by reducing albedo (the ability to reflect sunlight) when deposited on snow and ice. Black Carbon stays in the atmosphere for periods of days to weeks, whereas CO_2 has an atmospheric lifetime of more than 100 years.

1.2 MEASUREMENT METHOD

1.2.1 Aethalometer instrument and data processing

Aethalometers quantify Black Carbon on filter samples based on the transmission of light through a sample. The sample is collected onto a quartz tape, and the change in absorption coefficient of the sample is measured by a single pass transmission of light through the sample, measured relative to a clean piece of filter. The system evaluates changes in two optical sensors (sample and reference), with the light source both on and off, such that independent measurements of the change in attenuation of the sample are produced for averaging periods of typically five minutes. The absorption coefficient for material added during the period, α [m^{-1}], is calculated from the attenuation change, and the area and volume of the sample, and converted to a Black Carbon concentration for the period, as a first approximation, using a mass extinction coefficient [16.6 m^2 g^{-1}] chosen by the manufacturer to give a good match to Elemental Carbon. In practice this mass extinction coefficient will vary with factors such as particle size, sample composition and quantity of material already on the filter, as discussed below.

The Aethalometers run on the Network operate at 2 wavelengths, 880nm and 370 nm. The 880nm wavelength is used to measure the Black Carbon (BC) concentration of the aerosol, while the 370nm wavelength gives a measure of the "UV component" of the aerosol. At wavelengths shorter than about 400 nm, certain classes of organic compounds (such as polycyclic aromatic hydrocarbons, and also certain compounds present in tobacco smoke and smoke from wood burning) start to show strong UV absorbance. The UV component can therefore in principle be used as an indicator of oil and solid fuel emissions.

The UV component concentration presented in this Report is obtained by subtracting the measured BC concentration from the concentration measured by the 370nm source. The UV component is not a real physical or chemical material, but a parameter based on UV absorption due to the mix of organic compounds measured at this wavelength. This fictional material 'UVPM' is expressed in units of 'BC Equivalent'.

It is well known that the assumption of constant mass extinction coefficient does not hold as the filter spot darkens, leading to nonlinearity in the Aethalometer response. The effect of this nonlinearity results is that the Aethalometer under-reads at high filter tape loadings. To correct for this nonlinearity, the model developed by A Virkkula[3] has been used to correct for increased attenuation due to spot darkening during sampling. This uses a simple equation $BC_{corrected} = (1+k.ATN)\ BC_{uncorrected}$, where ATN is the light attenuation by the filter spot, and k is a parameter determined for each filter spot such that continuity between adjacent filter spots is greatly improved. All of the Black Carbon and UV component results in this report have been corrected by this method.

1.2.2 Sampling

At all sites, ambient air is drawn into the sampling system through a standard stainless steel rain cap mounted on the end of a vertical stainless steel tube. Size selection of the sampled aerosol is made by a $PM_{2.5}$ cyclone placed close to the inlet of the Aethalometer. All of the tubing before the cyclone is constructed from stainless steel. Sampling has been standardised across the network by using this size selective inlet before the Aethalometer, which was not possible with the Black Smoke method.

2.0 NETWORK INFRASTRUCTURE

The following sections present the design of the Network, describe its operation and the changes to the Network in 2010.

2.1 NETWORK SITES AND DESIGN

Figure 1 shows the locations of the Aethalometers.

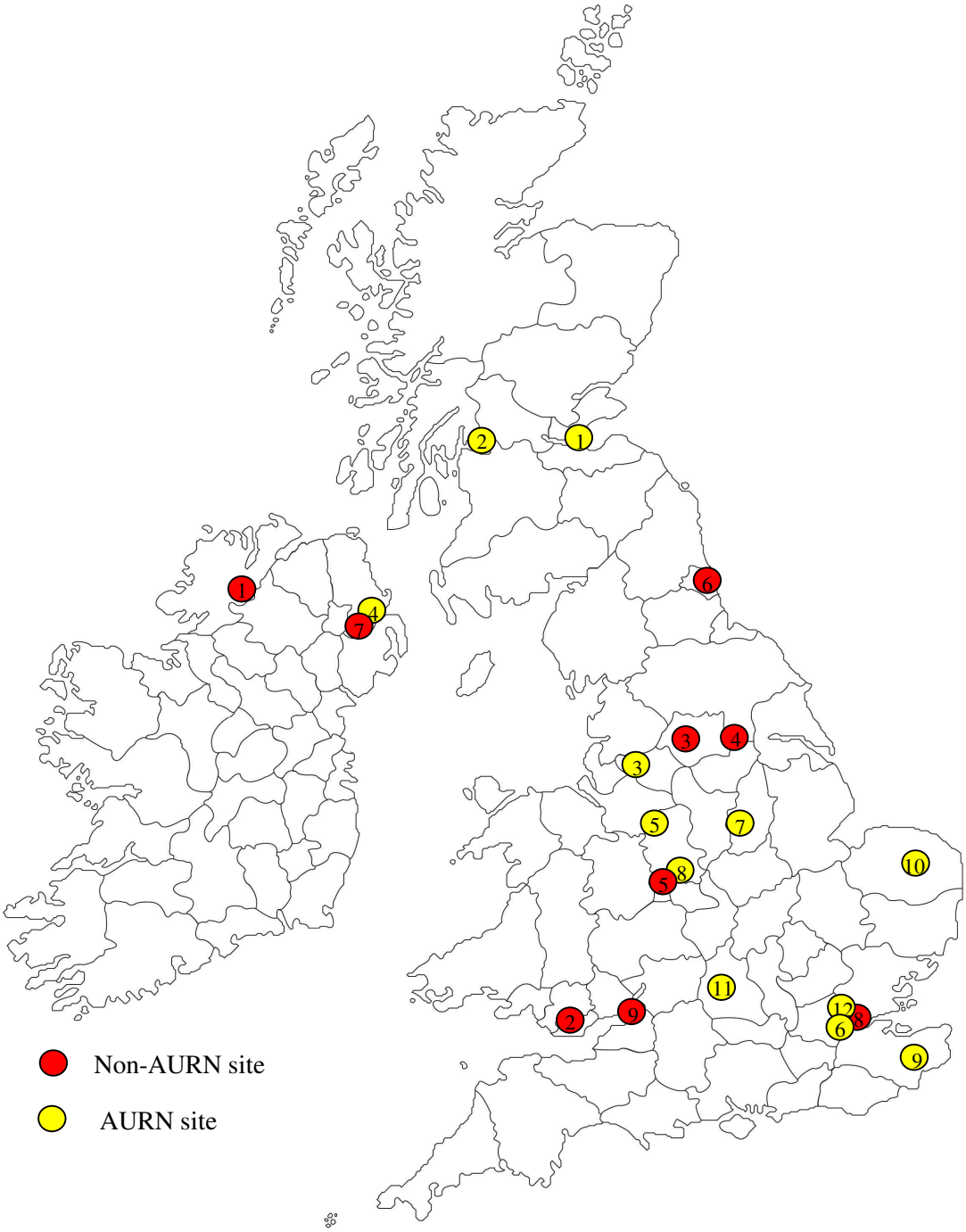


Figure 1 Location of Aethalometers making up the UK Black Carbon Network (key on next page)

Tables 1 and 2 below give the site names and classifications for the UK Black Carbon Network:

Key	Site Name	Classification
1	Strabane 2	Urban Background
2	Cardiff 12	Urban Background
3	Halifax 17	Urban Background
4	South Kirkby 1	Urban Background
5	Dudley Central	Urban Background
6	Sunderland 8	Urban Background
7	Dunmurry 3	Urban Background
8	Woolwich 9	Urban Background
9	Bath 6	Roadside

Table 1 Non-AURN

Key	Site Name	Classification	Other Analysers
1	Edinburgh St Leonard's	Urban Background	FDMS TEOM PM_{10} + $PM_{2.5}$
2	Glasgow Centre	Urban Centre	FDMS TEOM PM_{10} + $PM_{2.5}$
3	Manchester Piccadilly	Urban Centre	FDMS TEOM $PM_{2.5}$
4	Belfast Centre	Urban Centre	FDMS TEOM PM_{10} + $PM_{2.5}$
5	Stoke Centre	Urban Centre	FDMS TEOM PM_{10} + $PM_{2.5}$
6	North Kensington	Urban Background	FDMS TEOM PM_{10} + $PM_{2.5}$ + anions + EC/OC + number counting + manual $PM_{2.5}$
7	Nottingham Centre	Urban Centre	FDMS TEOM PM_{10} + $PM_{2.5}$
8	Birmingham Tyburn	Urban Background	FDMS TEOM PM_{10} + $PM_{2.5}$
9	Folkestone, Kent Network	Rural	TEOM PM_{10}
10	Norwich	Urban Background	FDMS TEOM PM_{10} + $PM_{2.5}$
11	Harwell	Rural	FDMS TEOM PM_{10} + $PM_{2.5}$ + anions + EC/OC + number counting + manual $PM_{2.5}$
12	Marylebone Road	Roadside	FDMS TEOM PM_{10} + $PM_{2.5}$ + anions + EC/OC + number counting + manual $PM_{2.5}$

Table 2 AURN sites

2.2 NETWORK OPERATION

The operation of the Network was set up to mirror that of the AURN, to include a Central Management and Control Unit (CMCU) and a Quality Assurance and Quality Control Unit (QA/QC). The Environmental Research Group at King's College London (KCL) carries out the CMCU activities. These activities include the routine collection of data from site, initial data validation and instrument fault finding, routine liaison with the Local Site Operators (LSO) and the Equipment Support Unit (ESU). The QA/QC activities are performed by NPL and include: site audits, inter-laboratory performance schemes, data ratification and reporting.

As the Aethalometer produces real-time continuous data it was decided to perform remote data collection and diagnostics at each site via a modem to maximise data capture and minimise LSO costs. A summary of this activity is outlined below:

Measurements are collected from the 20 sites on the Network between 6 am and 7 am every morning and again between 6 pm and 7pm in the evening. Measurements of Black Carbon, UV carbon, flow and the raw attenuation signals since the last data collection are requested from the Aethalometer and written to a text file on the server at KCL. These files are placed in a queue and processed into the central Microsoft SQL database. This database is mirrored to a second, on site server every hour and backed up to tape on a daily basis; these tapes are stored off site for added database security. When the files are processed, the 5 minute mean measurements are averaged to 15 minute means so that the averaging period is the same as measurements made using gaseous and particulate monitors on the AURN. A valid 15 minute measurement is only calculated where two valid 5 minute measurements exist in that 15 minute period. A range of sensibility checks are undertaken at this point to ensure measurements are above zero and below a maximum limit (100 µg m^{-3}); the flow data is also checked to ensure it is 4 l/min (±10 %).

The data from each site is assessed using a range of algorithms/criteria, which determine whether the site requires a manual check; this is 'risk-based' data checking and provides a method for improving the efficiency of the data checking procedure. The list of algorithms/criteria examine whether:

- Data warning flags have been attached to the data, either from the instrument or from the sensibility checks during processing.
- Data checking resulted in any notes or actions on the previous day.
- There are any services, local site operator visits or audits being undertaken that day.
- The data is stable for more than 6 consecutive 15 minute periods.
- The data capture over the previous 24 hours is less than 90 %.
- The site was not manually checked the previous day.

If any of these tests produce a positive result, the site is included in a list of sites to be examined manually. Where necessary, this manual validation is undertaken using MONNET every working day; a screen shot of the 5 day data checking graph is shown in Figure 2. This shows the Black Carbon and UV carbon measurements and the flow measured by the instrument. Where NO_X measurements are available from the site (such as North Kensington and Marylebone Road) these are included as a method of assessing the impact of local traffic emissions. Further manual checks are made comparing the measurements between sites across the network to identify any outliers.

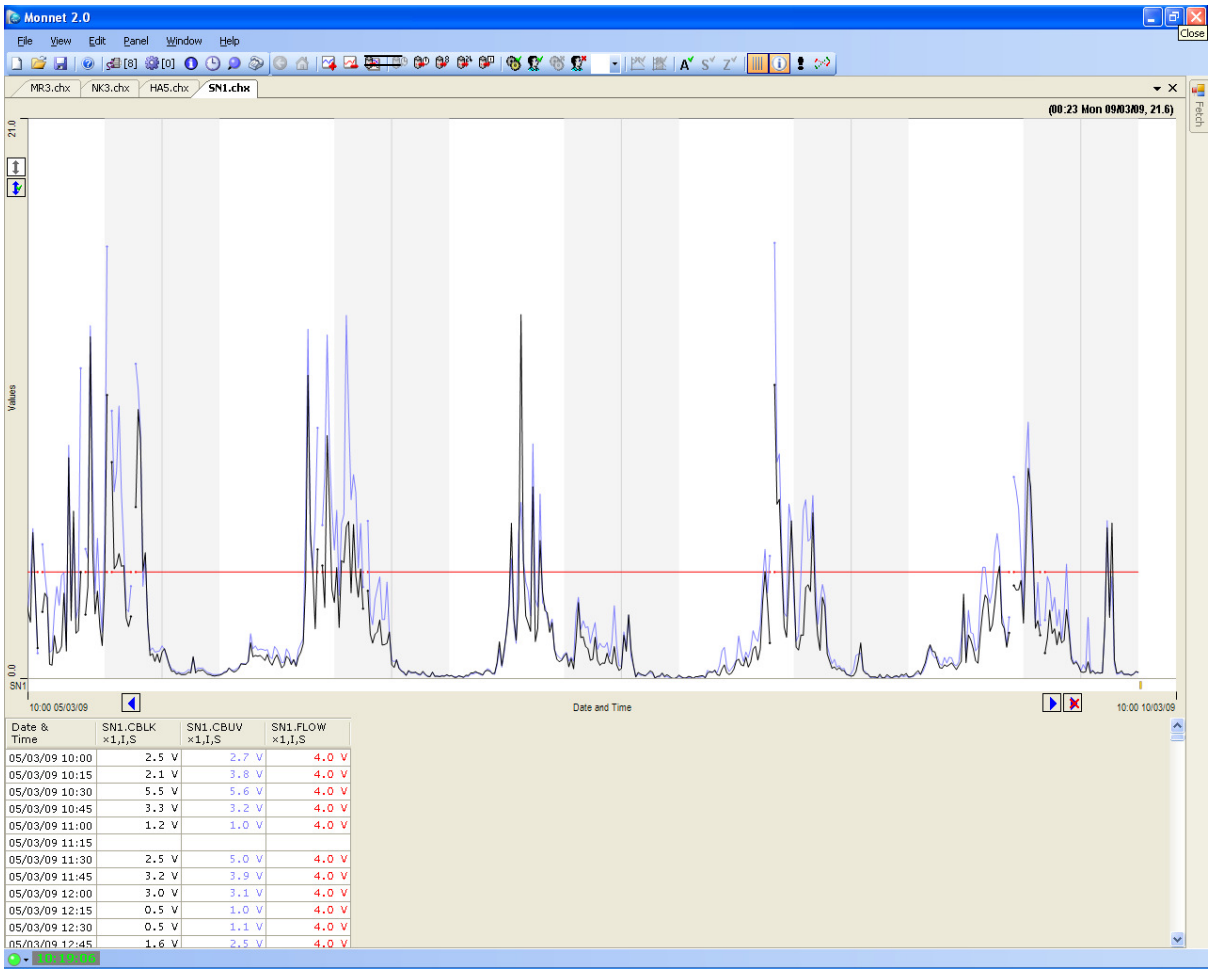


Figure 2 MONNET data checking graph

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 local site operator (LSO) or the equipment support unit. If this is the case a visit request is sent to either the LSO or Air Monitors. The reports generated from these visits are processed at KCL and stored according to the site that they pertain to. The directory is mirrored to the web server and accessible via a password protected web portal for access during ratification.

2.3 CHANGES TO THE NETWORK

There were no changes to the Network infrastructure in 2010.

3.0 QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC)

Quality Assurance and Quality Control activities cover two main areas: site audits and instrument calibration. The first addresses sampling issues and the second ensures the consistency and accuracy of the measured attenuation for Black Carbon.

3.1 SITE AUDITS

Table 3 gives the site audit dates and serial numbers of the Aethalometer audited.

Site	Date	Serial Number
Birmingham Tyburn	25/06/2010	859
Dudley Central	25/06/2010	849
Bath	30/06/2010	869
Cardiff 12	30/06/2010	868
Folkestone	01/07/2010	853
Marylebone Road	02/07/2010	864
North Kensington	02/07/2010	850
Woolwich	05/07/2010	865
Norwich Lakenfields	14/07/2010	855
Manchester	09/09/2010	858
South Kirkby	09/09/2010	852
Halifax	09/09/2010	860
Stoke	13/09/2010	861
Belfast	14/09/2010	863
Dunmurry	14/09/2010	862
Strabane	14/09/2010	848
Harwell	23/09/2010	851
Nottingham	15/11/2010	857
Edinburgh St Leonard's	16/11/2010	866
Sunderland	16/11/2010	854
Glasgow Centre	17/11/2010	867

Table 3 Site Audit Visits

3.1.1 Sampler Leak Rate and Calibration of Sample Flow

The leak rate for Aethalometers is measured by simultaneously measuring the flow rate at the input and exhaust of the analyser and requires the use of two calibrated flow meters.

According to the manufacturer, the maximum acceptable leak rate is 20%. Black Carbon concentrations are not corrected for leak rate, but the leak rate is included in the uncertainty budget.

The absolute value of the inlet flow measured during the leak test is used to calibrate the sample flow of the instrument.

Both flow meters used were calibrated against National Standards. When taking into account the repeatability of the measurements in the field, the flow inlet and exhaust flows were measured with an uncertainty of ±2.5%, expressed with a level of confidence of 95%.

Table 4 gives the measured leak rates and sample flows for each site:

Site	% Leak Rate	Indicated Flow	Inlet Flow
Birmingham Tyburn	6.8	4.0	4.320
Dudley Central	2.7	3.9	4.283
Bath	3.6	4.0	4.427
Cardiff 12	4.5	4.0	4.610
Folkestone	6.4	4.0	4.487
Marylebone Road	8.3	4.0	4.030
North Kensington	4.6	4.0	4.467
Woolwich	4.4	4.0	4.110
Norwich Lakenfields	2.6	4.0	4.453
Manchester	7.3	4.0	4.520
South Kirkby	3.7	4.0	4.320
Halifax	3.7	4.0	4.320
Stoke	3.5	4.0	4.310
Belfast	6.7	4.0	4.183
Dunmurry	6.5	4.0	4.170
Strabane	6.1	4.0	4.457
Harwell	8.1	4.0	4.137
Nottingham	7.2	4.0	3.940
Edinburgh St Leonard's	2.7	4.0	4.543
Sunderland	9.9	4.0	4.090
Glasgow Centre	7.9	4.0	4.250

Table 4 Aethalometer leak rates and sample flows

3.1.2 Optical Calibration

The Aethalometer measurement does not depend on any absolute calibration of the detectors' response signals, but instead relies upon their ability to determine very small relative changes in optical transmission.

Due to the physical limitations of the optical system in the Aethalometer the signal strength measured by the detectors is dependent on the separation of the source and detector heads. Any changes in path length in the reference or sensing beams changes the optical performance of the detection system. Therefore, inserting a filter of known attenuation on top of the tape does not give a traceable calibration of absolute attenuation. However this method can be used to give an indication of performance.

A neutral density filter with a calibrated attenuation of 14.8% was measured 9 times by a single Aethalometer, resulting in a mean measured attenuation of 10.4% for the reference beam and 7.1% for the sensing beam. The standard deviations of the two measurements were 1.0% attenuation and 0.8% attenuation respectively for the reference and sensing beams.

Each Aethalometer measured a neutral density filter with a measured attenuation of 14.8% at the Annual Audit visit and the results are given in Table 5.

Site	Reference Beam Attenuation, %	Sensing Beam Attenuation, %
Birmingham Tyburn	12.3	6.9
Dudley Central	14.7	16.5
Bath	9.3	6.8
Cardiff 12	10.0	6.8
Folkestone	9.1	8.7
Marylebone Road	7.3	4.3
North Kensington	10.5	6.6
Woolwich	9.9	6.5
Norwich Lakenfields	11.8	5.2
Manchester	8.6	7.9
South Kirkby	10.2	6.5
Halifax	10.2	8.0
Stoke	10.1	8.1
Belfast	9.5	4.5
Dunmurry	10.8	8.3
Strabane	10.4	6.3
Harwell	10.5	7.2
Nottingham	5.5	2.2
Edinburgh St Leonard's	8.5	5.5
Sunderland	9.0	9.4
Glasgow Centre	10.3	6.6

Table 5 Results of attenuation measurements on neutral density filter

Dudley and Nottingham could be considered to be outliers, but these results can easily be attributed to the problems of consistent optical path length and are not necessarily an indication of poor performance. These measurements are considered to be of limited value, and improved QA/QC procedures have been developed in consultation with the manufacturer. These will be described in future reports.

A better indication of instrument performance can be gained by examining the zero noise of the Aethalometer, as this should give an indication of the optical and electrical stability over the measurement period. This is carried out by generating nominally particle free air using a High Efficiency Particle (HEPA) filter and examining the reported concentrations over the following few measurement periods. The Aethalometer concentration should fall quickly to a stable value around zero, whose noise is due to noise in the optical system and electronics. Figure 3 shows a typical Aethalometer response to this test. The sample period is 5 minutes; the same as in the Network.

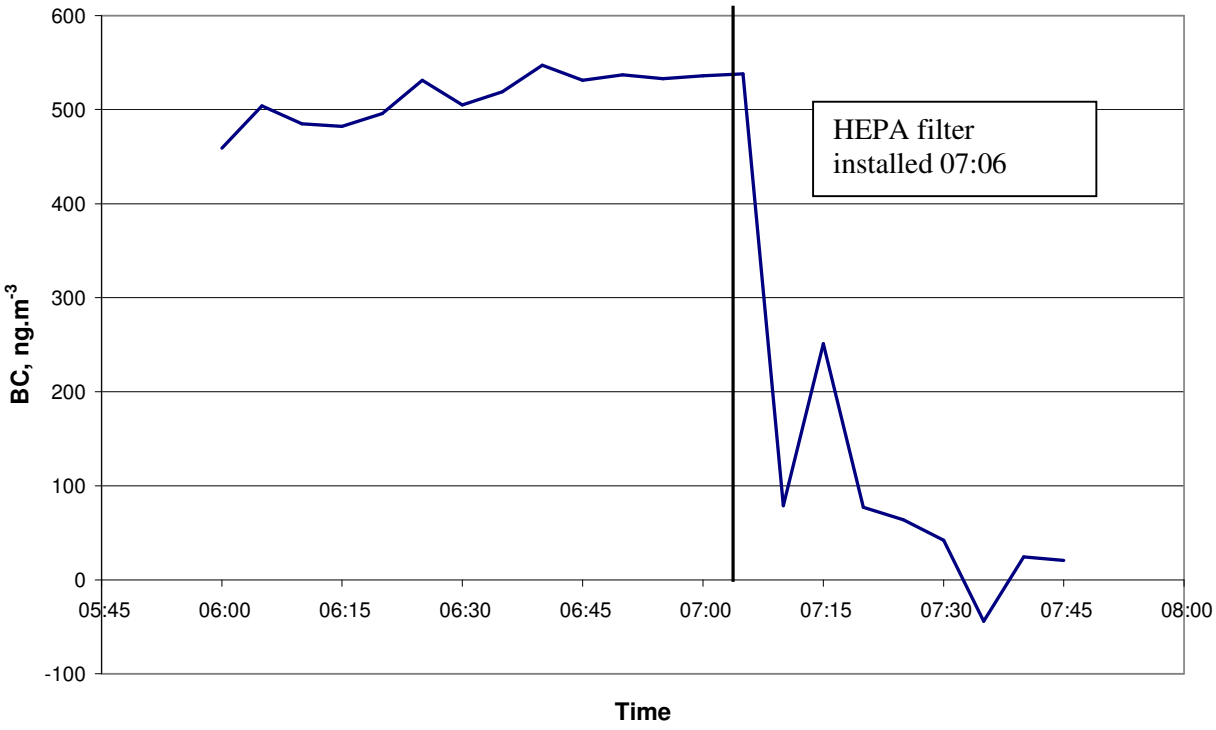


Figure 3 Aethalometer sampling unfiltered and HEPA filtered air

HEPA filter tests have been performed at a few sites with encouraging results. This test is being refined and will be incorporated in the 2011 audit round.

4.0 MEASUREMENT UNCERTAINTY

4.1 SAMPLE VOLUME

From measurements at the site audit the sample volume can be determined with an uncertainty of ±9.0%, expressed with a level of confidence of 95%. Included in this uncertainty are contributions from flow rate accuracy, repeatability, drift and leaks.

The leak rate is not used to correct the results, but is included as an uncertainty if the sampler passes the leak test at audit. The manufacturer's tolerance for leak rate is 20%. In the case of this uncertainty calculation the average value of leak rate determined in the 2010 audits was used. As leak rate is considered to be a rectangular distribution, its contribution to the standard uncertainty in sample volume is 3.2%.

4.2 MEASUREMENT OF ABSORPTION

The Aethalometer measurement does not depend on any absolute calibration of the detectors' response signals, but instead relies upon their ability to determine very small relative changes in optical transmission. Determining the zero noise of the system gives relevant information on the instrument's ability to measure small changes in optical transmission. Preliminary results from the HEPA filter tests show that the stability of the optical / electrical system is approximately 5%.

4.3 CORRECTION FOR SPOT DARKENING

The Virkkula model[3] was used to correct the measured concentrations due to the fact that the Aethalometer shows nonlinearity with attenuation. This effect and its correction introduce an uncertainty into the measurements. At most sites the correction can be seen to work well on the 15-minute data, in that there is minimal discontinuity when the spot location changes, and the associated uncertainty is considered to be small compared to other components. At sites where the concentration is changing quickly, such as Marylebone Road, this uncertainty in the 15-minute data becomes significant. When hourly averages have been produced from this 15-minute data the effect is less significant.

The differences between using individual spot corrections versus seasonal or monthly corrections have been examined, with the conclusion that individual spot correction is the most suitable method.

The uncertainty due to this effect cannot be directly determined and has not been included in the overall measurement uncertainty.

4.4 PRELIMINARY OVERALL MEASUREMENT UNCERTAINTY

As QA/QC procedures are still being developed, the overall measurement uncertainty is a preliminary value. Further work is being done in collaboration with the instrument manufacturer to develop these procedures and will be incorporated in the 2011 site audits.

When the contributions from sample volume and measurement of adsorption are combined, the overall measurement uncertainty for Black Carbon concentrations is 13.5%, expressed with a level of confidence of 95%. This is an indicative measurement uncertainty for the Aethalometer method and is calculated from the results of the 2010 audit data. The site specific overall measurement uncertainty may differ from this value, and any effect from the spot darkening correction will be additional.

5.0 RESULTS

The concentration data for 2010 are presented in the following sections as time series graphs, summary graphs and tables of the annual mean concentration and data capture.

All of the Black Carbon and UV Component data have been corrected for spot darkening using the Virkkula method[3].

The hourly data set for Black Carbon and UV component concentrations can be downloaded from Defra's UK-AIR: Air Information Resource Web Pages found at:

http://uk-air.defra.gov.uk/

5.1 TIME SERIES

The following sections present time series graphs of the Black Carbon and UV component concentrations.

5.1.1 Black Carbon

The following charts show the Black Carbon concentrations measured by the UK Black Carbon Network for 2010. The time resolution of the measurements is hourly. Data has been split into regions of the UK for presentation purposes. The y-axis on these charts has been set to 50µg.m^{-3} to enable easy comparison between charts.

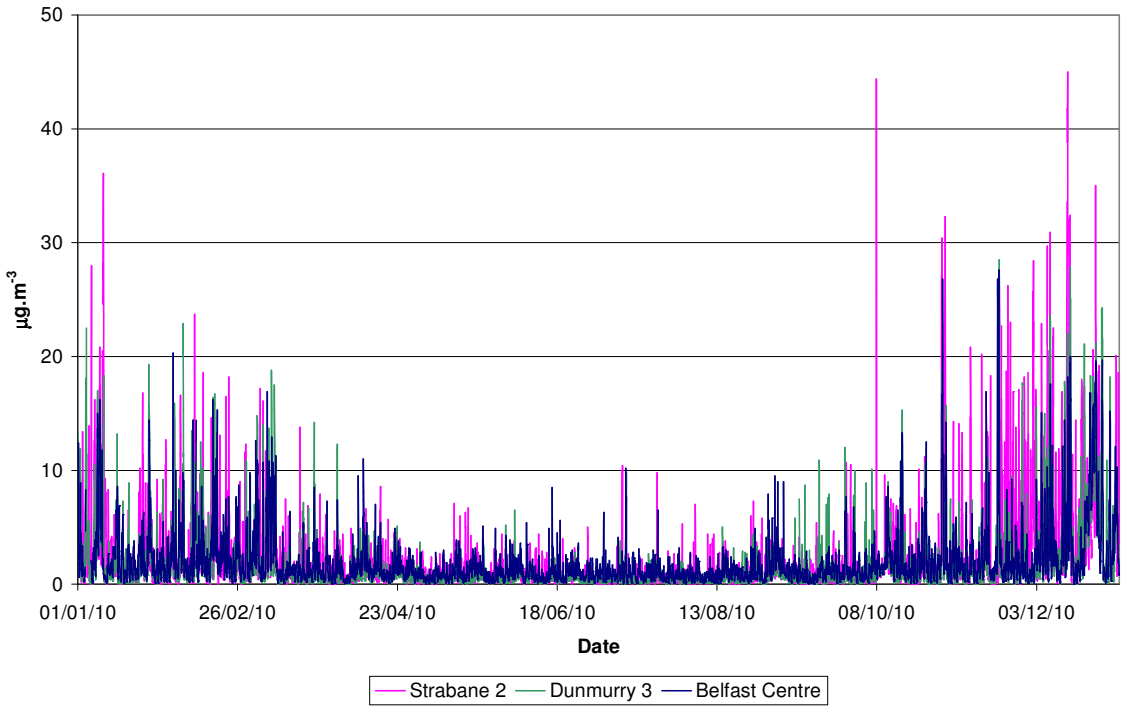


Figure 4 Black Carbon concentrations during 2010 in Northern Ireland

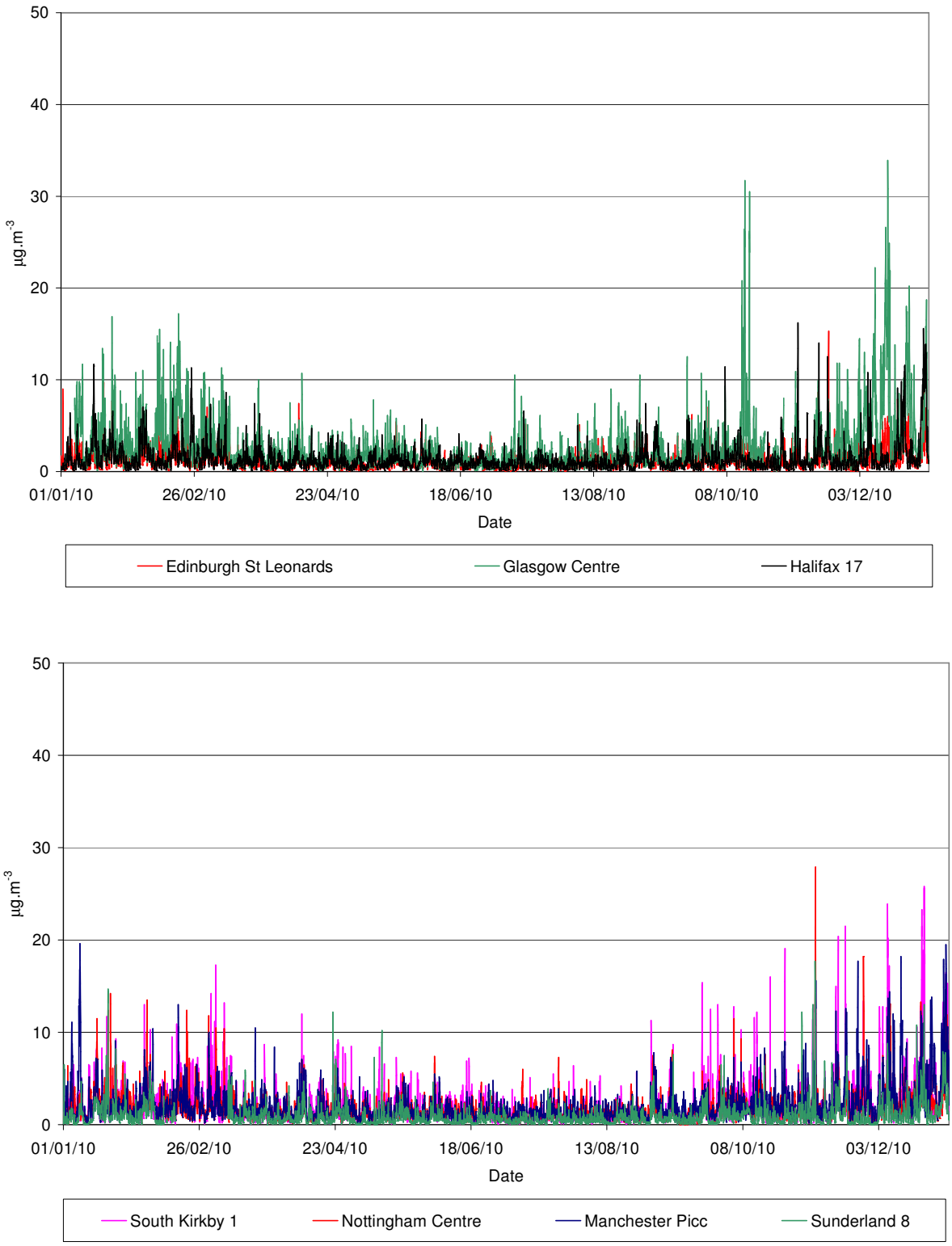
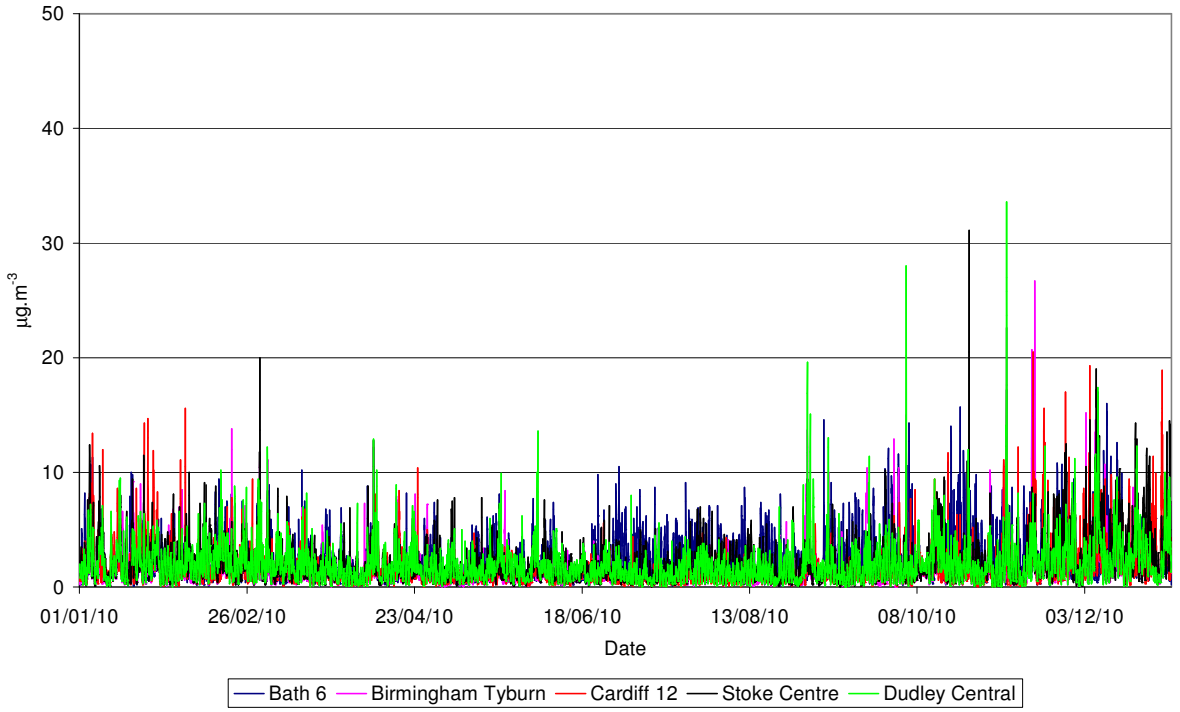
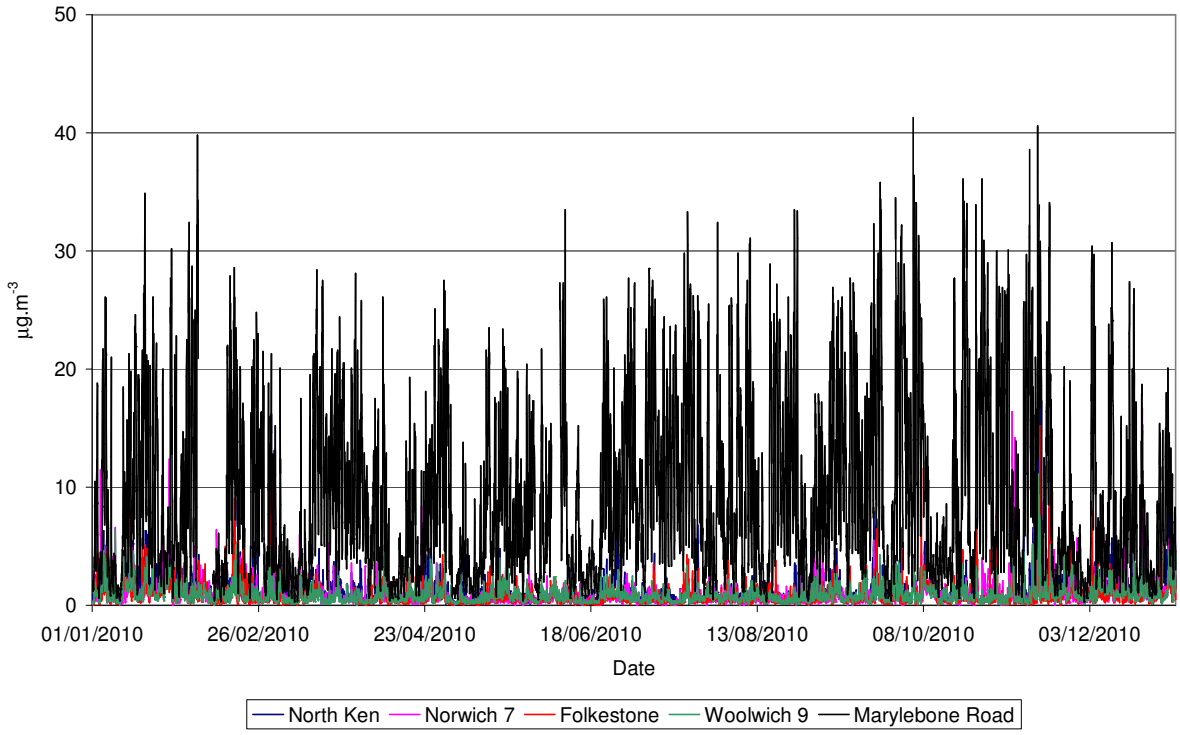


Figure 5 + 6 Black Carbon concentrations during 2010 in Scotland and Northern England





Figures 7 + 8 Black Carbon concentrations during 2010 in Southern England and Wales

All sites measured increased concentrations during the cold periods in November and December of 2010, with most sites showing the quick drop in concentrations on Boxing Day as the weather changed from stable cold conditions to the warmer and wetter normally prevailing westerly direction.

Glasgow Centre measured higher than normal concentrations over the period 14th to 17th October. This

was traced to generator situated near to the monitoring site being used to power a Continental Market. The monitoring site is situated in a busy pedestrian shopping square and anybody visiting this area would have been exposed to this source of particulates. Data from the AURN has also been treated as valid, with the $PM_{2.5}$ TEOM / FDMS reporting hourly concentrations up to 300 $\mu g.m^{-3}$.

5.1.2 UV Component

The following charts show the UV component concentrations measured by the UK Black Carbon Network for 2010. The time resolution of the measurements is hourly. Data has been split into regions of the UK for presentation purposes. The y-axis on the UV component time series graph has not been fixed to the same value for every chart, because the UV component is much more dependent on local site-specific conditions.

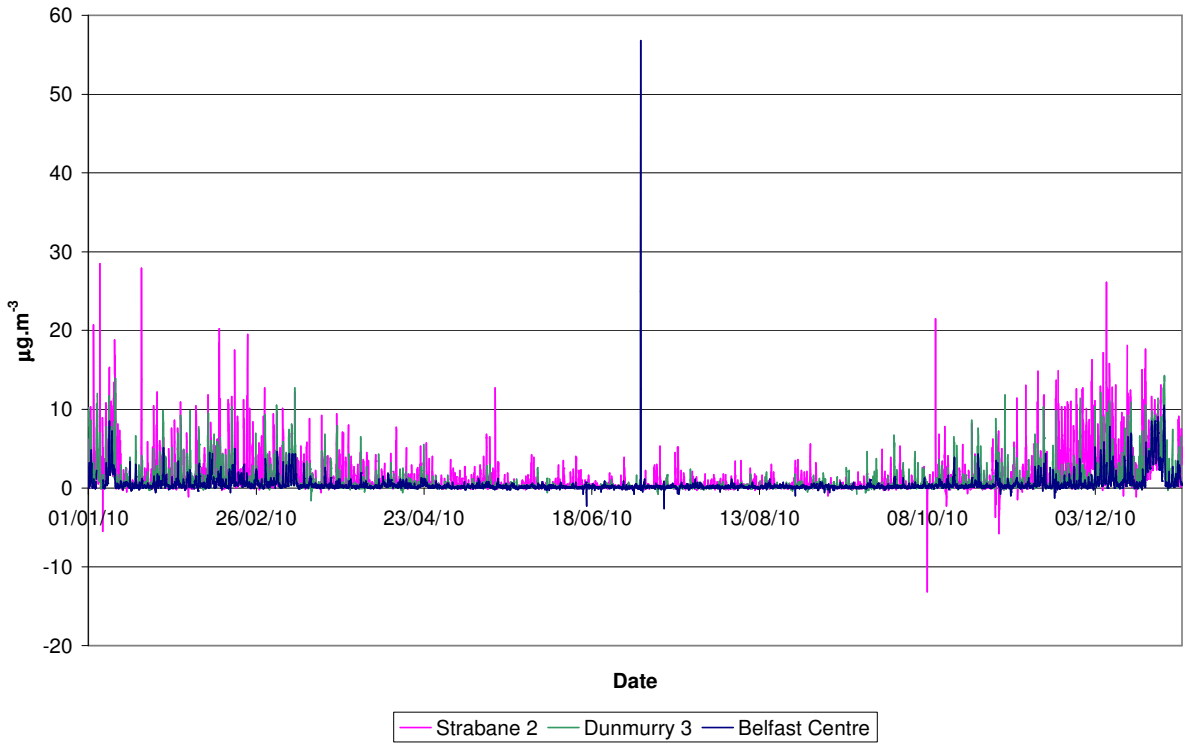
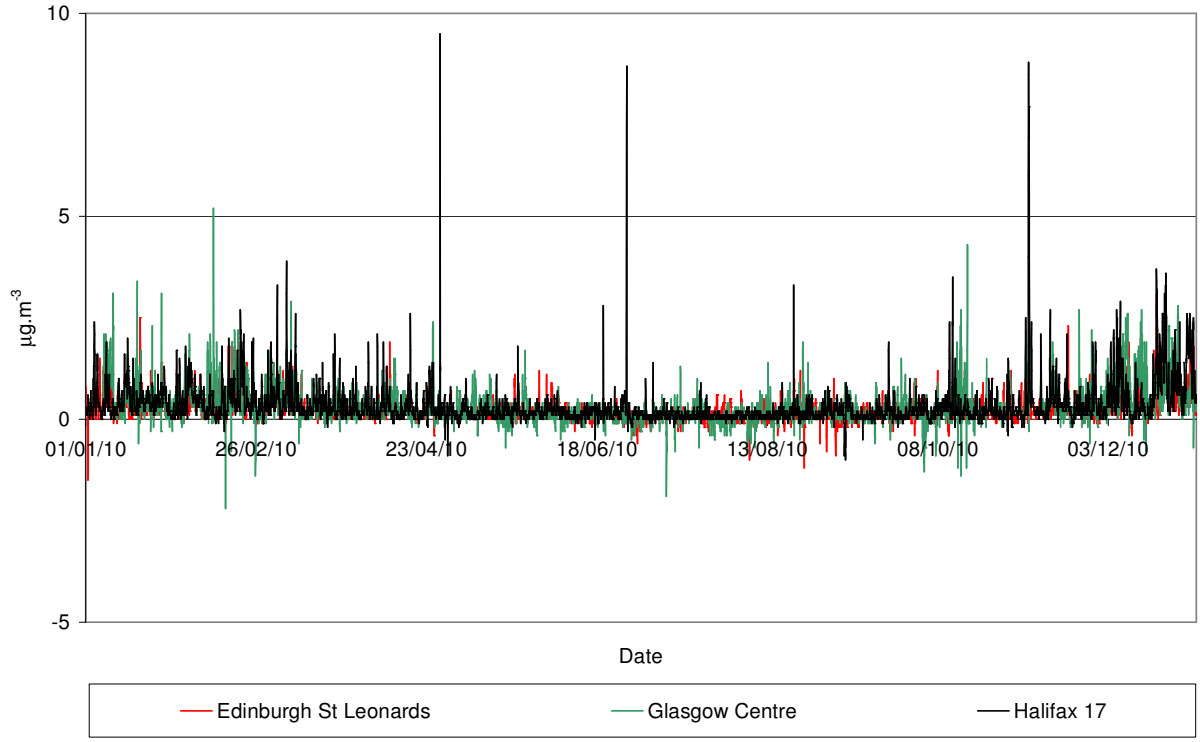


Figure 9 UV component concentrations during 2010 in Northern Ireland



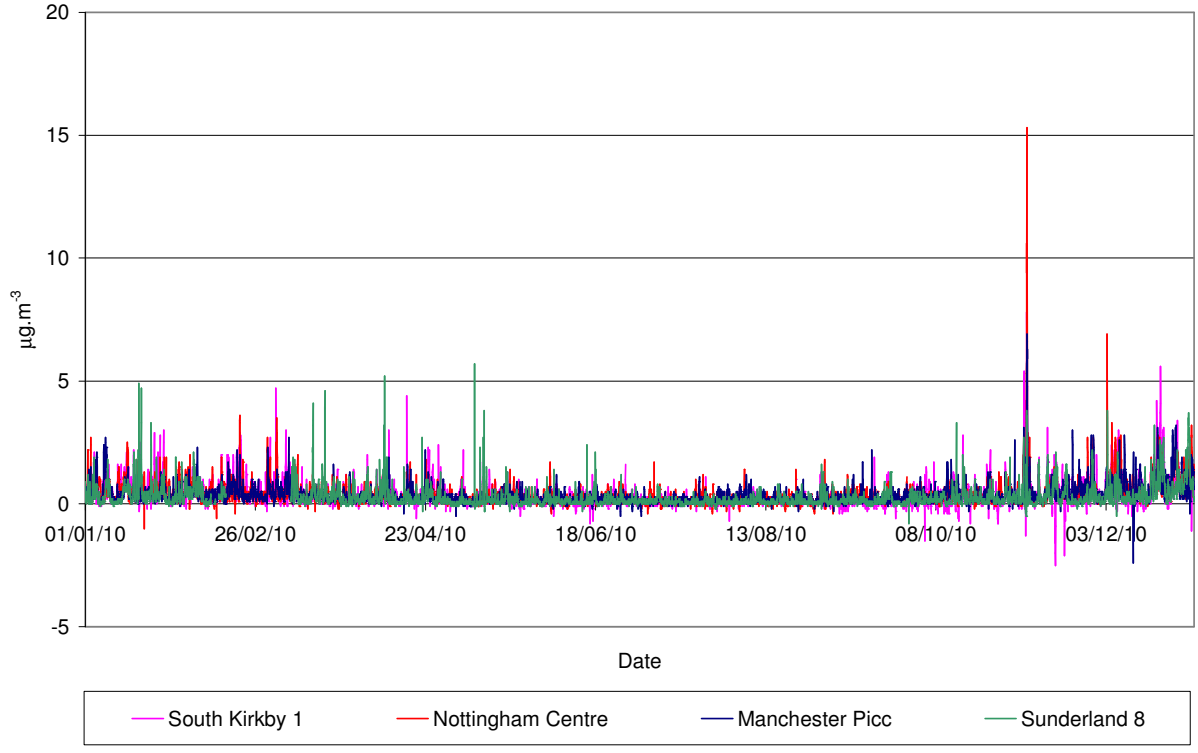
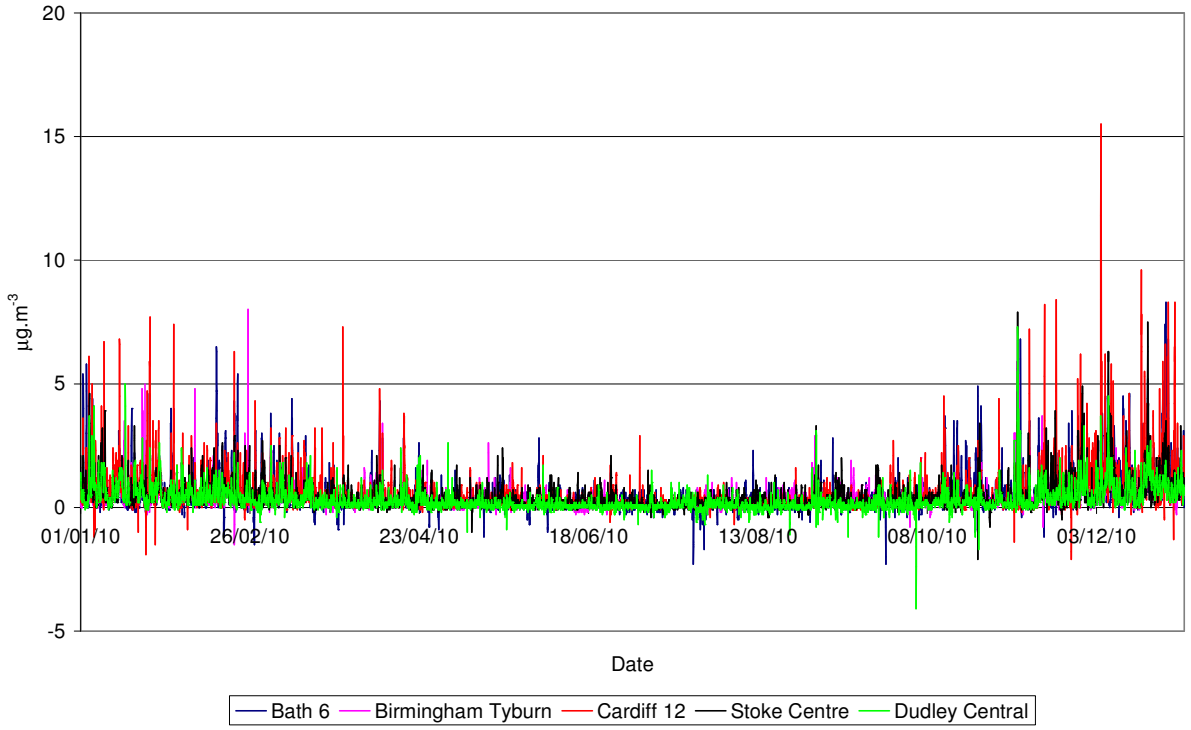


Figure 10+11 UV component concentrations during 2010 in Scotland and Northern England



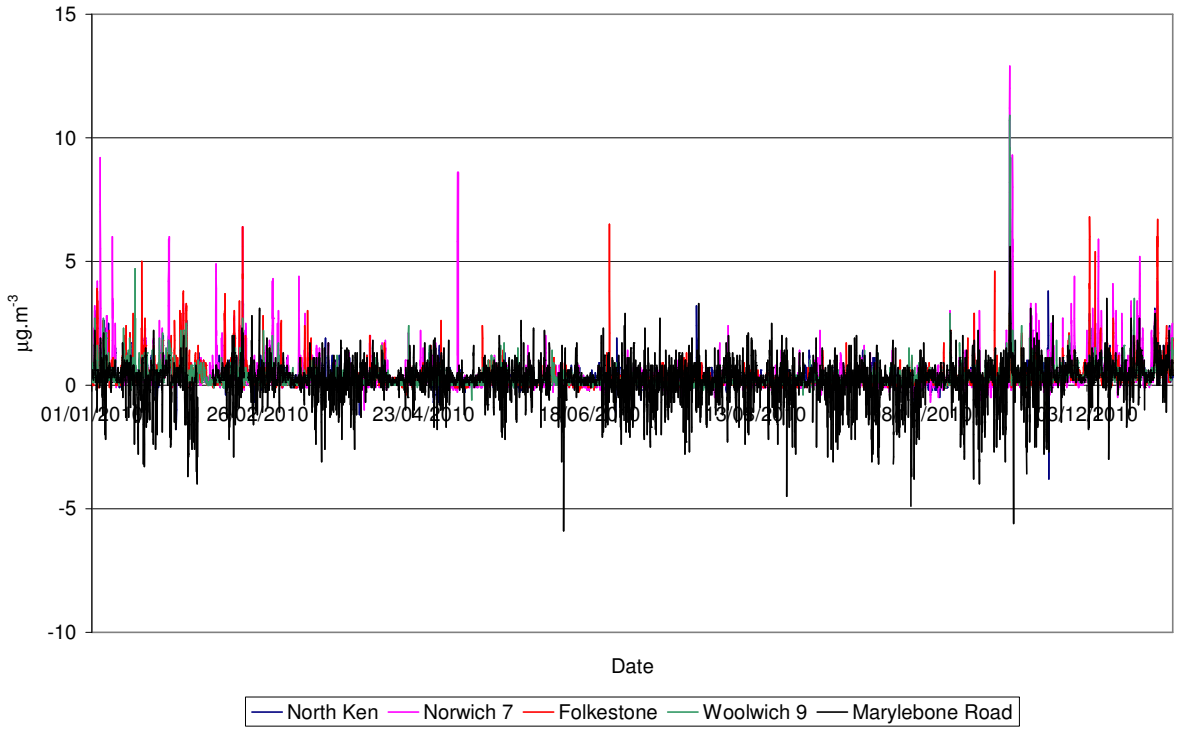


Figure 12 + 13 UV component concentrations during 2010 in Southern England and Wales

The cause of the occurrence of negative concentration spikes in the "UV component", especially at roadside sites, is not clear. It may be due to the semi-volatile nature of the aromatic organic species that adsorb at the 370mm wavelength. In well-aged ambient air samples these volatile organics will be found almost exclusively in the gas phase, and the UV response of the Aethalometer will show little enhancement over the BC response. However, combustion exhaust streams may contain filterable particles at high concentrations together with semi-volatile UV-active material that will be temporarily

retained on the filter tape leading to a distinct increase in UV absorption. Over time these organic species boil off the tape and reduce the enhanced UV adsorption. If equilibrium between organic species deposit and boil off is not reached due to cleaner air being sampled, the amount of organic enhancement will drop and will lead to negative UV Component concentrations.

Another possible reason for positive and negative spikes in roadside data is the internal timing of the measurement process within the Aethalometer. The UV Channel reading is made around 20 seconds after the Black Carbon channel reading. If concentrations are changing rapidly, the subtraction of the Black Carbon concentration from the "UV" concentration could give misleading results.

These effects will be most prevalent at Marylebone Road due to the closeness of the inlet to the curb, high traffic flow and predominantly diesel based exhaust signatures from HGVs, busses and taxis. At Bath the inlet is further from the road, there is less traffic flow and a higher proportion of petrol fuelled vehicles. The Dudley site is located in a car park so is also susceptible to directly sampling exhaust emission streams and quickly changing concentrations.

5.2 AVERAGES AND DATA CAPTURE

The following sections present the annual average Black Carbon and UV component concentrations along with the data capture statistics

5.2.1 Black Carbon

Table 6 gives the annual average for each site for 2010.

Site	**Mean concentration $\mu g.m^{-3}$**
Bath 6	2.2
Belfast Centre	1.9
Birmingham Tyburn	1.5
Cardiff 12	1.5
Dudley Central	1.9
Dunmurry 3	1.7
Edinburgh St Leonard's	1.2
Folkestone	0.8
Glasgow Centre	2.7
Halifax 17	1.3
Harwell	0.5
Manchester Piccadilly	2.0
Marylebone Road	8.8
North Kensington	1.5
Norwich Lakenfields	1.0
Nottingham Centre	1.8
South Kirkby 1	2.0
Stoke Centre	2.1
Strabane 2	2.0
Sunderland 8	0.9
Woolwich 9	0.9

Table 6 Annual Mean Black Carbon Concentration for 2010

The increments in concentration from the rural background site at Harwell to the suburban site in Folkestone to the urban background sites in London (North Kensington and Woolwich) and from these to the Marylebone Roadside site in Central London are 0.3 $\mu g.m^{-3}$, 0.4 $\mu g.m^{-3}$ and 7.0 $\mu g.m^{-3}$ respectively.

The annual mean concentrations are presented as a bar graph (Figure 14) to aid the comparison of sites:

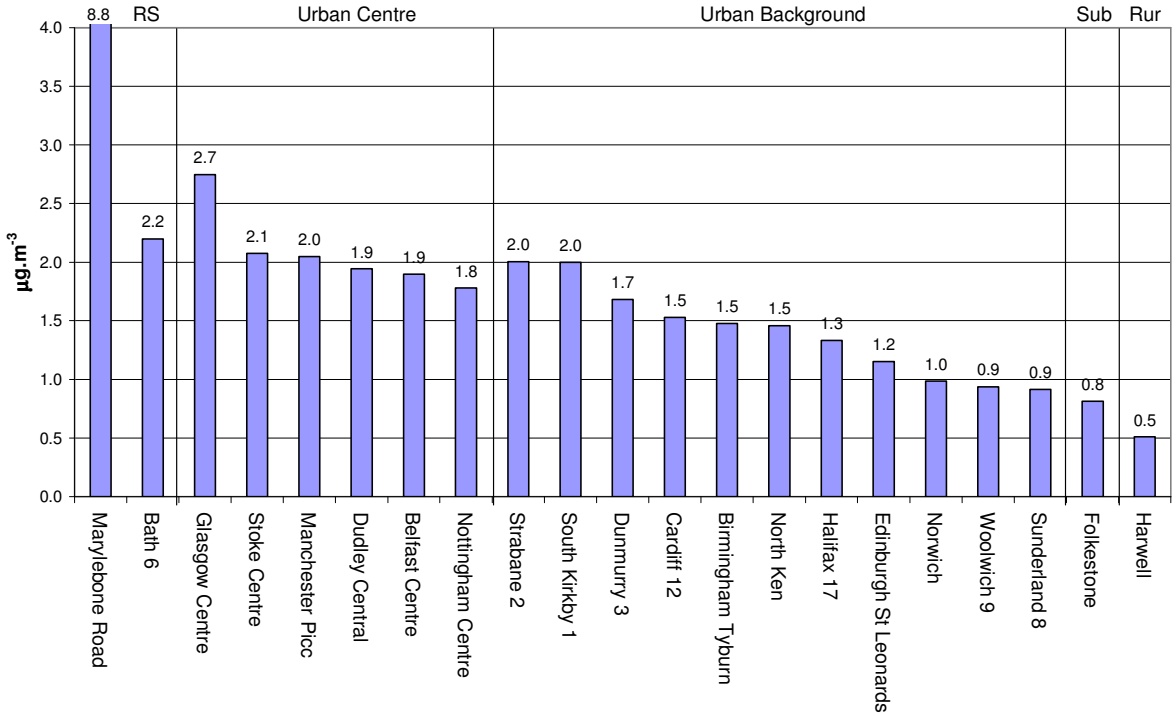


Figure 14 Annual Mean Black Carbon Concentration for 2010

5.2.2 UV Component

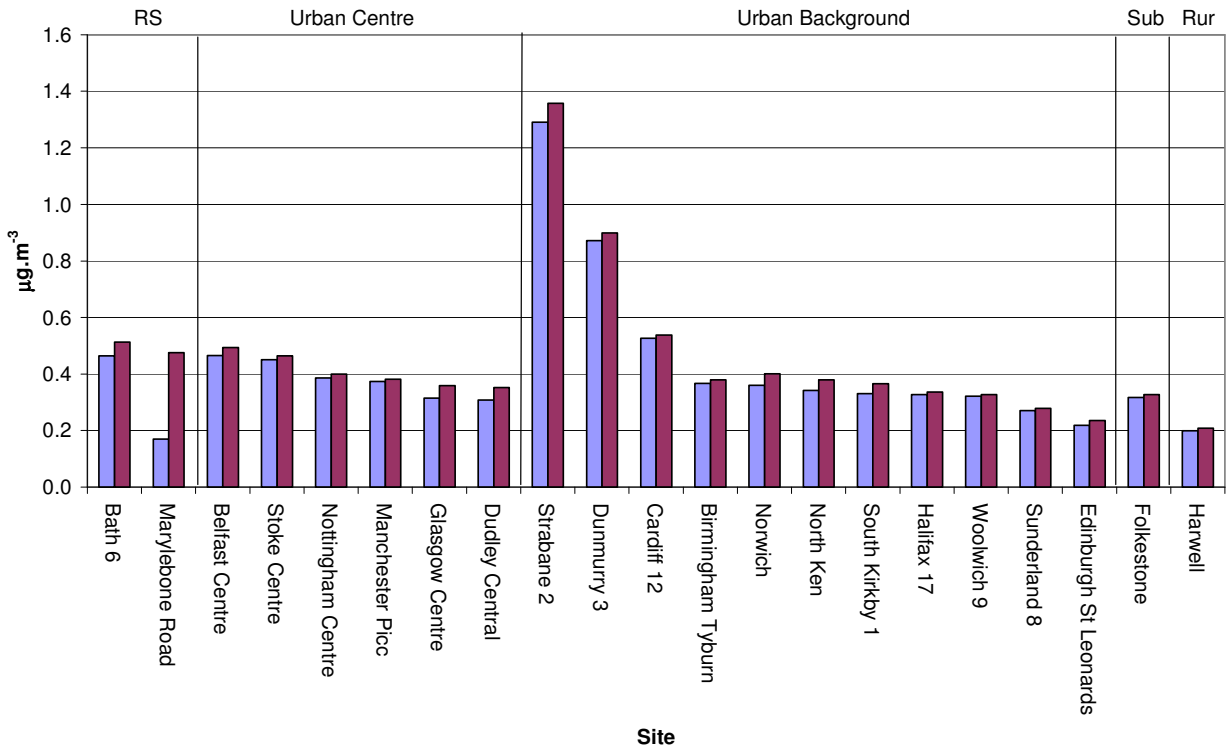
Table 7 gives the annual average for each site for 2010.

Site	Mean concentration, (all measurements included) $\mu g.m^{-3}$	Mean concentration, (negative measurements excluded) $\mu g.m^{-3}$
Bath 6	0.5	0.5
Belfast Centre	0.5	0.5
Birmingham Tyburn	0.4	0.4
Cardiff 12	0.5	0.5
Dunmurry 3	0.9	0.9
Edinburgh St Leonard's	0.2	0.2
Folkestone	0.3	0.3
Glasgow Centre	0.3	0.4
Dudley Central	0.3	0.4
Halifax 17	0.3	0.3
Manchester Piccadilly	0.4	0.4
Marylebone Road	0.2	0.5
North Ken	0.3	0.4
Norwich Lakenfields	0.4	0.4
Nottingham Centre	0.4	0.4
South Kirkby 1	0.3	0.4
Stoke Centre	0.5	0.5
Strabane 2	1.3	1.4
Sunderland 8	0.3	0.3
Woolwich 9	0.3	0.3
Harwell	0.2	0.2

Table 7 Annual Mean UV Component Concentration for 2010, all data included

It can be seen that by excluding all the negative UV component concentrations, the Marylebone Road mean becomes comparable to other sites.

The annual mean concentrations are presented as a bar graph (Figure 15) to aid the comparison of sites:



Key:

Mean of all data

Mean of all negative concentrations excluded

Figure 15 Annual Mean UV component concentration for 2010

The concentrations of the UV component measured at the suburban site in Folkestone, the urban background sites in London (North Kensington and Woolwich) and the Marylebone Road site in Central London are comparable with no obvious urban or roadside increment. Concentrations at Harwell and Folkestone are also comparable.

5.2.3 Data Capture

Table 8 gives the data capture for each site for 2010.

Site	Data Capture %
Bath 6	100
Belfast Centre	99
Birmingham Tyburn	94
Cardiff 12	100
Dudley Central	99
Dunmurry 3	98
Edinburgh St Leonard's	99
Folkestone	97
Glasgow Centre	95
Halifax 17	100
Harwell	100
Manchester Piccadilly	100
Marylebone Road	97
North Kensington	88
Norwich Lakenfields	100
Nottingham Centre	100
South Kirkby 1	100
Stoke Centre	100
Strabane 2	98
Sunderland 8	93
Woolwich 9	100

Table 8 Data capture rates of the Aethalometers for 2010

The reasons for the site with data capture below 90% is given below:

North Kensington (88%)

Combinations of faults over the year lead to the reduced data capture. The faults are detailed below:

06/04/10 – 20/04/10 Very noisy instrument replaced with network spare.

29/05/10 – 10/06/10 Optics fault, instrument replaced with repaired original instrument from 20th April.

26/10/10 – 08/11/10 Tape advance fault, instrument returned to workshop repair before being returned to site.

5.3 CYCLICAL VARIATIONS

The following section presents analysis of the Black Carbon and UV component concentrations with regards to the hour of the day, the day of the week and the month in which the measurements are made during 2010.

These results have been grouped by site and are batched together by site classification. The site order for the Roadside and Urban Centre sites is in decreasing Black Carbon Concentration, while the site order for the Urban Background, Suburban and Rural Background sites is in decreasing UV component concentration. The units on the y-axis are: $\mu g.m^{-3}$ for Black Carbon and equivalent $\mu g.m^{-3}$ for the UV component. All negative values for the UV component have been included in the data set. The results are presented in Figures 16 to 19.

The data has been plotted in local time (GMT/BST) as the pollution sources are primarily attributed to human activity sources and not solar driven atmospheric chemistry sources.

Chart Key

The top chart of each figure shows the average concentration measured each hour through the week and is labelled “hour”.

The bottom left chart shows the same data just grouped by hour of the day.

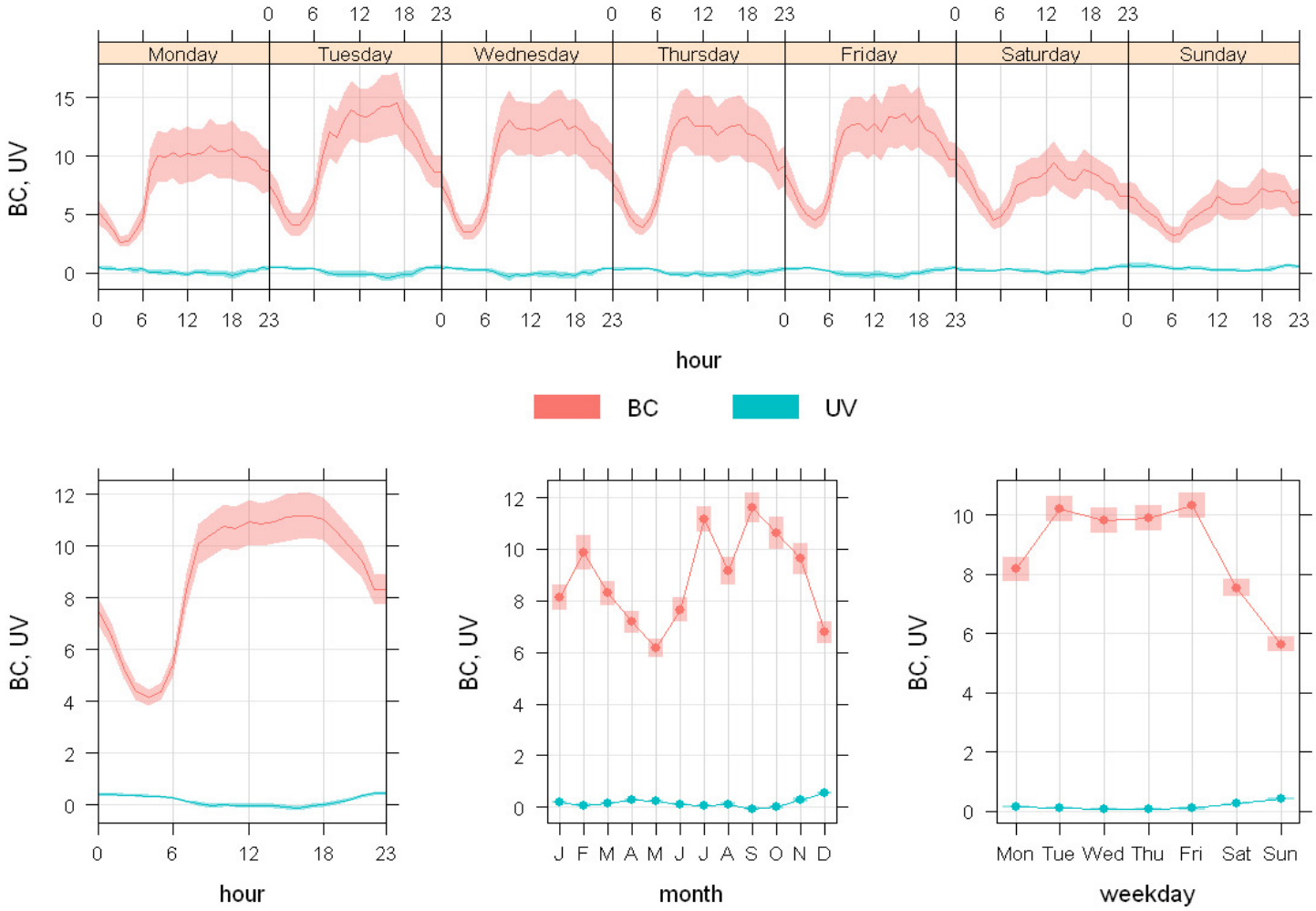
The bottom centre chart shows the same data grouped by month of the year.

The bottom right chart shows the same data grouped by day of the week.

For all of the charts, the shaded area on the y-axis represents the uncertainty in the mean y-value due to the spread of the results over that averaging period, expressed with a level of confidence of 95%. It is not the overall measurement uncertainty. The shaded area on the x-axis in the by month chart (bottom centre) is for display purposes only, to allow the uncertainty in the mean value to be seen more clearly.

Acknowledgement

Figures 16 to 19 are generated using the Open-Air Tools run on the R software platform[7,8].



Marylebone Road

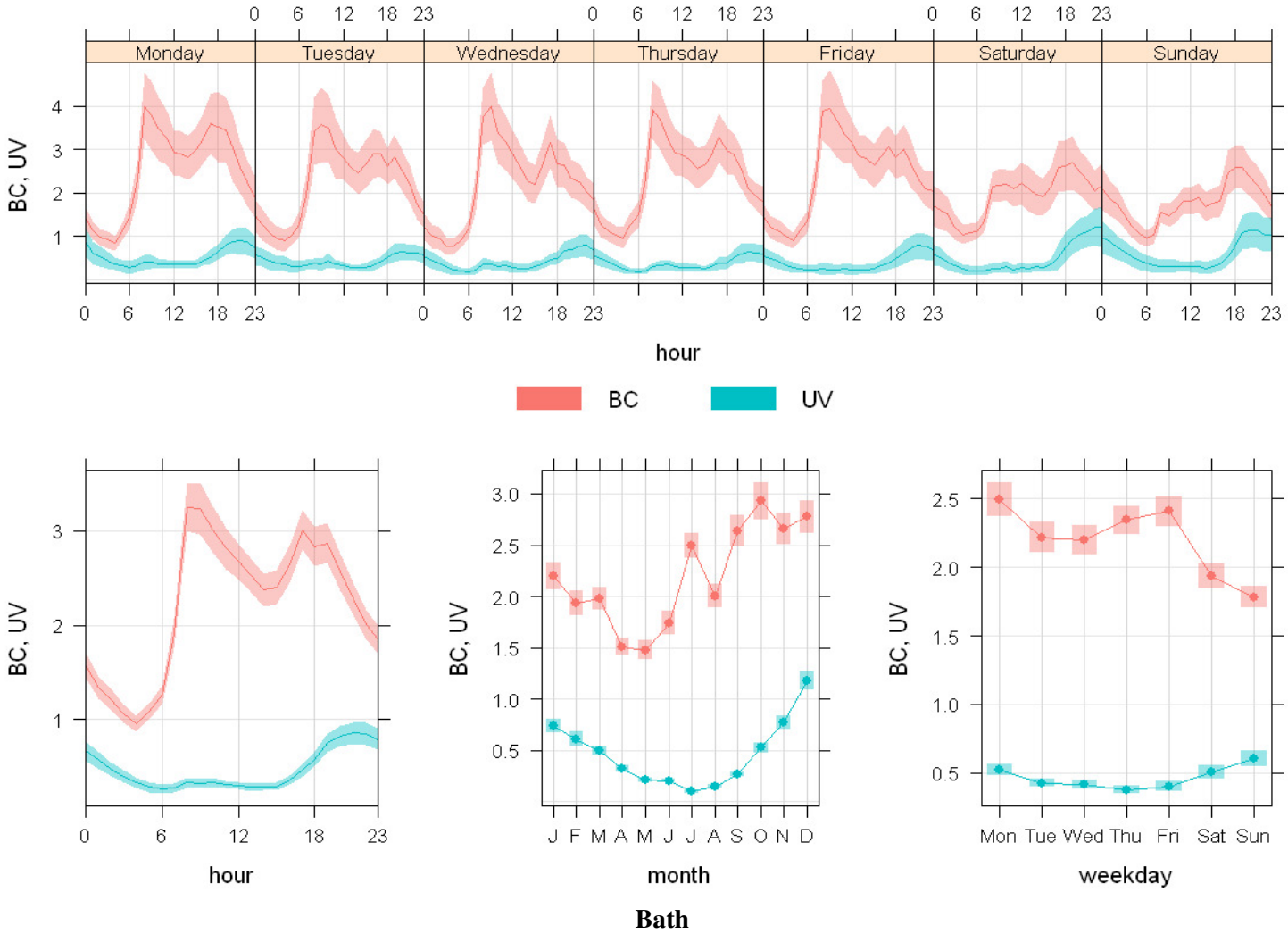
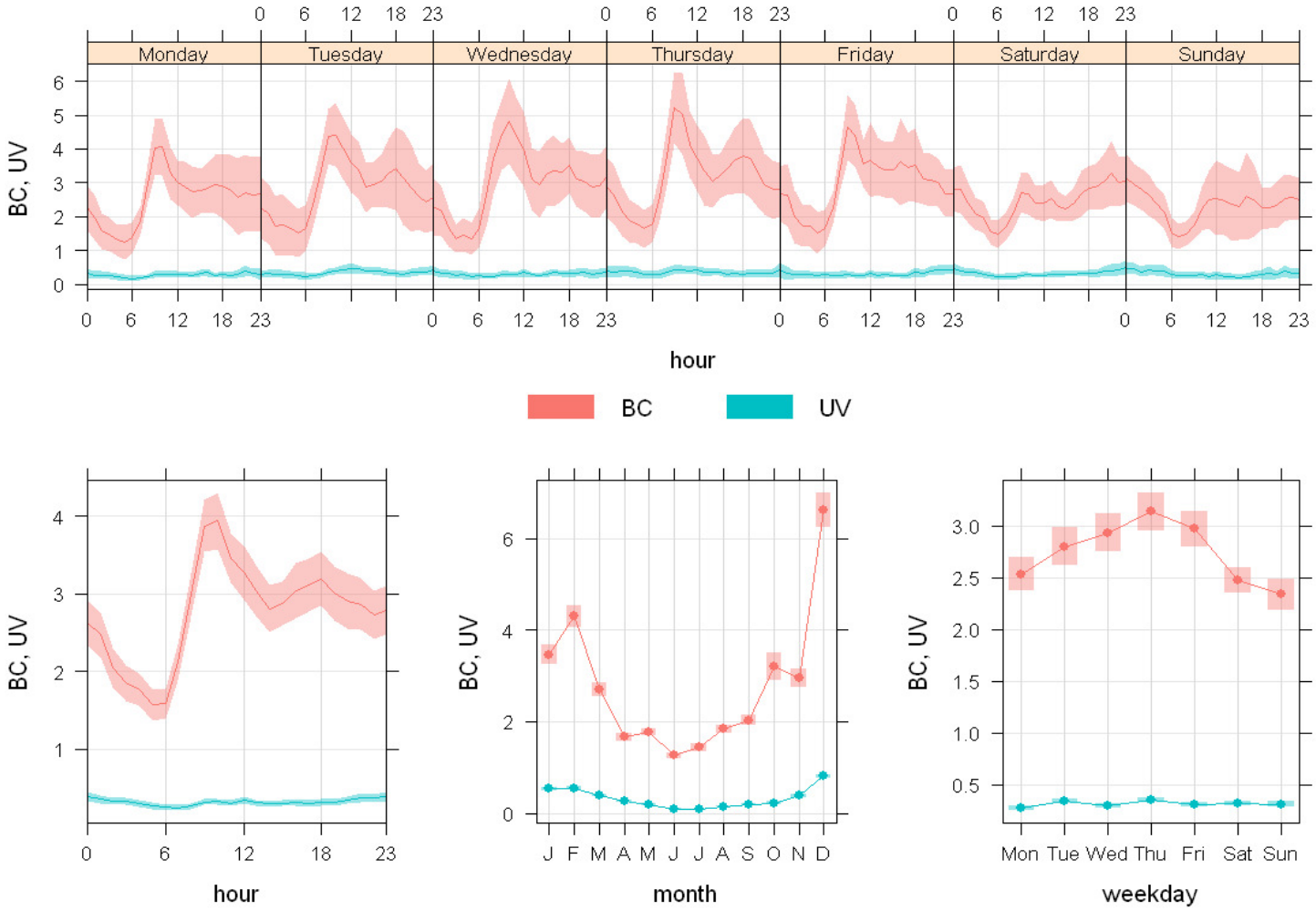
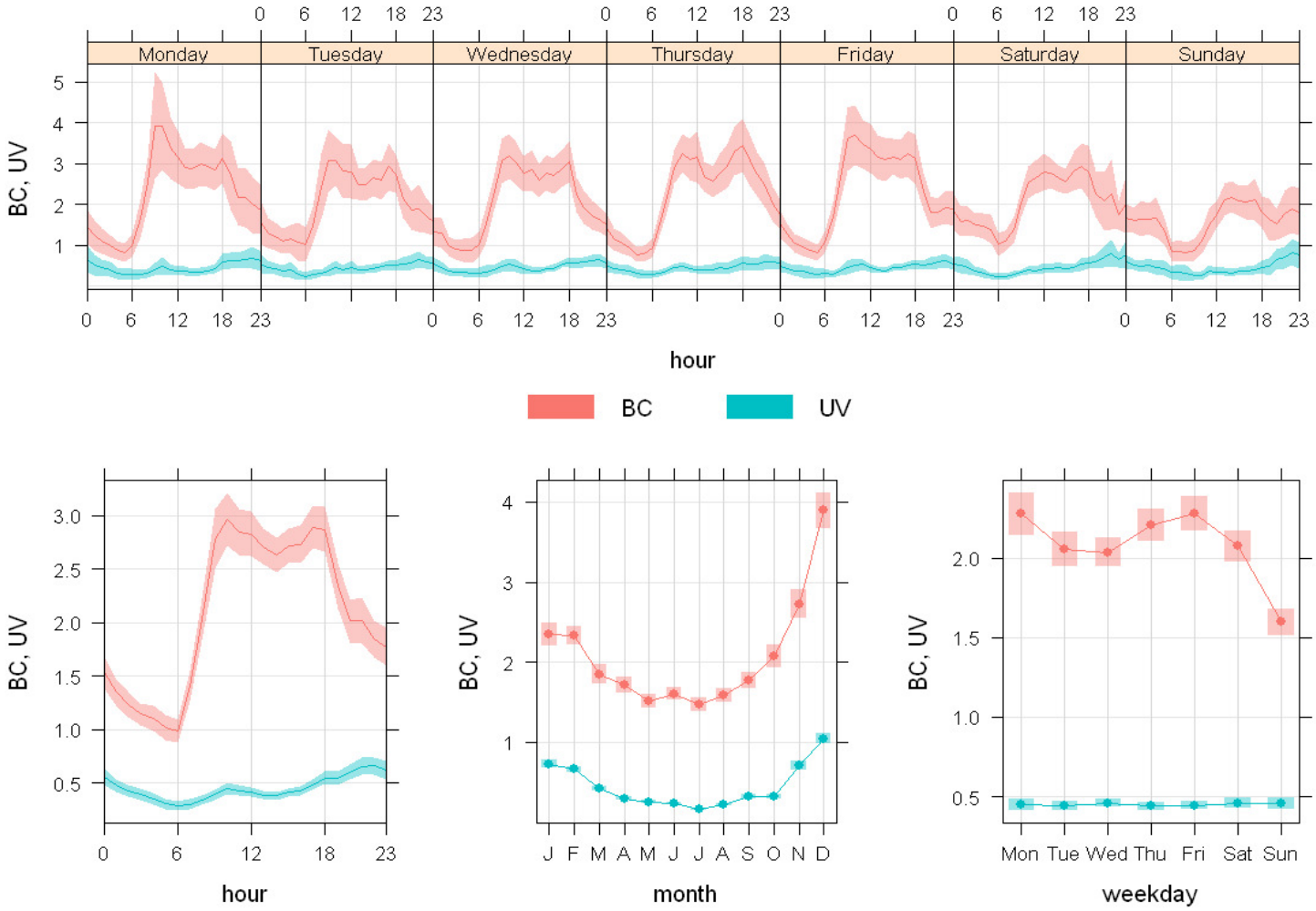


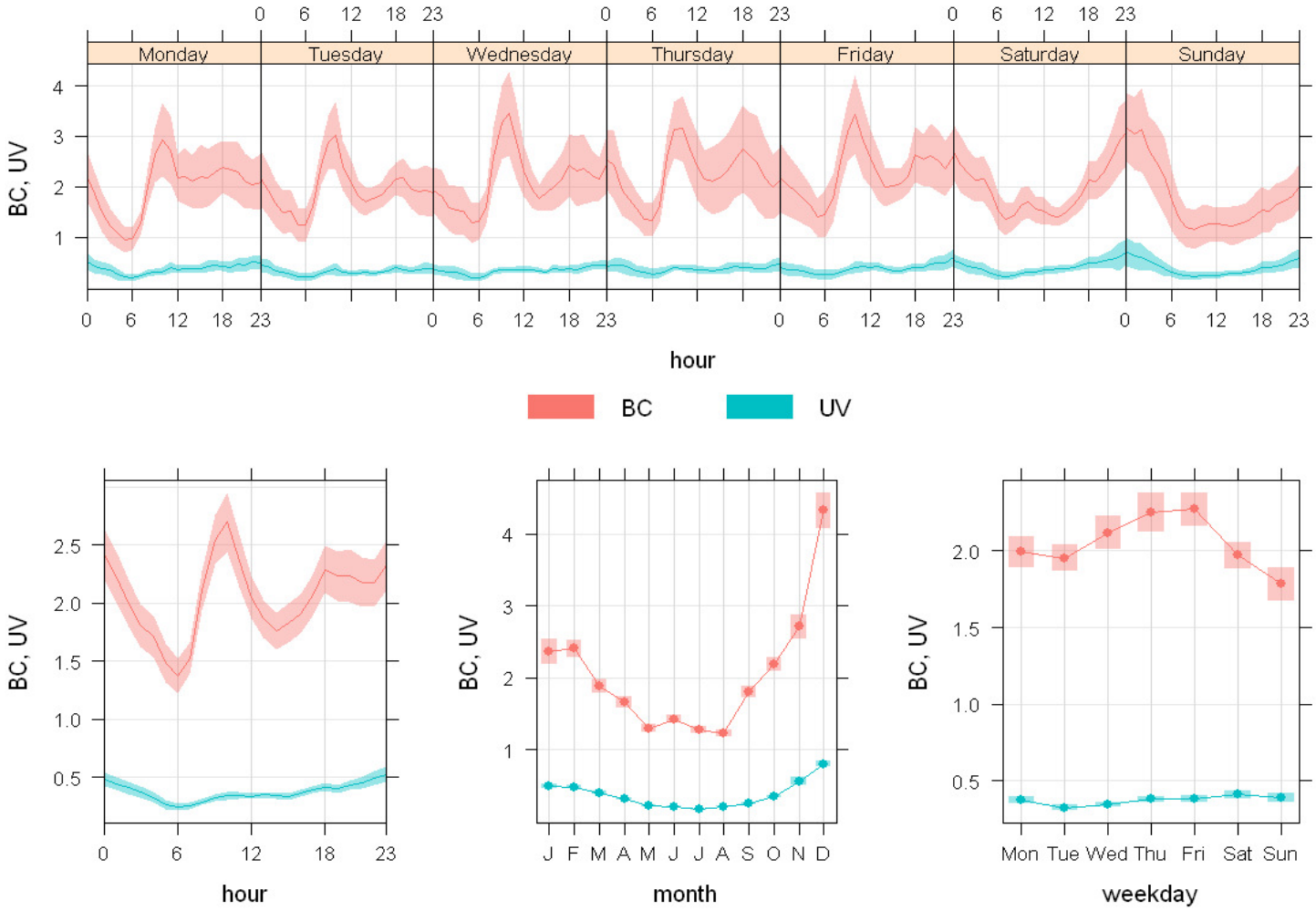
Figure 16 Roadside Sites



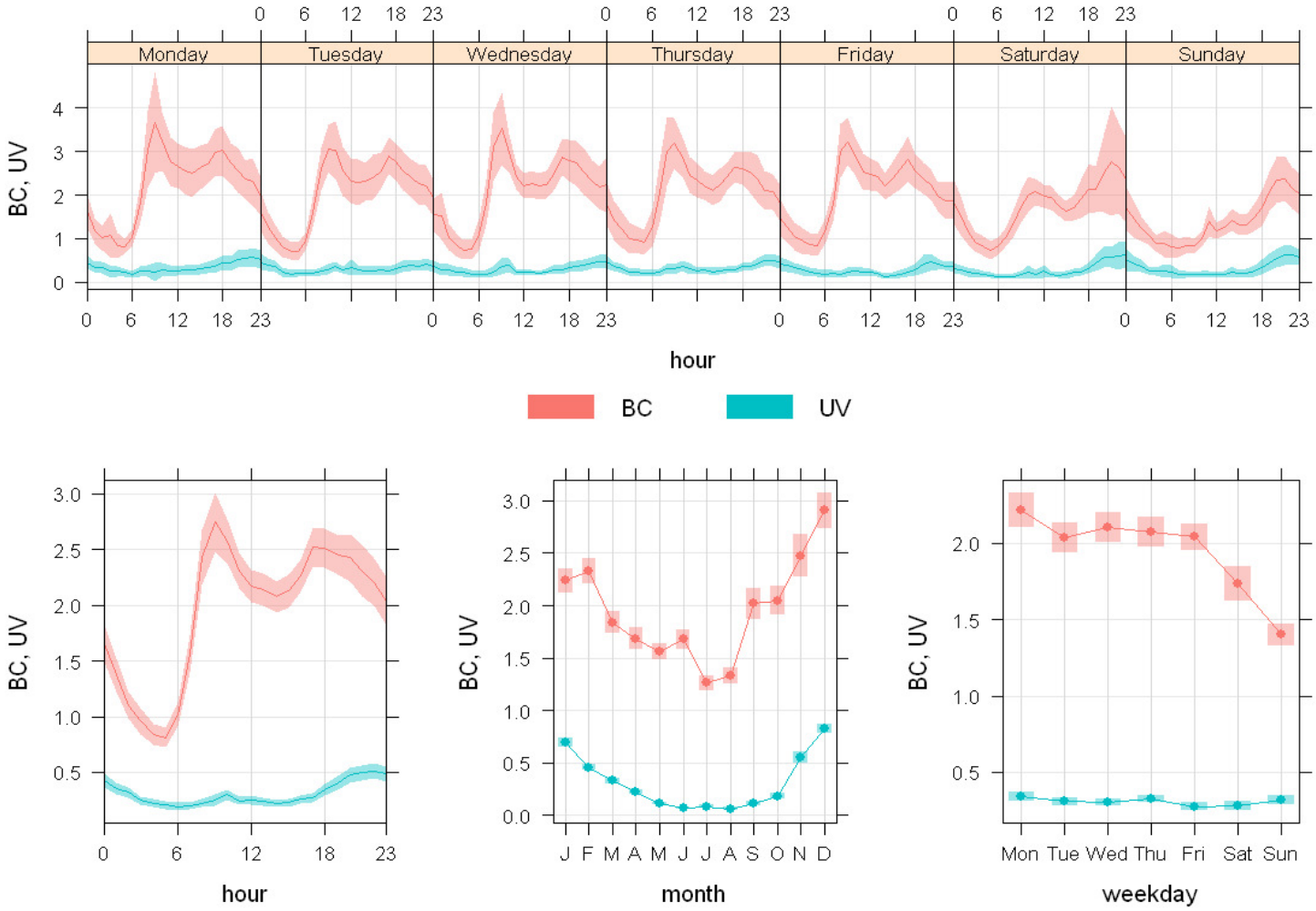
Glasgow Centre



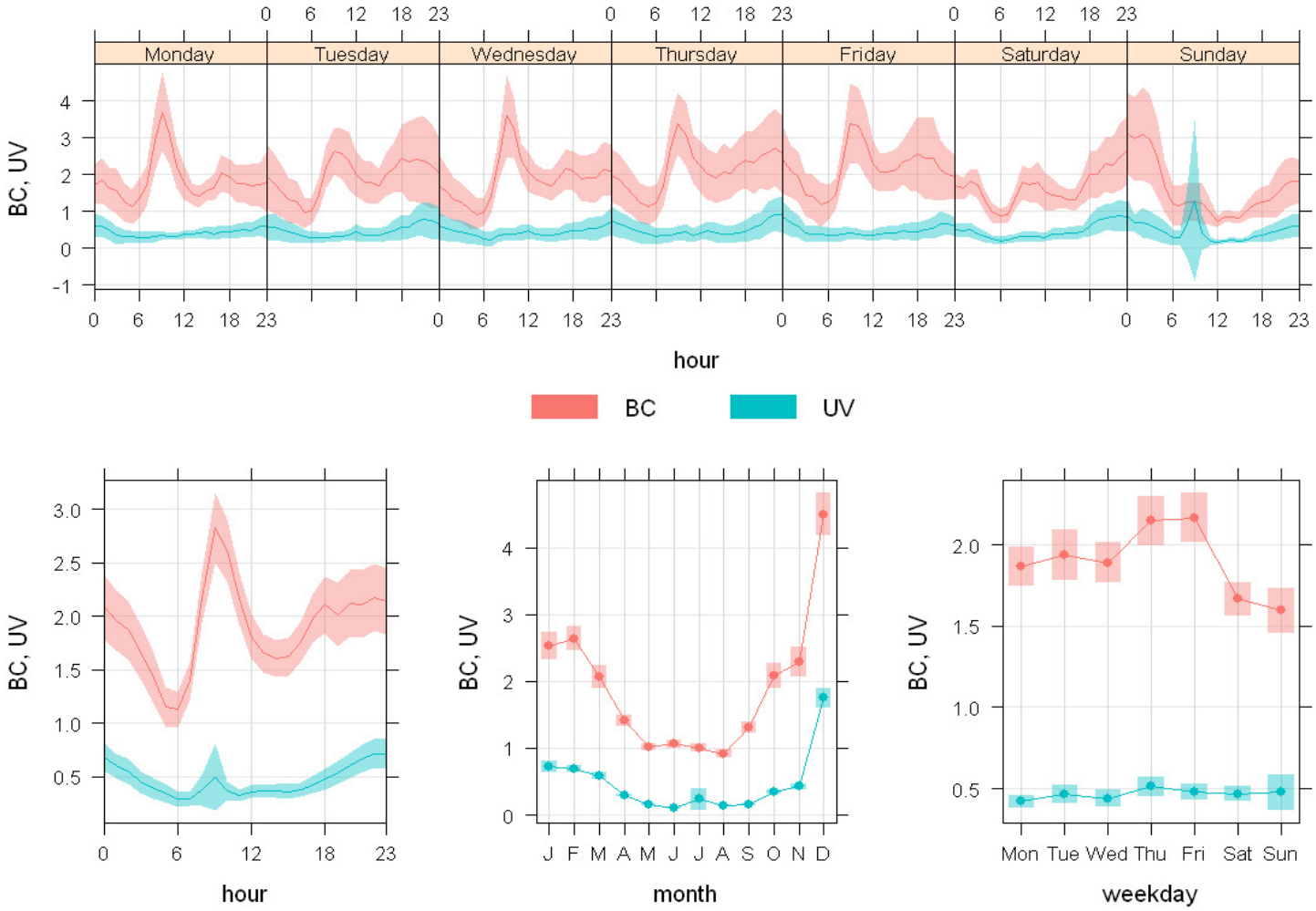
Stoke Centre



Manchester Piccadilly



Dudley Central



Belfast Centre

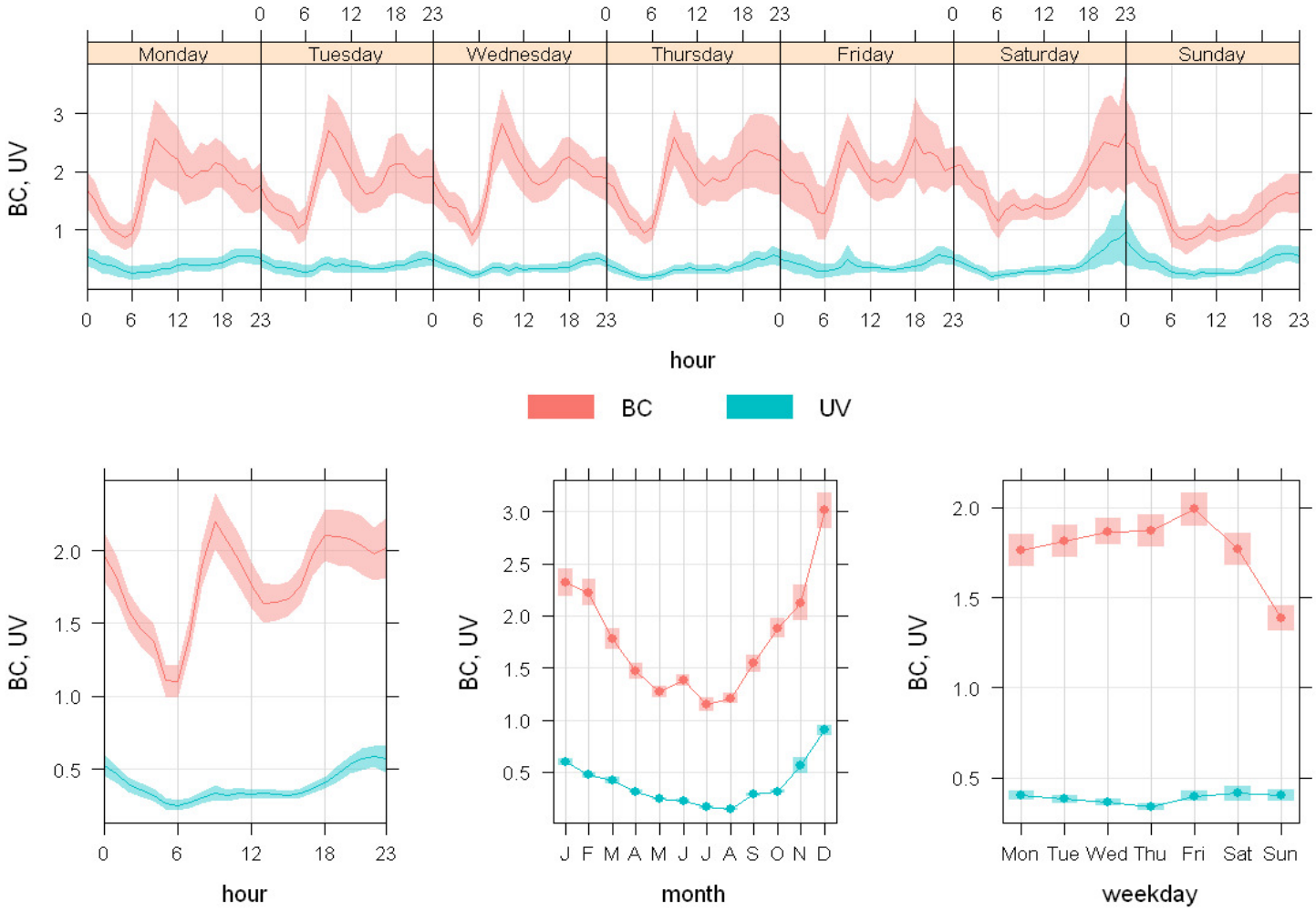
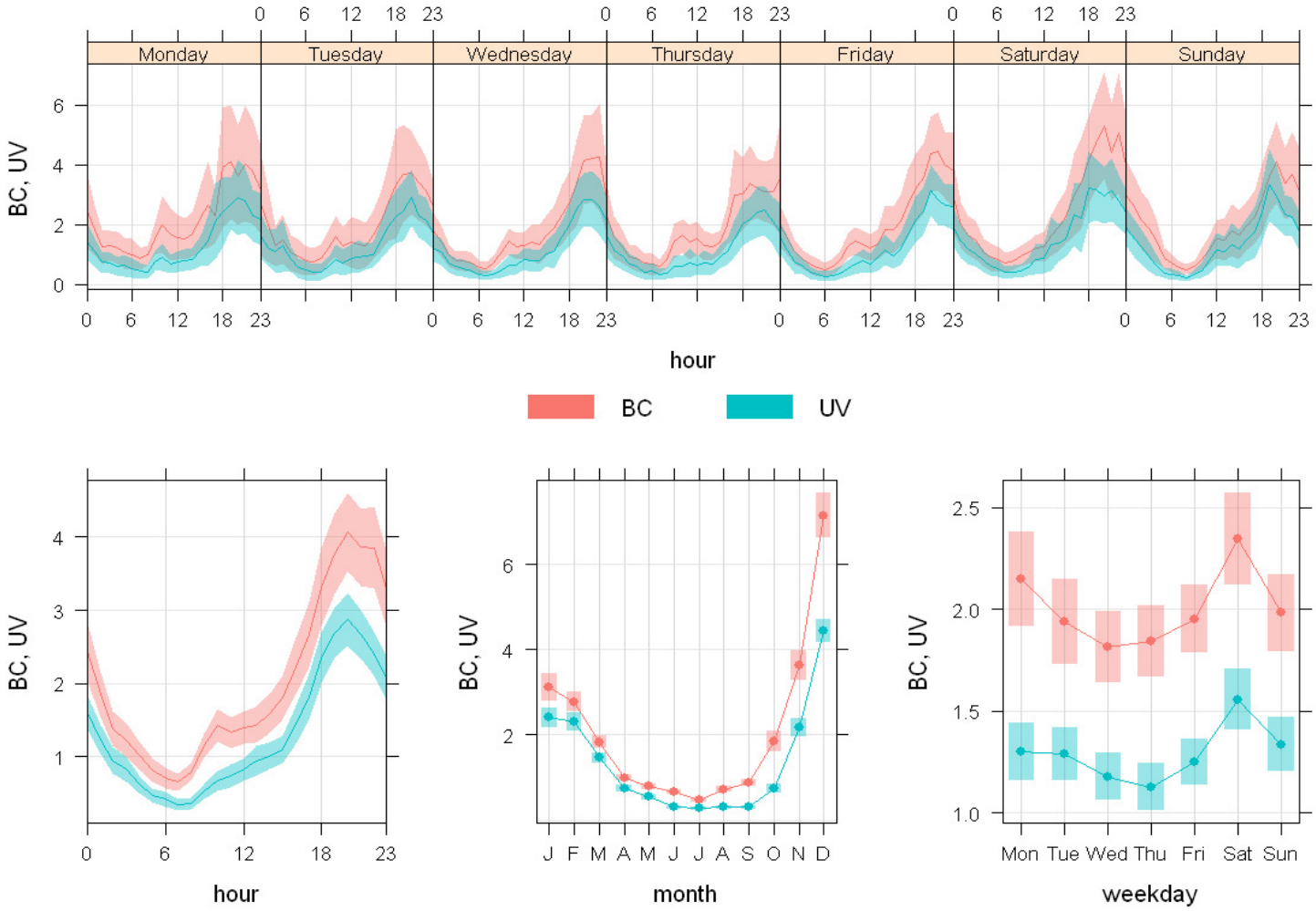


Figure 17 Urban Background Sites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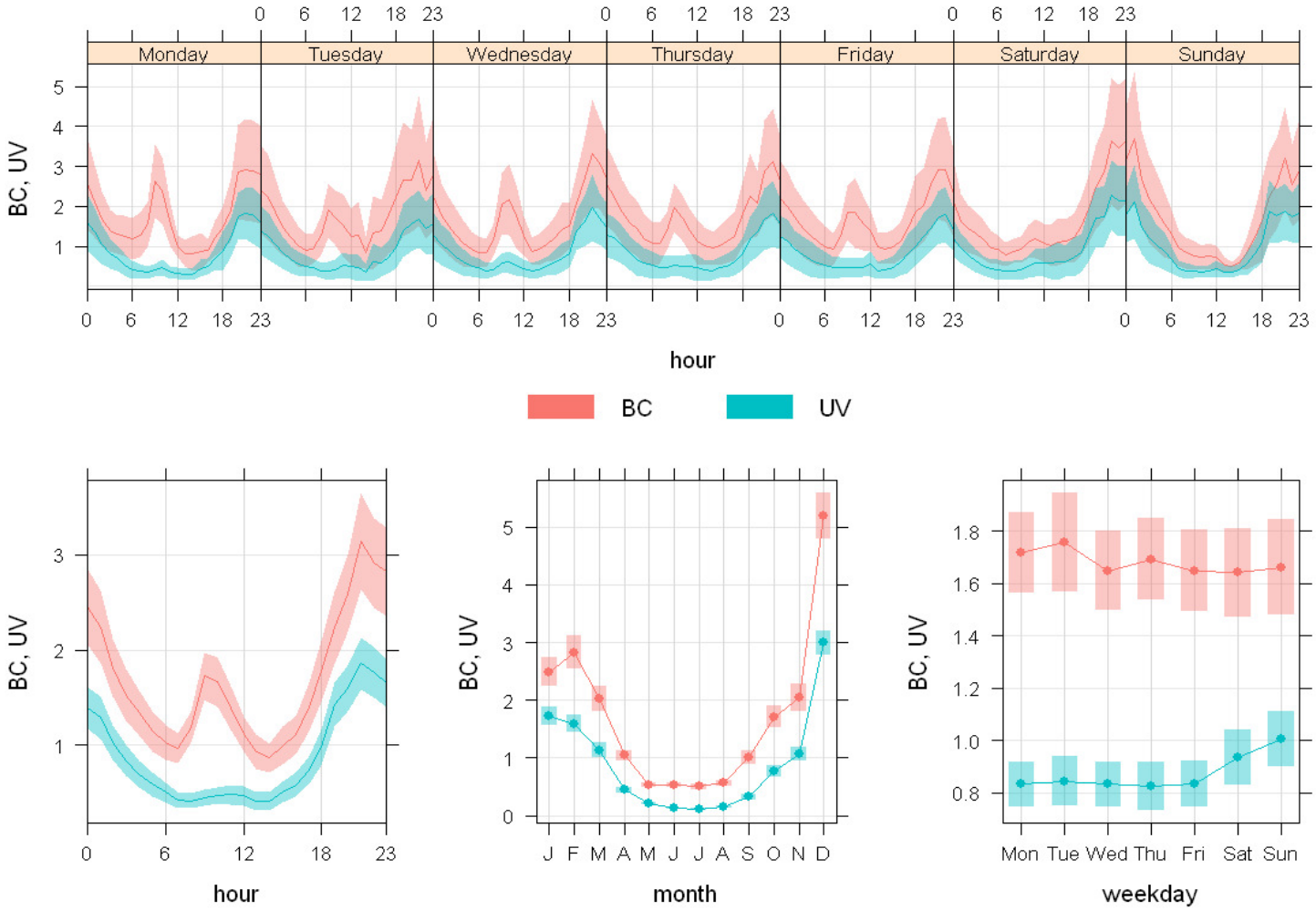
Strabane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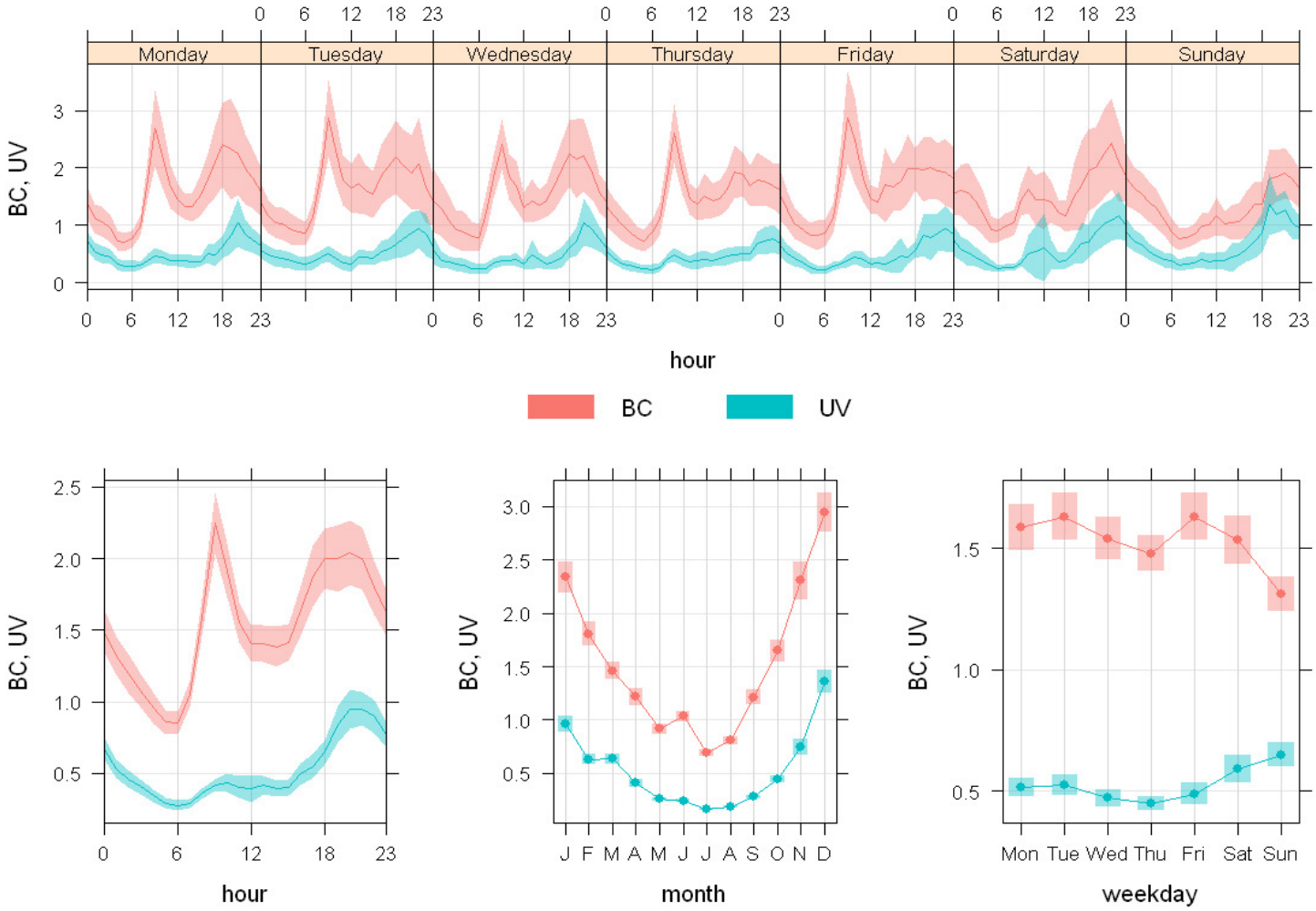
Dunmurry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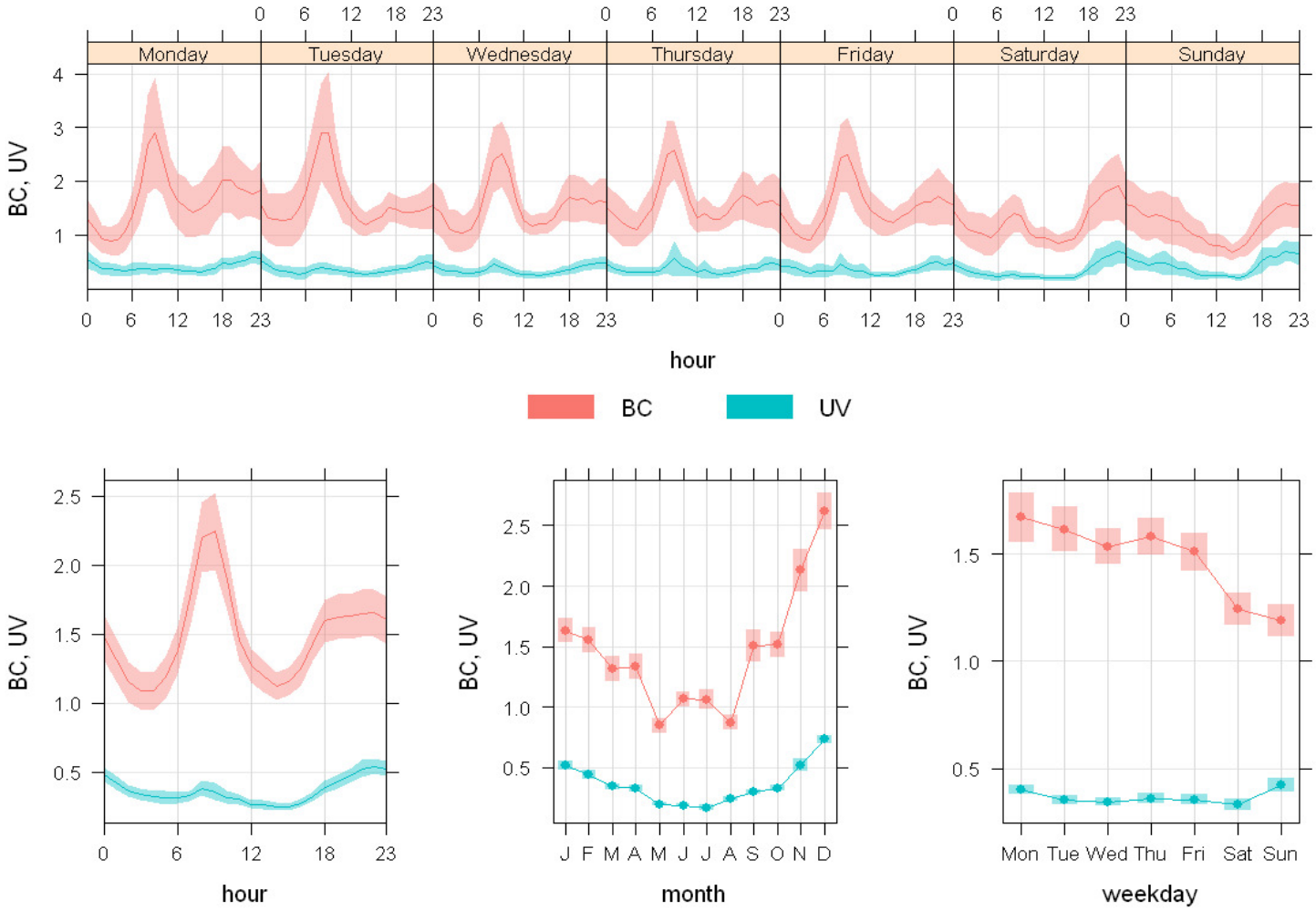
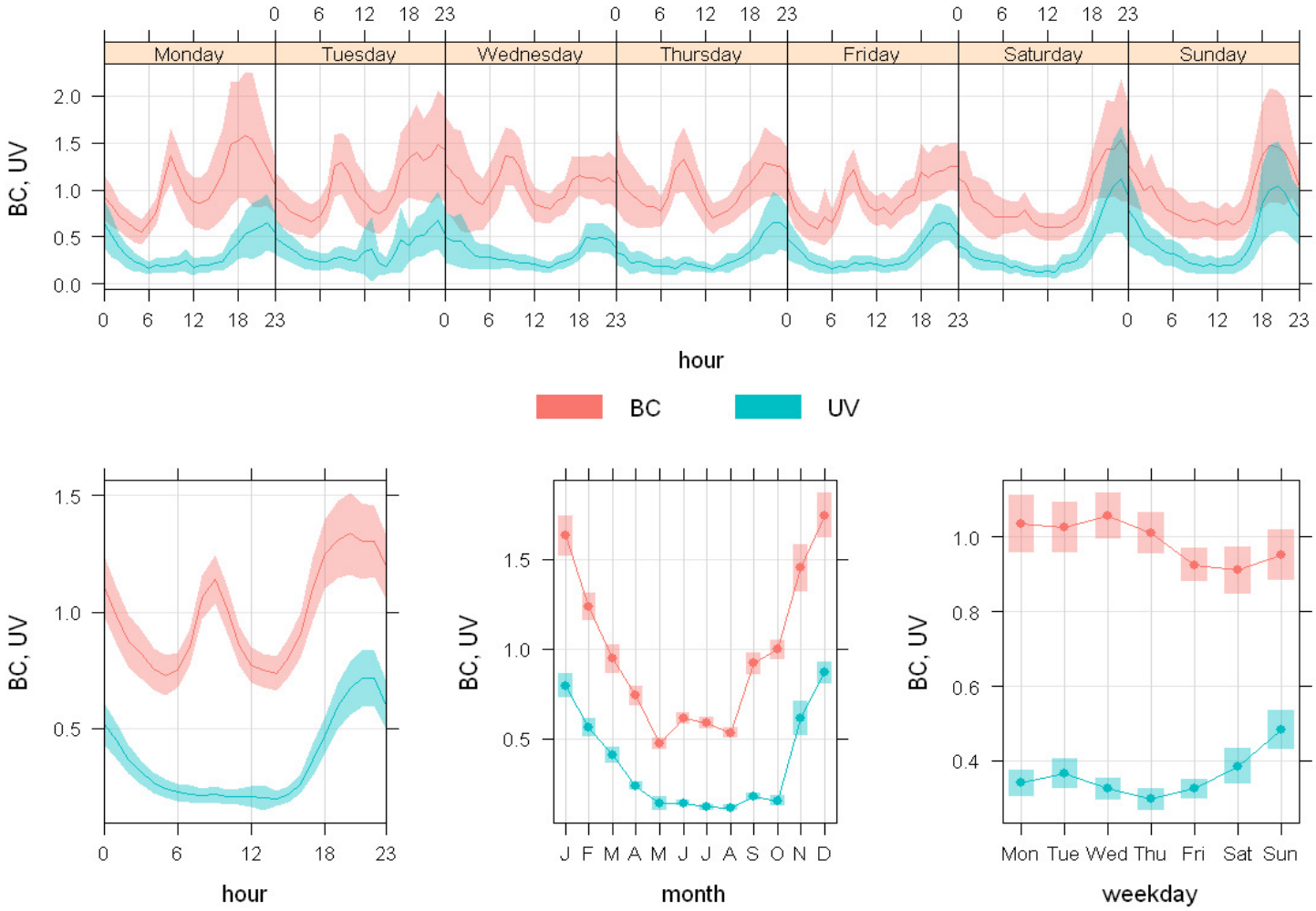
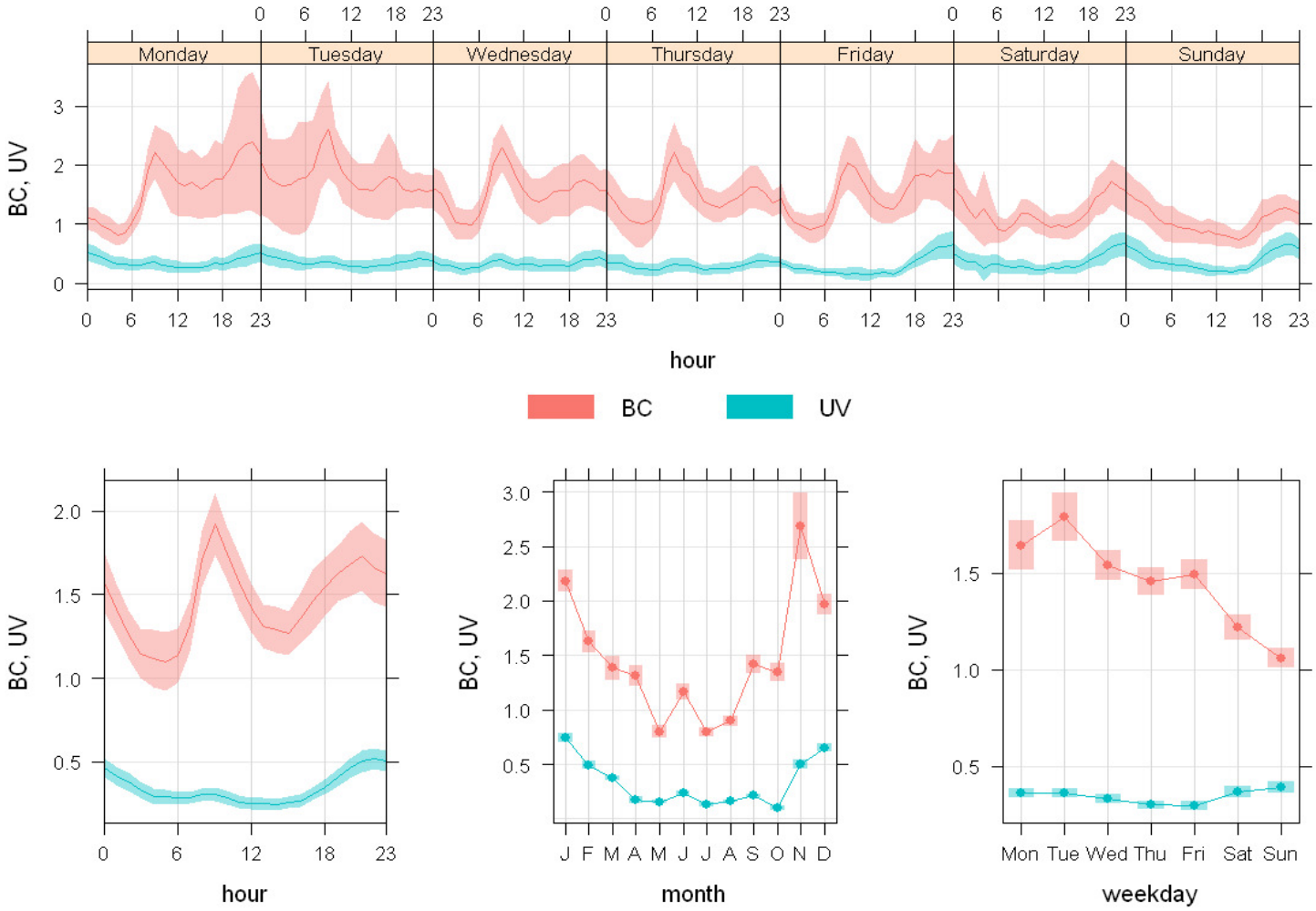
Cardiff



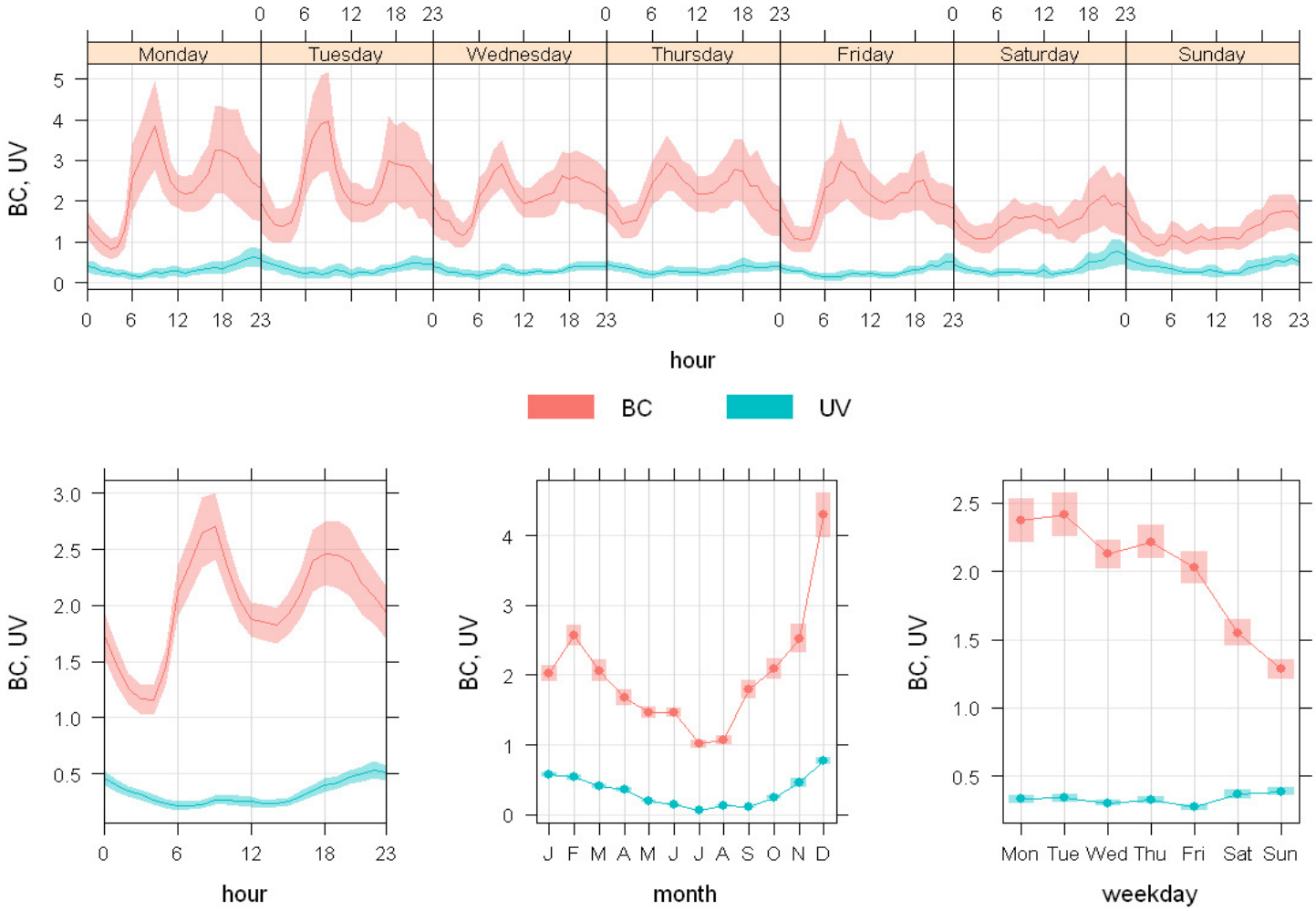
Birmingham Tyburn



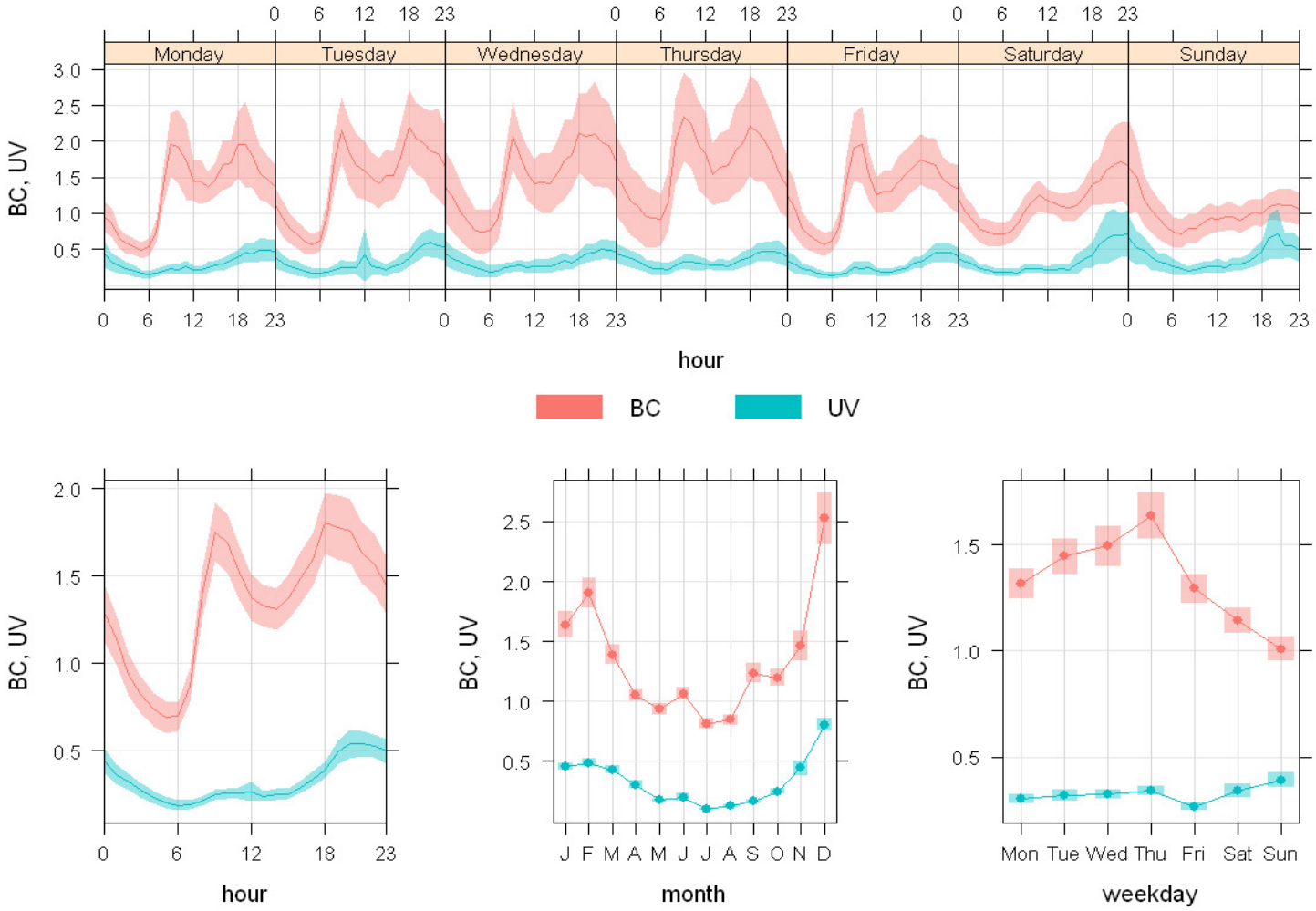
Norwich Lakenfields



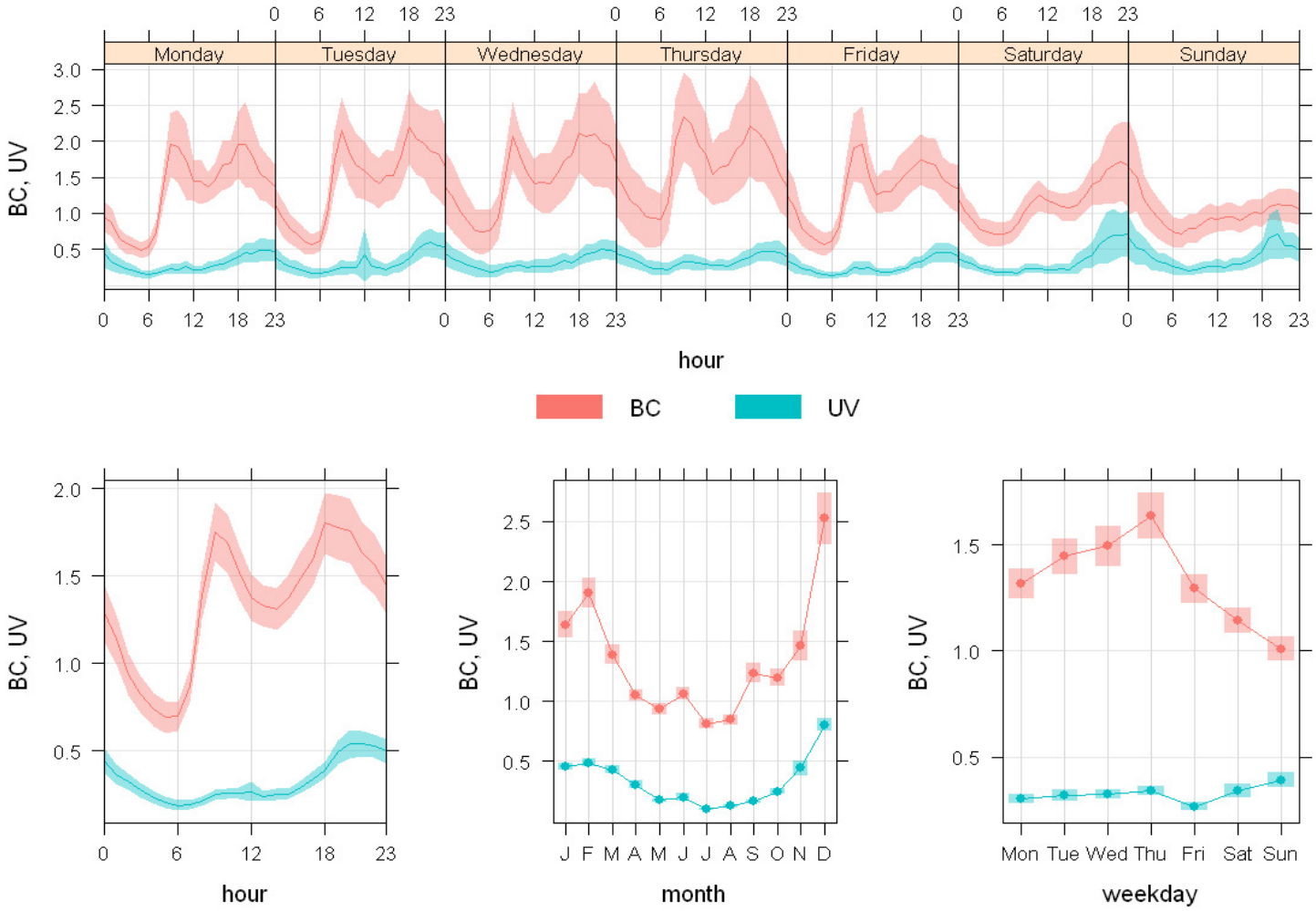
North Kensington



South Kirkby



Halifax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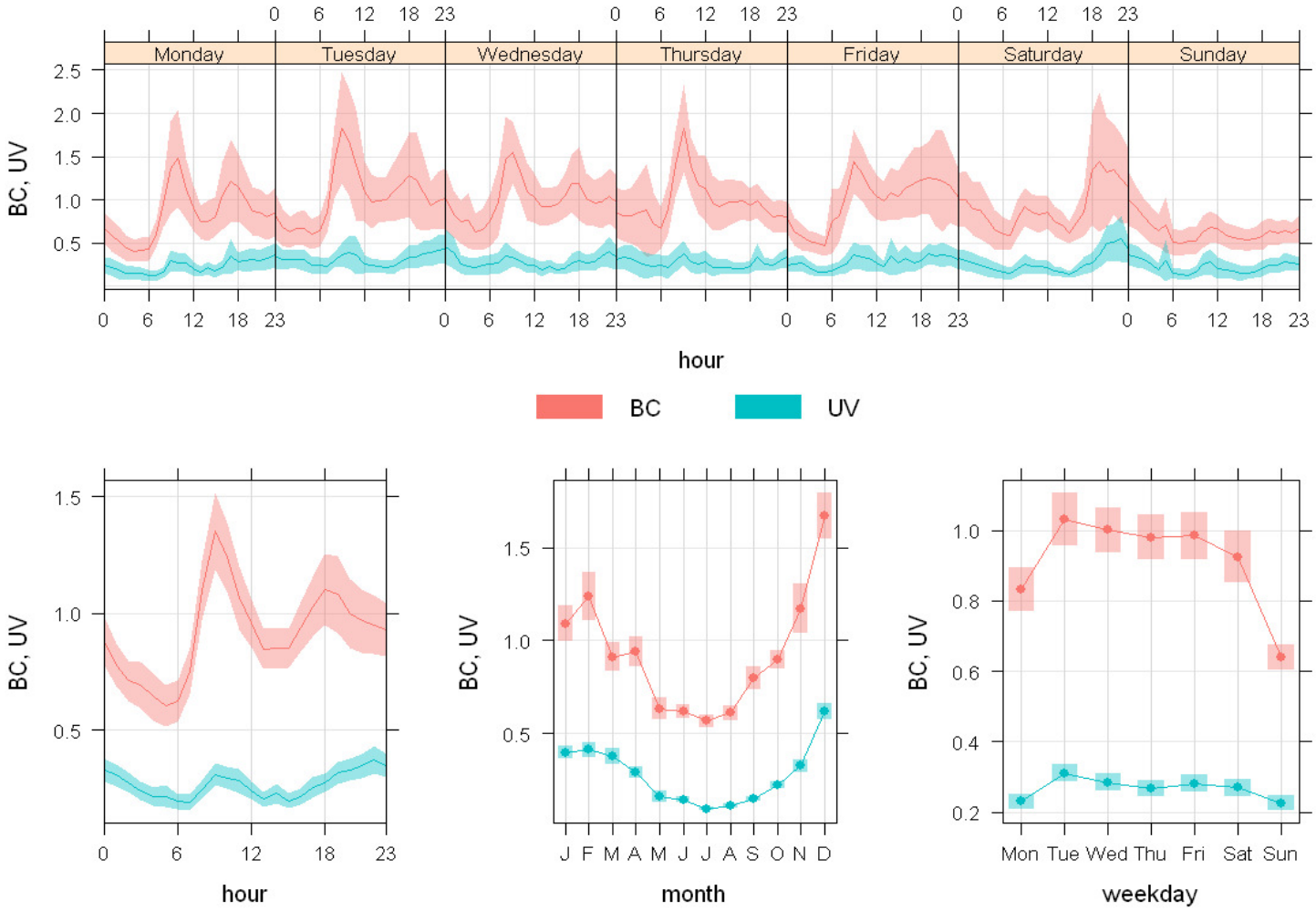
Woolwich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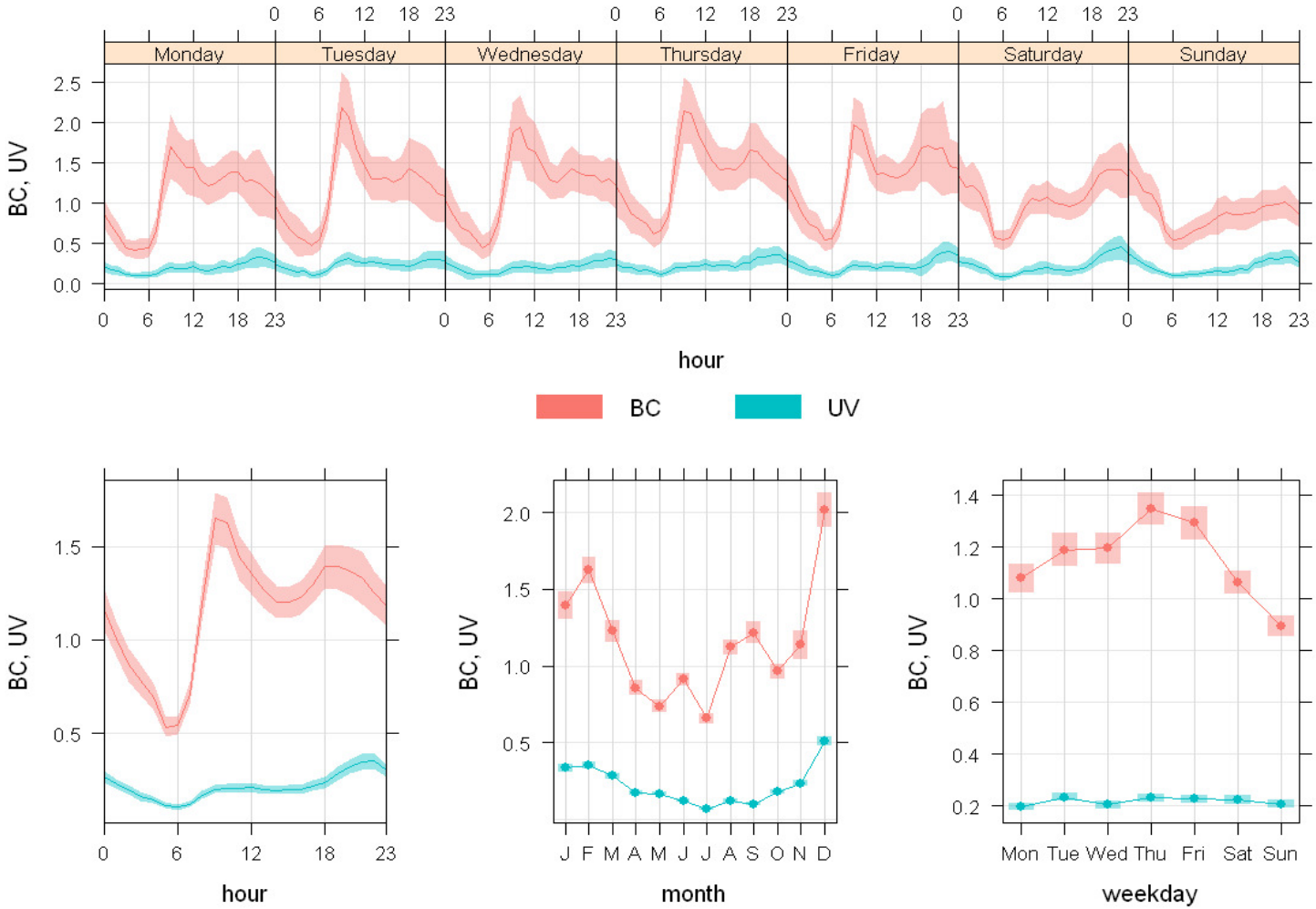
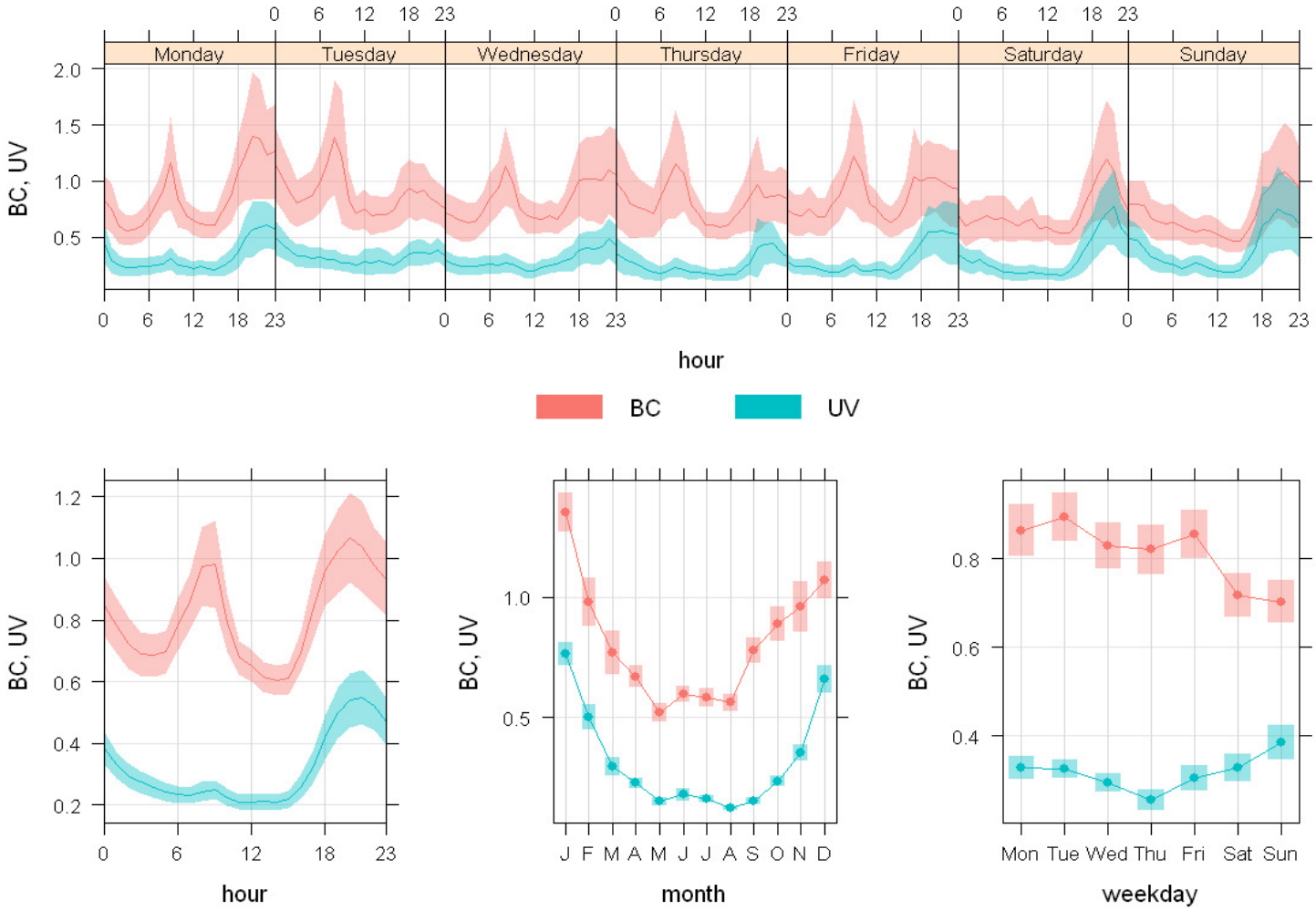
Sunderland



Edinburgh St Leonard's

Figure 18 Urban Centre Sites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Folkestone

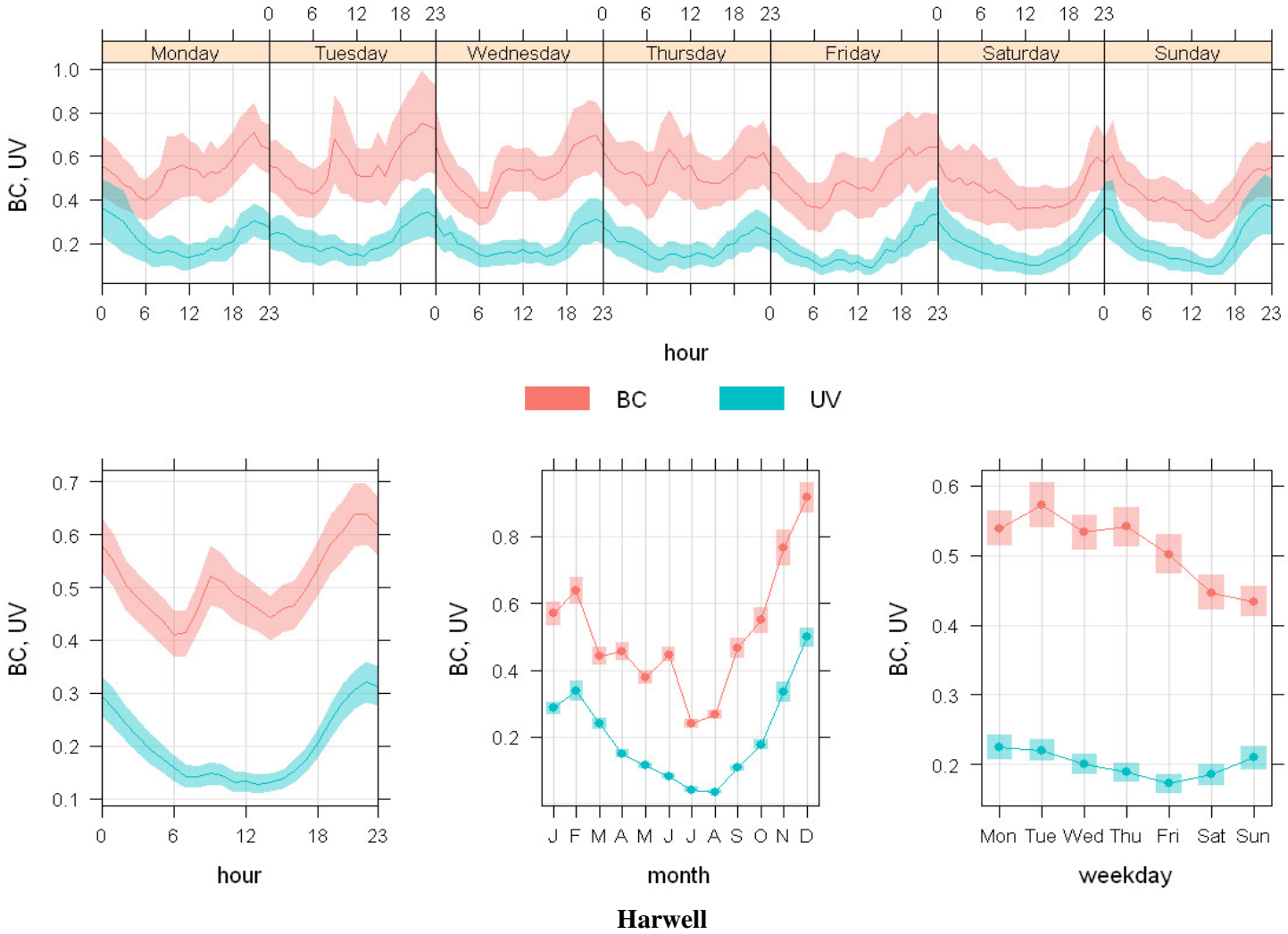

Figure 19 **Suburban and Rural Background Sites**

Roadside sites

It can be seen that the Black Carbon concentrations at the roadside sites follow the expected profile for traffic movements through the day, with raised concentrations in the morning and evening rush hours.

Marylebone Road shows a drop off in Black Carbon concentrations at the weekend which is in line with the reduced traffic and change in vehicle fleet over the weekend. There is a considerable drop in the number of heavy goods vehicles at the Marylebone Road site over the weekend. There is no apparent seasonal trend in either black Carbon or UV component.

Bath shows an increase in UV component concentrations in the evening consistent with it being in a residential area, with possible wood burning sources. The UV component concentration also shows a decrease in concentration over the summer months and an increase in concentration in the winter months.

Urban Centre sites

The city centre sites also show an increase in Black Carbon concentrations coinciding with the morning rush hour, but the concentrations remain raised for longer into the evening than the roadside sites. All of the sites except Stoke Centre show an increased Black Carbon concentration late on Saturday evening / early Sunday morning, which can be assumed to be due to evening entertainment journeys.

Black Carbon concentrations are generally lower at the weekends compared to the working days.

All urban centre sites show some UV component signature in the evenings, probably due to domestic urban heating and possible wood burning sources.

Both black Carbon and UV component concentrations show some seasonality dependence, with a decrease in concentration over the summer months and an increase in concentration in the winter months.

The 09:00 hrs increment in Black Carbon concentration at Belfast Centre may be due to lorries parking next to the site while they unload goods to the local shops; there are a significant number of lorry movements past the site at this time.

Urban Background sites

The urban background sites are affected by the morning rush hour to a lesser extent but do show some increase in Black Carbon concentration. These sites also show an increase in concentration in the evening, which is probably due to local domestic heating.

The reason for the increased variation in Black Carbon concentrations at North Kensington on Monday evenings and Tuesday mornings is unknown. It could be due to use of the community centre next to the site.

The Strabane, Dunmurry and Norwich concentrations are dominated by evening fuel use, probably due to the use of oil and solid fuel burning as a domestic fuel. At these sites the UV component concentration is significant, reaching up to 70% of the Black Carbon concentration.

Both Black Carbon and UV component concentrations show strong seasonality dependence, with a marked decrease in concentration over the summer months and a significant increase in concentration in the winter months. This is most apparent in the Strabane and Dunmurry sites due to the

meteorological conditions in the last two months of 2010. This is illustrated in Figure 20 showing the Strabane diurnal concentrations for Black Carbon and UV component split into seasons.

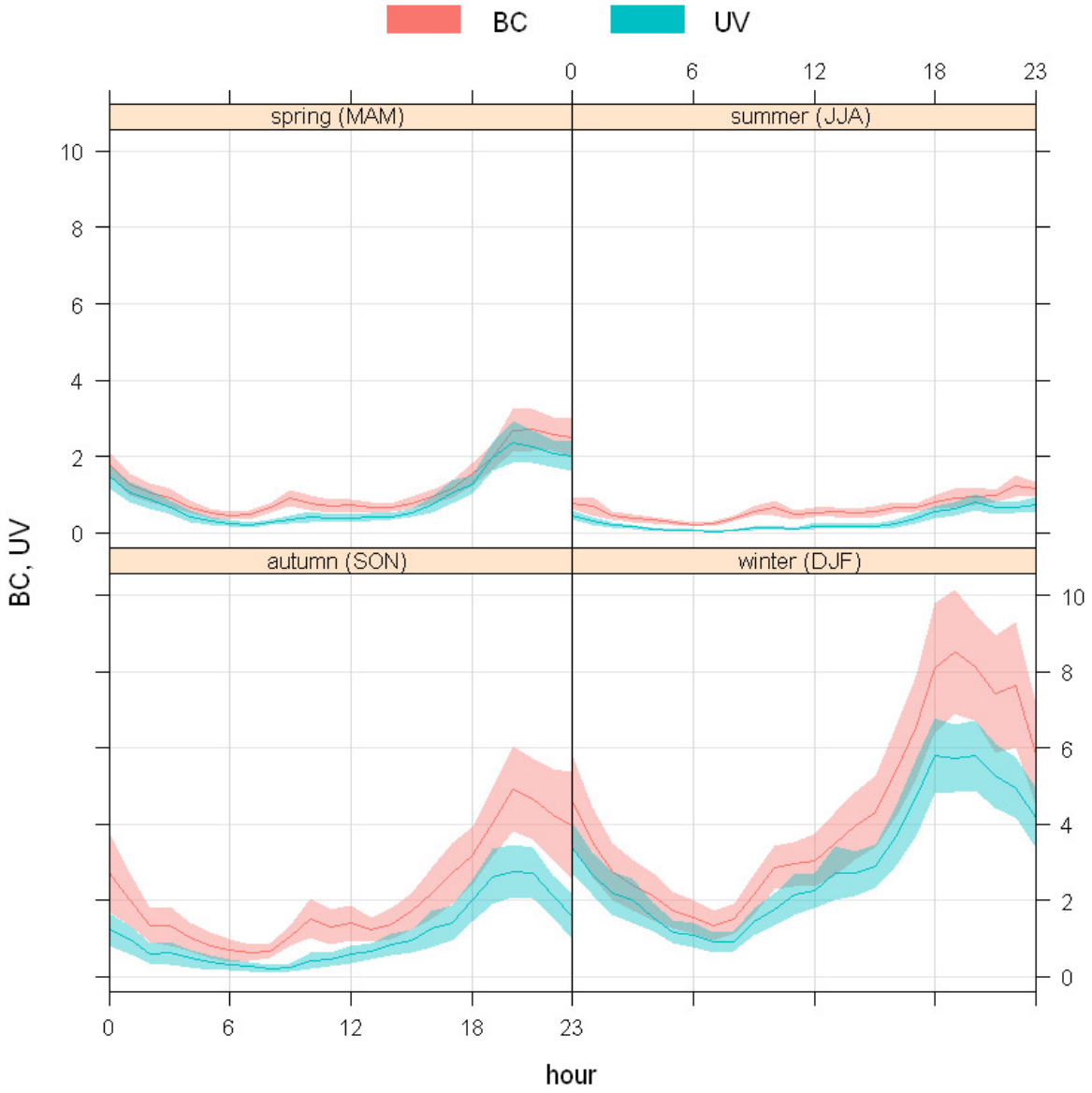

Figure 20 **Seasonal Black Carbon and UV component concentrations measured at Strabane in 2010**

In the above chart the shaded area on the y-axis represents the uncertainty in the mean y-value, expressed with a level of confidence of 95%.

Acknowledgement

Figures 20 is generated using the Open-Air Tools run on the R software platform[7,8].

Suburban and Rural Background sites

The suburban and rural background site concentrations are lower than the other site classifications as expected. This effect of local heating can also be seen in the concentrations at the Folkestone suburban site.

Diurnal discrepancies

The diurnals for the following sites have been influenced by short pollution episodes of unknown origin skewing the average hourly concentration:

Belfast	Saturday 09:00hrs	4th July high UV component
Norwich	Tuesday 13:00hrs	4th May high UV component
Halifax	Tuesday 12:00hrs	27th April and 27th June high UV component

PM measurements in other sites in Belfast also show an increase in PM concentration on the morning of 4th July, consistent with raised PM levels across the city.

Measurements of PM_{10}, $PM_{2.5}$ and NO_2 at Norwich also peak at 13:00hrs on 4th May, while ozone remains around 65 $\mu g.m^{-3}$ throughout the day, showing a possible influx of polluted air from the European continent.

Unfortunately there is not an AURN station in Halifax and all the Local Council Samplers are based at roadside locations, which are not representative of the Halifax Aethalometer monitoring site.

5.3.1 Weekly Periodicity

Tables 9a and 9b shows the difference between the Monday to Friday average concentration and the Sunday average concentration for Black Carbon and UV component. The sites have been sorted into site classification and are in descending order of annual average in each site classification.

Site	Monday - Friday	Sunday	Ratio
Roadside			
Marylebone Road	9.7	5.6	1.73
Bath 6	2.3	1.8	1.32
Urban Centre			
Glasgow Centre	2.9	2.3	1.24
Stoke Centre	2.1	1.6	1.36
Manchester Picc	2.1	1.8	1.20
Dudley Central	2.1	1.4	1.50
Belfast Centre	2.0	1.6	1.28
Nottingham Centre	1.9	1.4	1.36
Urban Background			
Strabane 2	1.9	2.0	0.99
South Kirkby 1	2.2	1.3	1.74
Dunmurry 3	1.7	1.7	1.02
Cardiff 12	1.6	1.3	1.20
Birmingham Tyburn	1.6	1.2	1.34
North Ken	1.6	1.1	1.51
Halifax 17	1.4	1.0	1.44
Edinburgh St Leonard's	1.2	0.9	1.39
Norwich Lakenfields	1.0	0.9	1.07
Woolwich 9	1.0	0.8	1.30
Sunderland 8	1.0	0.6	1.54
Suburban			
Folkestone	0.9	0.7	1.22
Rural			
Harwell	0.5	0.4	1.25

Table 9a Average Monday to Friday and Sunday Concentrations of Black Carbon

It can be seen that Black Carbon concentrations on Sundays are significantly lower than those on Mondays to Fridays, except for Strabane and Dunmurry.

Site	Monday - Friday	Sunday	Ratio
Roadside			
Bath 6	0.43	0.61	0.71
Marylebone Road	0.11	0.41	0.26
Urban Centre			
Belfast Centre	0.46	0.47	0.98
Stoke Centre	0.45	0.45	0.99
Nottingham Centre	0.38	0.40	0.95
Manchester Picc	0.36	0.39	0.93
Glasgow Centre	0.32	0.31	1.02
Dudley Central	0.31	0.32	0.98
Urban Background			
Strabane 2	1.23	1.33	0.92
Dunmurry 3	0.83	1.01	0.83
Cardiff 12	0.49	0.65	0.75
Birmingham Tyburn	0.36	0.42	0.87
Norwich Lakenfields	0.33	0.48	0.68
North Ken	0.33	0.39	0.84
South Kirkby 1	0.31	0.38	0.82
Halifax 17	0.31	0.39	0.81
Woolwich 9	0.31	035	0.88
Sunderland 8	0.28	0.22	1.24
Edinburgh St Leonard's	0.22	0.21	1.07
Suburban			
Folkestone	0.30	0.38	0.79
Rural			
Harwell	0.20	0.21	0.96

The results are averages of all measurements, including negative values

Table 9b Average Monday to Friday and Sunday Concentrations of the UV Component, all data included

It can be seen that the negative concentrations at Marylebone Road are dominant in the Monday to Friday period, suggesting that this effect is dominated by vehicle exhaust, probably from commercial vehicles rather than the private fleet. Concentrations at urban centre sites are generally constant over the week, while concentrations at urban background and suburban sites are significantly higher at the weekend than in the week.

5.4 COMPARISONS WITH OTHER POLLUTANTS

Comparisons are possible between Elemental Carbon and Black Carbon concentrations at three sites, and between PAH and UV component concentrations at one site.

Comparisons were also made with particle mass measurements where these instruments were collocated with the Aethalometer.

5.4.1 Elemental Carbon

Daily Elemental Carbon (EC) measurements are made at the North Kensington, Marylebone Road and Harwell sites by the Particle Number and Speciation Network[5]. Aethalometer concentrations (BC) at these sites have been averaged into daily measurements and plotted as scatter plots against the elemental carbon (EC) concentrations in Figures 21 to 23.

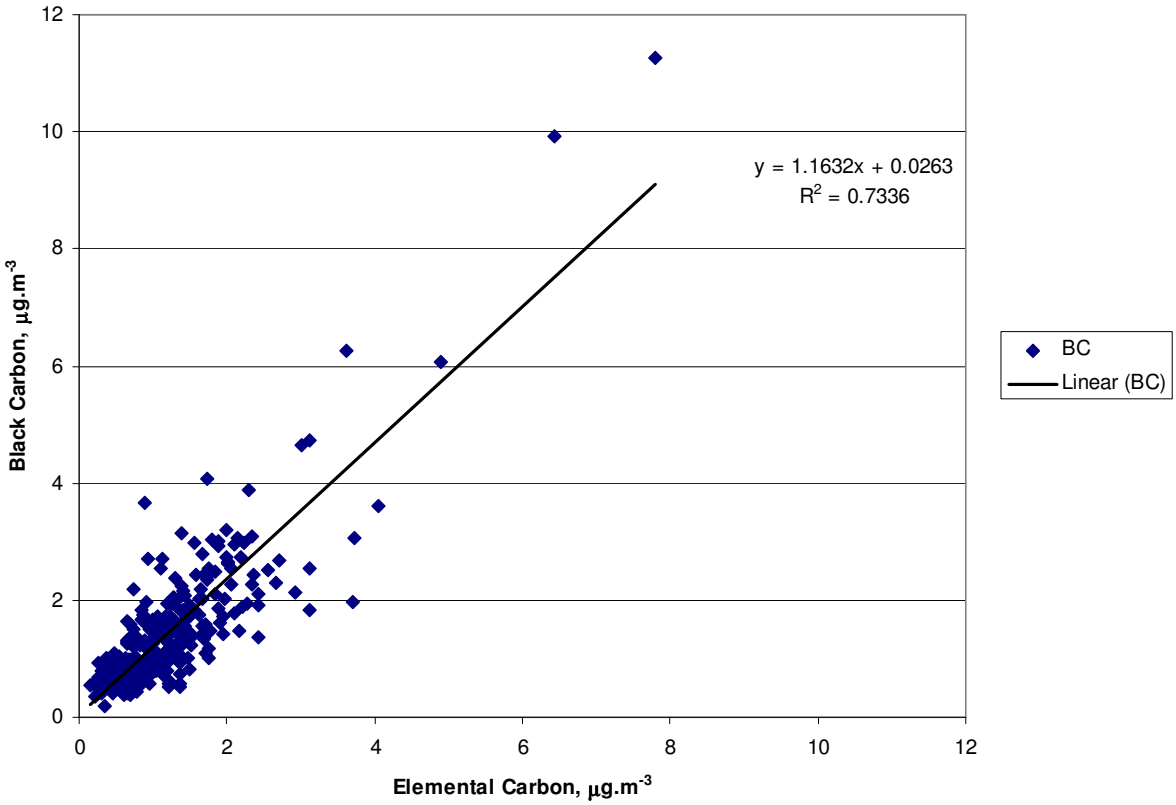

Figure 21 2010 EC and BC Measurements at North Kensington

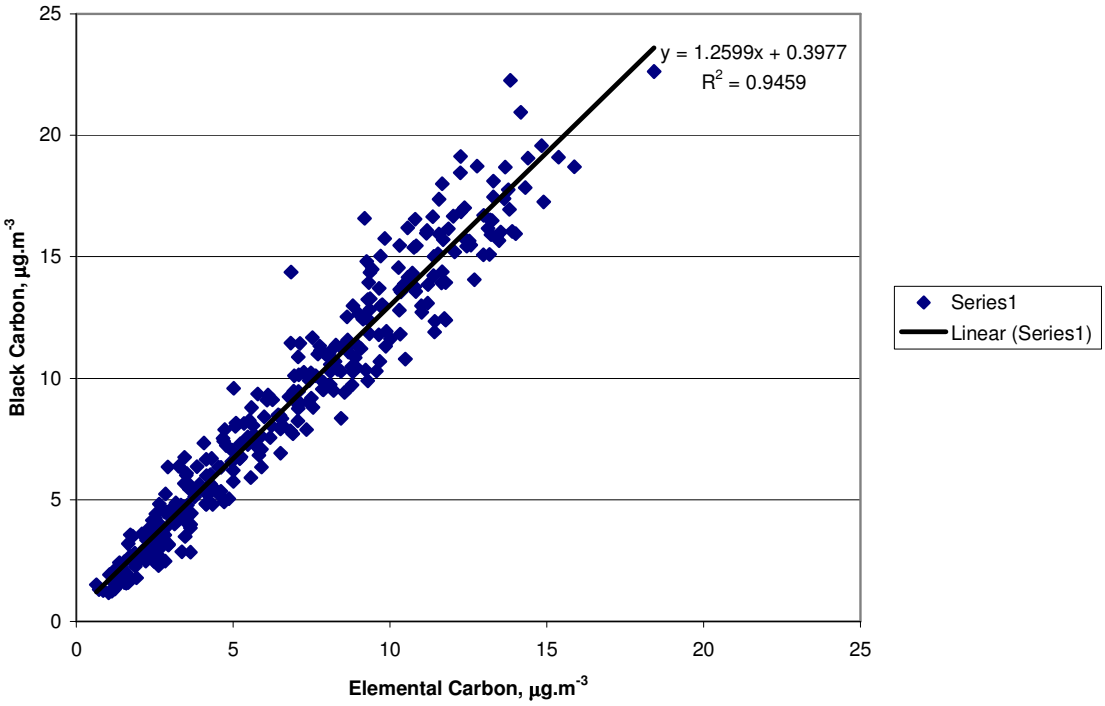

Figure 22 2010 EC and BC Measurements at Marylebone Road

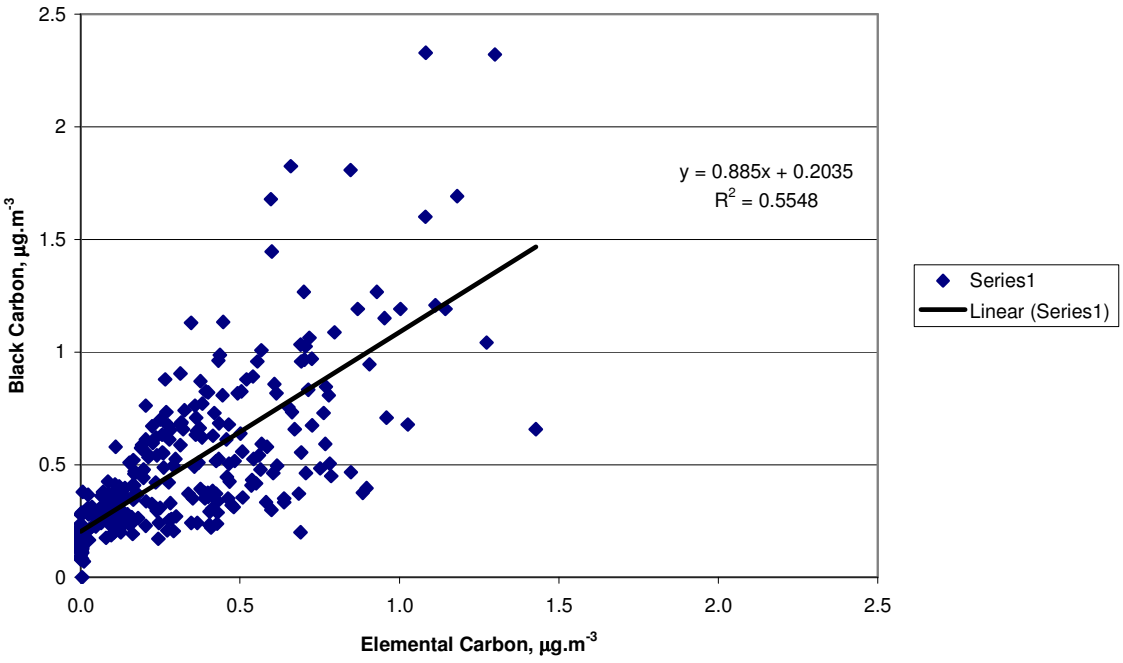

Figure 23 2010 EC and BC Measurements at Harwell

It can be seen that there is a good relationship between the EC and BC concentrations measured at North Kensington and Marylebone Road, while the relationship starts to breakdown at Harwell. The lack of agreement is likely to be due to measurement method issues at low concentrations, as described in a joint 2009 paper[6].

5.4.2 Poly Aromatic Hydrocarbons (PAH)

Monthly concentrations of Benzo[a]pyrene are measured at the Dunmurry site under the UK PAH Network. Aethalometer concentrations (UV component) have been averaged into monthly measurements and plotted as a time series with the Benzo[a]pyrene concentration in Figure 24

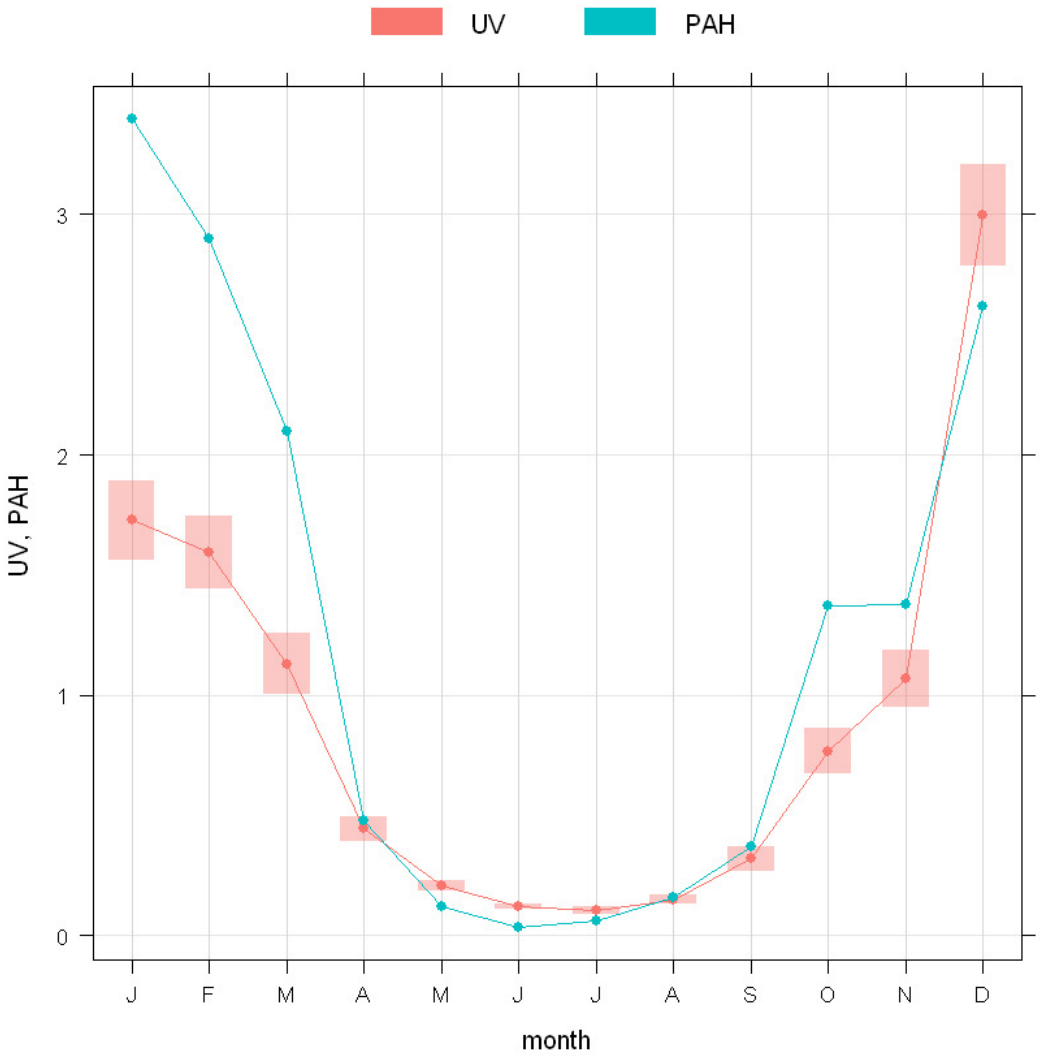

Figure 24 **Benzo[a]pyrene and UV component concentrations measured at Dunmurry in 2010**

The shaded area on the y-axis represents the uncertainty in the mean y-value due to the spread of the results over that averaging period, expressed with a level of confidence of 95%. It is not the overall measurement uncertainty. As the PAH measurements are a monthly average there is no spread in the result over the month and therefore no uncertainty displayed in the y-value. The shaded area on the x-axis is for display purposes only, to allow the uncertainty in the mean value to be seen more clearly.

The units are different for the two quantities, the PAH measurements are represented in $ng.m^{-3}$ while the UV Component is represented as $\mu g.m^{-3}$, however it can be seen that there is good temporal agreement between the two species due to similar emission sources such as solid fuel burning.

5.4.3 Particulate Mass

The annual average particulate mass concentration was compared with the Black Carbon concentration at collocated sites where automatic particulate mass instrumentation was installed. Three different types of instruments provide particulate mass concentrations across the Black Carbon Network: TEOM FDMS Model CB drier, TEOM Model AB and MetOne BAM – reference equivalent. As different automatic methods provide different results the concentrations reported by these automatic instruments have been separated into instrument type and the results shown in Table 10.

Site	BC $\mu g.m^{-3}$	TEOM FDMS PM10 $\mu g.m^{-3}$	TEOM FDMS PM2.5 $\mu g.m^{-3}$	MetOne BAM PM10 $\mu g.m^{-3}$	TEOM Model AB PM10 $\mu g.m^{-3}$	Percent BC PM10 %	Percent BC PM2.5 %
Marylebone Road	8.8	31.6	22.7			28	39
Stoke Centre	2.1	22.2	16.6			9	13
Belfast Centre	1.9	21.8	13.5			9	14
Edinburgh St Leonard's	1.2	14.2	9.5			8	12
Nottingham Centre	1.8	23.1	15.8			8	11
North Kensington	1.5	21.4	14.0			7	10
Birmingham Tyburn	1.5	25.5	18.4			6	8
Norwich Lakenfields	1.0	17.9	12.7			6	8
Harwell	0.5	16.0	10.3			3	5
Glasgow Centre	2.7		12.5				22
Dudley Central	1.9				13.8	14	
Strabane	2.0			22.8		9	
Dunmurry	1.7	20.3	19.5			8	9
Folkestone	0.8				14.3	6	

Grey shaded cells indicate no measurements were made or data capture is less than 50 %.

$PM_{2.5}$ measurements at Marylebone Road and PM_{10} measurements at North Kensington have a data capture less than 75%, but greater than 50%

Table 10 Comparison of Black Carbon and Particulate Mass Concentrations

The particulate mass measurements made by the bottom four sites are made by Local Authorities and may not have the same QA/QC procedures applied to the data as that applied to the AURN sites shown in Table 10.

It can be seen that the PM_{10} and $PM_{2.5}$ mass concentration measured at Marylebone Road have a much higher percentage of Black Carbon than the other sites. The $PM_{2.5}$ result at Glasgow may be skewed due to the high Black Carbon measurements made during the pollution episode at Glasgow Centre in October 2010, as discussed in Section 5.1.1.

The Dudley Central site also shows an elevated percentage of Black Carbon in the PM_{10} mass, probably due to the sites location in a car park and its sampling of car exhausts.

It can be seen that Black Carbon represents a significant proportion of the total particulate mass at sites influenced by road traffic emissions. Any reduction in Black Carbon emissions from road traffic will lead to a reduction in PM_{10} and $PM_{2.5}$ mass concentrations.

If the same comparison is made between particulate mass and the UV Component then only the sites at Strabane and Dunmurry show a percentage contribution of particulate mass of greater than 3%.

Site	BC µg.m^{-3}	TEOM FDMS PM10 µg.m^{-3}	TEOM FDMS PM2.5 µg.m^{-3}	MetOne BAM PM10 µg.m^{-3}	Percent BC PM10 %	Percent BC PM2.5 %
Strabane	1.29			22.8	6	
Dunmurry	0.87	20.3	19.5		4	4

Table 11 Comparison of UV Component and Particulate Mass Concentrations

5.5 TRENDS

Short and long term trends in Black Carbon and UV components are given below.

5.5.1 Short-Term

Figures 25 and 26 below show the trend in Black Carbon and UV component concentrations as measured by the Aethalometer over the full calendar years 2009 and 2010.

5.5.1.1 BLACK CARBON

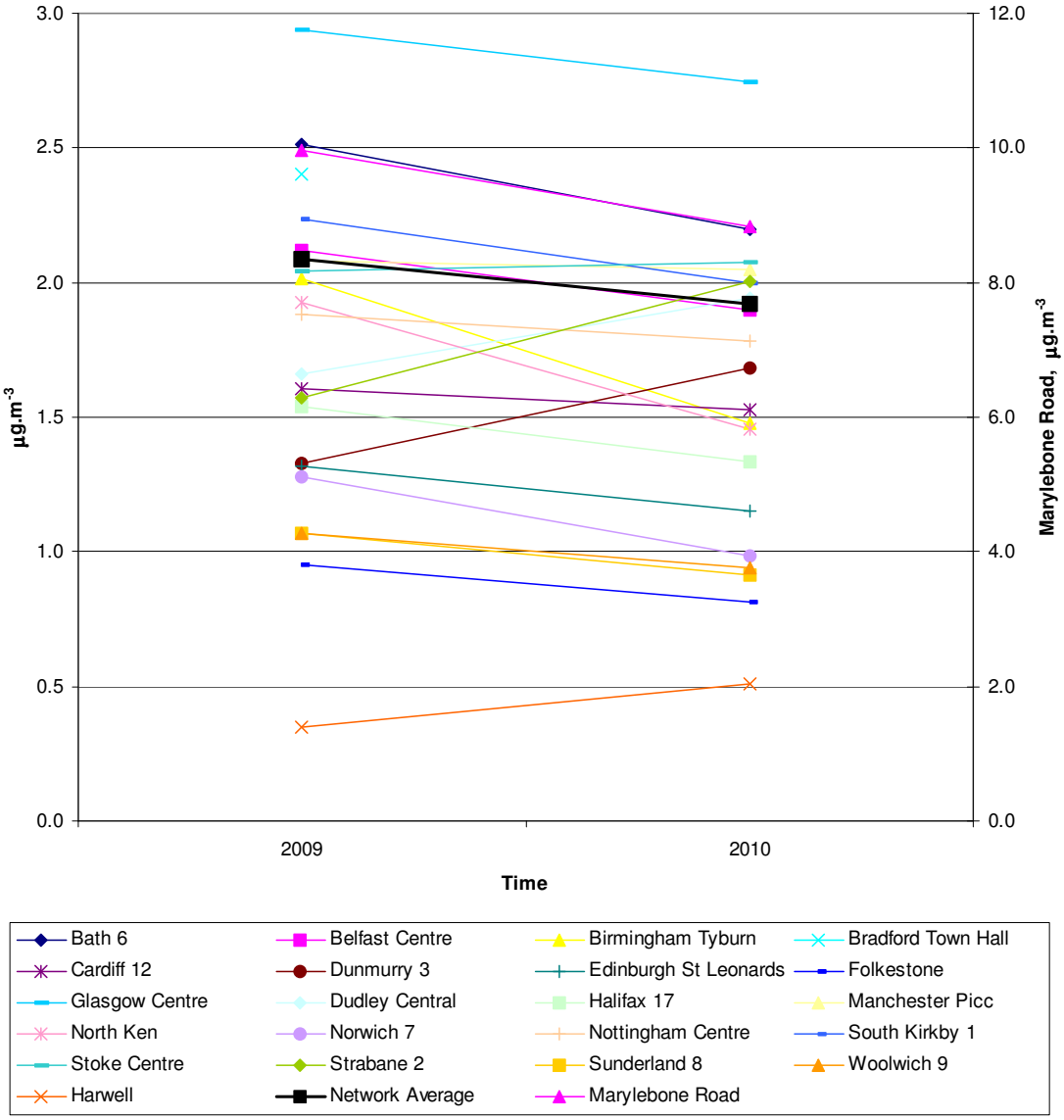

Figure 25 Black Carbon concentrations over the period of Network operation

The Nov – Dec 2008 results have not been included as this is biased due to only including data for the last two months of the year; when concentrations are normally higher than the annual concentration, see Figures 16 to 19. Concentrations in 2010 are generally lower than in 2009 with the exception of the Strabane, Dunmurry Harwell and Dudley Central sites. The Network mean concentrations ($\mu g.m^{-3}$) are: 2.1 and 1.9 for 2009 and 2010 respectively.

5.5.1.2 UV COMPONENT

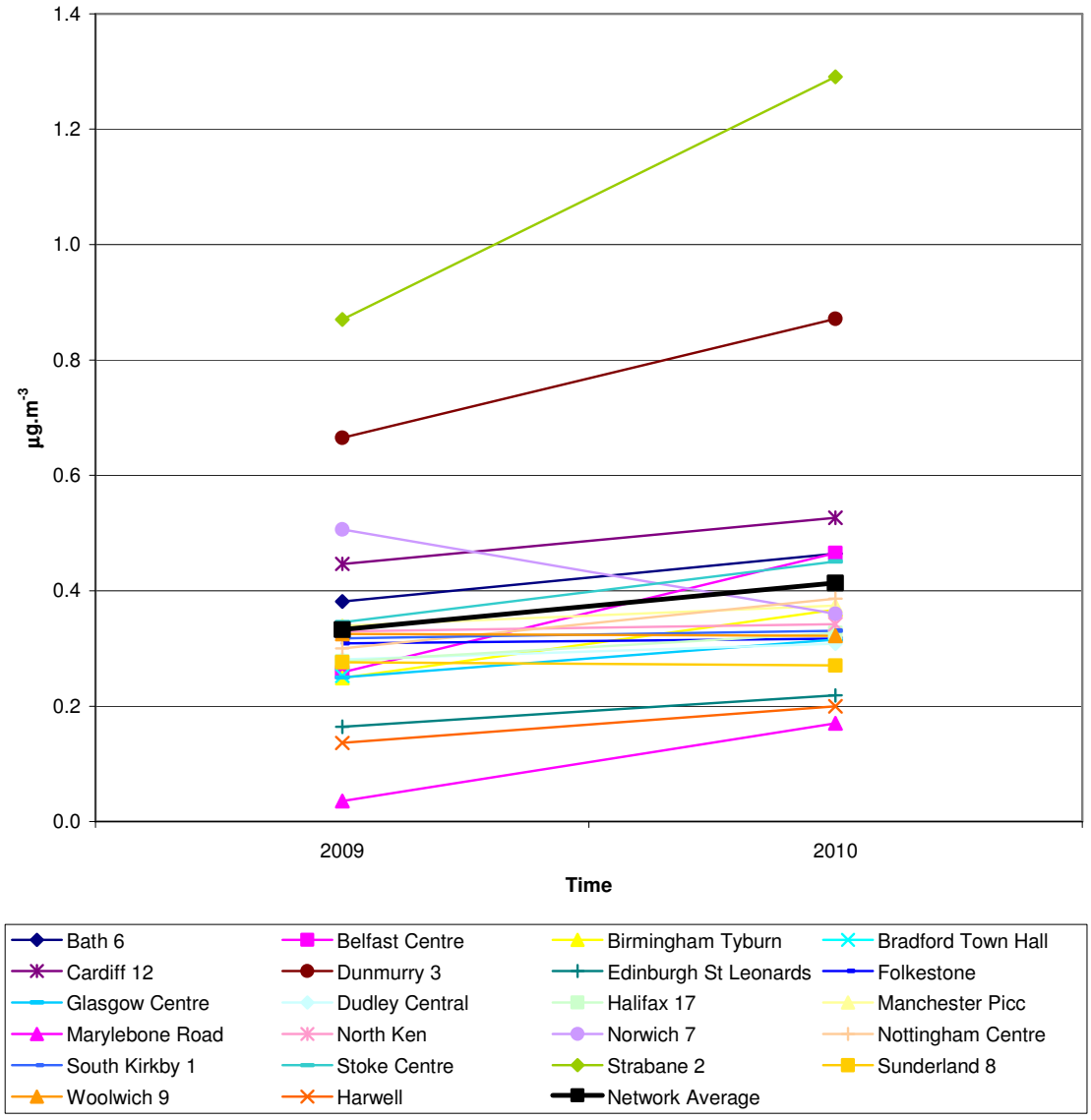

Figure 26 UV Component concentrations over the period of Network operation

The Nov – Dec 2008 result has not been included as this is biased due to only including data for the last two months of the year; when concentrations are normally higher than the annual concentration, see Figures 16 to 19. Concentrations in 2010 are generally higher than in 2009 with the exception of the Norwich site, which was only installed in October 2009 and therefore has the same winter high bias. The Network mean concentrations (µg.m^{-3}) for the period of operation are: 0.3 and 0.4 for 2009 and 2010 respectively.

5.5.2 Long-Term Trends

A publication is pending by Quincey et al[9] giving the results of the parallel running intercomparison performed in 2009 between the Aethalometer and the Black Smoke Method and tests the proposed

relationship between Black Smoke Index and Black Carbon measurements. This relationship, described by Equation 1 below, was used to convert Black Smoke Index measured between 2000 and 2008 into Black Carbon concentrations. The trends in these Black Carbon concentrations are given in Figure 27.

$$C_{BC} = \sqrt{4.18 I_{BS} + 59.6} - 7.72 \qquad \text{Eq 1}$$

where:

C_{BC} =Black Carbon concentration in µg.m^{-3}
I_{BS} =Black Smoke Index

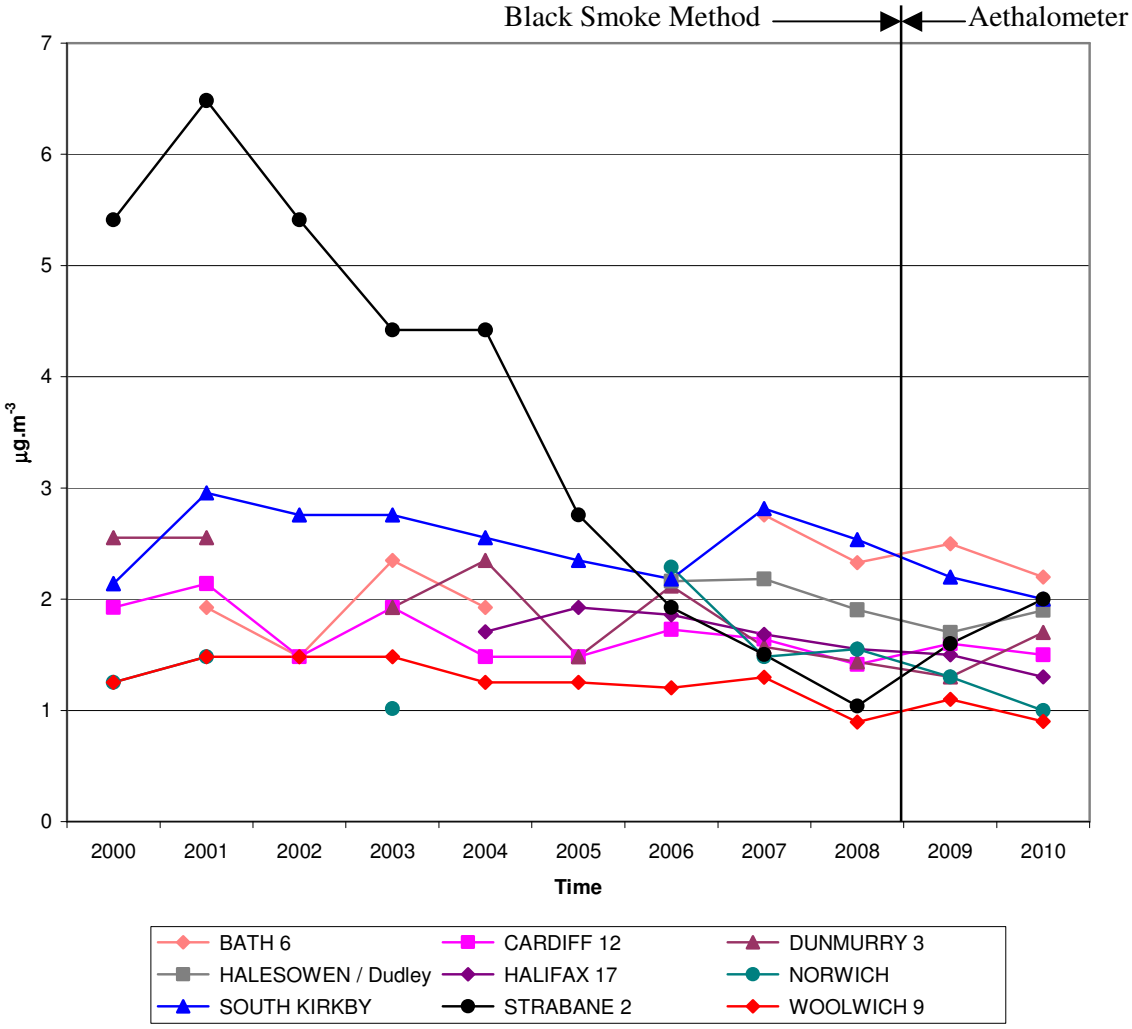

Figure 27 Trend in Black Carbon Concentrations 2000 to 2010

The drop in the Strabane 2 Black Smoke concentration since 2004 is attributable to the installation of oil fired central heating (generally replacing coal burning) in the estate of houses that surround the monitoring site on three sides. Central heating replacement started in 2003.

Apart from Strabane 2 there are no obvious trends in this recent data.

There is no evidence of discontinuity in the data as a result of the change in measurement method from Black Smoke Index to Black Carbon concentration by Aethalometry at the end of 2008.

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