NPL

NPL Report AS 97

2014 Annual Report for the UK Black Carbon Network

D Butterfield
S Beccaceci
P Quincey
B Sweeney
A Lilley
C Bradshaw
G Fuller
D Green
A Font Font

JULY 2015

2014 Annual Report for the UK Black Carbon Network

D Butterfield, S Beccaceci, P Quincey, B Sweeney, A Lilley and C Bradshaw
Analytical Science Division, NPL

G Fuller, D Green and A Font Font
Environmental Research Group, King's College London

ISSN: 1754-2928

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

Approved on behalf of NPLML by Martyn Sene, Operations Director

EXECUTIVE SUMMARY

This report covers the operation of the UK Black Carbon Network and the data collected by the Network in 2014. The Aethalometer instrument used on the Network makes measurements of Black Carbon (BC) and UV component.

The National Physical Laboratory (NPL) in partnership with the Environmental Research Group at King's College London 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 2009, when the Bradford site was closed after Defra reviewed its monitoring requirements. In early 2012 the Network underwent major restructuring to focus the network on targeted monitoring of specific emission sources. In late 2012 Aethalometers were installed at Goonhilly and Ballymena to investigate emissions from shipping and domestic fuel use, respectively. The Norwich Lakenfields site closed in May 2013, the Goonhilly site closed in November 2013 and the Cardiff 12 site closed in June 2014. 12 sites made full calendar year measurements in 2014.

The 2014 data capture for Aethalometer measurements was 96%. This is a remarkably high figure for an automatic monitoring network and shows the reliability of the Aethalometers and the effectiveness of daily on-line surveillance of the equipment.

2014 urban annual mean Black Carbon concentrations on the Network (with the corresponding 2013 concentrations in brackets) ranged from 1.0 (1.0) $\mu g.m^{-3}$ at Dunmurry Kilmakee to 6.6 (6.9) $\mu g.m^{-3}$ at Marylebone Road. Harwell (rural background) reported an average concentration of 0.5 (0.5) $\mu g.m^{-3}$, with similar values at the newly installed rural sites at Auchencorth Moss and Detling. The network mean for Black Carbon concentration was 1.6 (1.6) $\mu g.m^{-3}$.

The annual mean UV component concentrations ranged from 0.1 (0.1) $\mu g.m^{-3}$ at Auchencorth Moss to 1.1 (1.2) $\mu g.m^{-3}$ at Strabane. Roadside sites show many negative spikes in the UV component concentration, thought to be measurement artefacts caused by volatile components in fresh vehicle exhaust plumes. This effect is most prevalent at Marylebone Road. The network mean for UV component concentration was 0.2 (0.3) $\mu g.m^{-3}$. The figures in brackets are again the corresponding concentrations for 2013.

The new network design implemented in early 2012 allows urban increments in Black Carbon and UV component concentrations to be determined for London, Birmingham and Glasgow, and roadside increments for London and Birmingham. The urban increment for Black Carbon was similar for all locations while the roadside increment was roughly proportional to road traffic volumes, especially buses and taxis. There was no significant urban or roadside increment in UV component concentration.

Daily averages of the measurements show that the highest concentrations of Black Carbon are found on weekdays, 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, Ballymena and Dunmurry, in Northern Ireland, which show elevated levels from 15:00hrs to 23:00hrs, which is indicative of local residential 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 coal, wood and oil and solid fuel (coal and wood) for domestic heating. From the daily averages it can be seen that the UV component concentration is fairly consistent on weekdays with greater concentrations at the weekend. It can also be seen that UV component concentrations are inversely proportional ambient temperature providing extra evidence of domestic heating being a major emission source.

Comparisons between Black Carbon concentrations and Elemental Carbon concentrations showed good linear relationships between the measurements at North Kensington and Harwell, with R^2 values of 0.87 and 0.80. The scatter at Marylebone Road was smaller than in previous years (R^2 = 0.82). For North Kensington and Harwell the slopes were 1.68 and 2.02, with intercepts of 0.00 and -0.01 $\mu g.m^{-3}$. The slope and intercept for Marylebone Road were 1.32 and 0.25 $\mu g.m^{-3}$.

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 comprises 25% of the PM_{10} concentration and 37% of the $PM_{2.5}$ concentration, while at Birmingham Tyburn roadside Black Carbon forms 15% and 21% of PM_{10} and $PM_{2.5}$ respectively.

Monthly means of Black Carbon concentrations were examined over the period 2009 to 2014 to evaluate trends. The only site with a significant trend in Black Carbon concentrations was Marylebone Road. Here, Black Carbon concentrations have dropped over the last 3 years. Over the same period there were no sites with a significant slope in UV component concentration.

Using a published method for converting Black Smoke Index into Black Carbon concentration it can be shown that there is no significant discontinuity in results from the two methods and, apart from Strabane, there is no obvious long-term trend in the Black Carbon concentrations over the past 14 years.

CEN are currently formulating a standard for the measurement of elemental carbon and organic carbon deposited on filters. As part of this work there are field validation trials where automatic instruments, including an Aethalometer, are being evaluated in parallel with filter samplers.

CONTENTS

1.0 INTRODUCTION

1.1 GENERAL

The National Physical Laboratory (NPL) in partnership with the Environmental Research Group at King's College London 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 2009 when the Bradford site was closed after Defra reviewed its monitoring requirements.

In January 2012 a new contract was issued by Defra to run the Network, and this involved a major reorganisation of the monitoring sites. The focus of the Network changed to provide targeted monitoring of the major urban conurbations of London, Birmingham and Glasgow, plus additional sites to monitor specific emission sources. This involved the closing of 11 existing sites and the opening of 4 new sites, leaving a Network of 13 sites, plus Harwell which is run as part of Defra's Particle Numbers and Speciation Network. By targeting these urban areas a more detailed apportionment of emissions of Black Carbon emission sources should be provided.

Later in 2012 Defra took up two options to increase monitoring of specific emission sources which resulting in a site being installed at Goonhilly in Cornwall to assess Black Carbon from shipping, and at Ballymena in Northern Ireland to extend the work on monitoring emissions from solid fuel and biomass burning. The Goonhilly monitoring continued until November 2013. Aethalometer measurements stopped at the Norwich Lakenfields site in May 2013 as the site was no longer provided additional information on Black Carbon emissions above that already collected from the other sites on the Network.

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 has 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.

The terminology to be used for 'Black Carbon' data is currently receiving attention within, for example, the Global Atmosphere Watch special aerosol advisory group. This is mainly concerned with highlighting the assumptions used to convert optical data to mass concentration data. The procedures used for the Black Carbon Network are described within this report.

1 P Quincey, A relationship between Black Smoke Index and Black Carbon concentration, Atmospheric Environment 41 (2007) 7964–7968

1.3 MEASUREMENT METHOD

1.3.1 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, σ [m^{-1}], is calculated from the attenuation change, the filter area, and volume of the sample. This is 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 wood 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 metric termed '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 means that the Aethalometer has reduced sensitivity to black carbon at high filter tape loadings. To correct for this nonlinearity, the model developed by A Virkkula[2] has been used to correct for increased attenuation due to spot darkening during sampling. This uses the 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.

1.3.2 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 A Virkkula et al, A Simple Procedure for Correcting Loading Effects of Aethalometer Data, Journal of Air and Waste Management Association, 57:1214-1222, 2007

2.0 NETWORK INFRASTRUCTURE

The following sections present the design of the Network, describe its operation and the changes to the Network in 2014.

2.1 NETWORK SITES AND DESIGN

Figure 1 shows the locations of the Aethalometers during 2014. The sites are located to target the measurement of traffic emissions of Black Carbon in urban areas, solid fuel and biomass emissions in Northern Ireland & Cardiff.

Urban and traffic increments were targeted by having a rural background, an urban background and a roadside / kerbside siting combination across each conurbation. These site combinations are shown in Table 1.

Conurbation	Site Name	Site Classification
Glasgow	Auchencorth Moss	Rural Background
	Glasgow Townhead	Urban Background
	Glasgow High Street	Traffic
Birmingham	Harwell	Rural Background
	Birmingham Tyburn Background	Urban Background
	Birmingham Tyburn Roadside	Traffic
London	Harwell	Rural Background
	North Kensington	Urban Background
	Marylebone Road	Traffic
	Detling	Rural Background

Table 1 Sites to measure emissions of Black Carbon from traffic sources

The installation of a site at Glasgow High Street was seriously delayed due to planning restrictions.

Five other sites make up the Network. These sites measure specific non-traffic emission sources and are listed in Table 2.

Site Name	Site classification	Emission Source
Belfast Centre	Urban Background	Urban background
Lisburn Kilmakee	Urban Background	Solid fuel use / Urban background
Strabane	Urban Background	Solid fuel use
Ballymena	Urban Background	Solid fuel use
Cardiff 12	Urban Background	Urban background

Table 2 Sites to measure non-traffic related emission sources

The sites making up the Network are shown on a map in Figure 1.

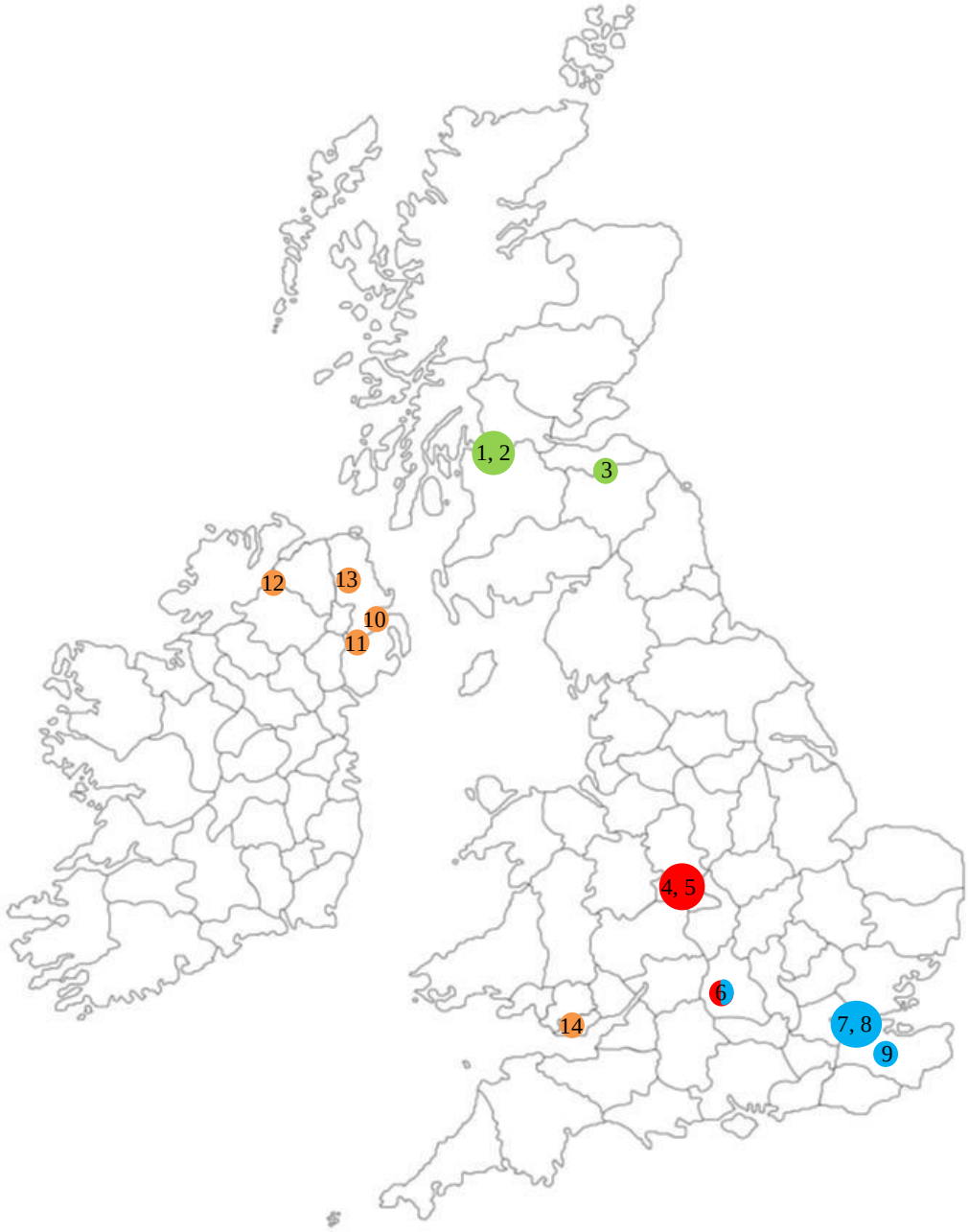


Figure 1 **Sites on the BC Network during 2014**
Key on next page

Key:

Emission source	Key	Site Name
Glasgow Urban Area	1	Glasgow High Street
	2	Glasgow Townhead
	3	Auchencorth Moss
Birmingham Urban Area	4	Birmingham Tyburn Roadside
	5	Birmingham Tyburn Background
Birmingham Urban Area + London Urban Area	6	Harwell
London Urban Area	7	North Kensington
	8	Marylebone Road
	9	Detling
Solid Fuel Use	10	Belfast Centre
	11	Lisburn Kilmakee
	12	Strabane
	13	Ballymena
Domestic Emissions	14	Cardiff 12

2.2 CHANGES TO THE NETWORK

In 2012 the Glasgow Centre site was closed due to redevelopment of the surrounding area. An urban background replacement site was found in 2013 and the Glasgow Townhead site commissioned in the last quarter of 2013. The Aethalometer did not survive its storage period very well and had numerous performance issues during the commissioning, resulting in valid measurements only starting in December 2013.

The Cardiff 12 site had to close in June 2014 due to the closure of Cardiff Scientific Services and demolition of the building housing the analyser. The analyser was relocated to the Cardiff Centre AURN site in the first quarter of 2015. The gap in the monitoring was due to the Cardiff Centre site having to be upgraded with a larger enclosure to house new monitors.

Planning issues affecting the new Glasgow traffic site were resolved in 2014 and the new Glasgow High Street site was commissioned on 4th March 2015.

2.3 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 (King's) 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 14 sites on the Network on a daily basis. Measurements of Black Carbon, UV carbon, flow, raw attenuation signals and tape life since the last data collection are requested from the Aethalometer and automatically loaded into King's database. The 5 minute mean measurements are averaged to 15 minute means in line with measurements made using gaseous and

particulate monitors on the AURN. A valid 15 minute measurement is only calculated where two or more 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 manual 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 the previous 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 the MONNET software package 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.

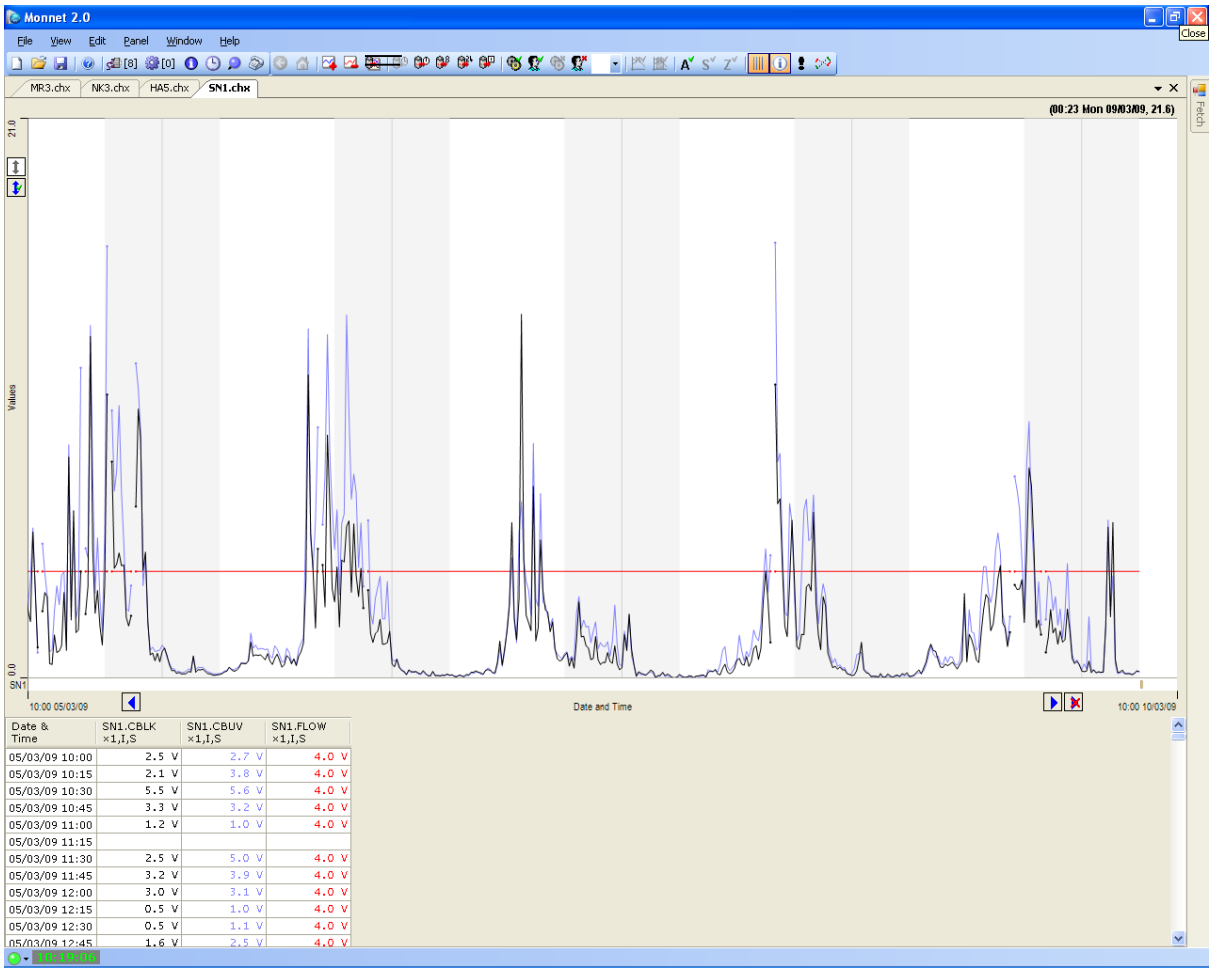


Figure 2 MONNET data checking graph

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 LSO or the ESU If this is the case a visit request is sent to either the LSO or ESU. The reports generated from these visits are processed at King's 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.

3.0 QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC)

Quality Assurance and Quality Control activities cover two main areas: site audits and instrument performance. The first addresses sampling issues and the second ensures the consistency and accuracy of the measurement of Black Carbon concentration.

3.1 SITE AUDITS

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

Site	Date	Serial No.
Auchencorth Moss	30/07/2014	862
Ballymena Ballykeel	01/07/2014	849
Belfast Centre	01/07/2014	863
Birmingham Tyburn RS	27/06/2014	869
Birmingham Tyburn UB	27/06/2014	859
Detling	18/06/2014	865
Glasgow Townhead	29/07/2014	856
Harwell	15/07/2014	851
Lisburn Kilmakee	30/06/2014	861
Marylebone Road	17/06/2014	866
North Kensington	17/06/2014	850
Strabane	03/07/2014	845

Table 3 Site Audit Visits

The Cardiff site was not audited as the site closed before the scheduled audit round had started.

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.

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%.

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.

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

Site	Leak Rate, %	Indicated Flow, lpm	Inlet Flow, lpm
Auchencorth Moss	5.7	4.0	4.210
Ballymena Ballykeel	4.5	4.0	3.670
Belfast Centre	4.8	4.0	4.033
Birmingham Tyburn RS	6.5	4.0	4.220
Birmingham Tyburn UB	4.5	4.0	4.090
Detling	0.0	4.0	4.257
Glasgow Townhead	2.4	3.9	3.980
Harwell	8.9	3.9	4.030
Lisburn Kilmakee	6.5	4.0	4.197
Marylebone Road	8.3	4.0	4.143
North Kensington	4.3	4.0	4.237
Strabane	4.8	3.7	3.820

Table 4 Aethalometer leak rates and sample flows

3.1.2 Instrument Performance

The best simple indication of instrument performance can be gained by examining the zero noise of the Aethalometer, as this gives 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 an extended period of time. The Aethalometer concentration falls quickly to a stable value around zero, with variations due to noise in the optical system and electronics. Figure 3 shows a typical Aethalometer response to this test running on the normal time base of 5 minutes. The data are from the Strabane site.

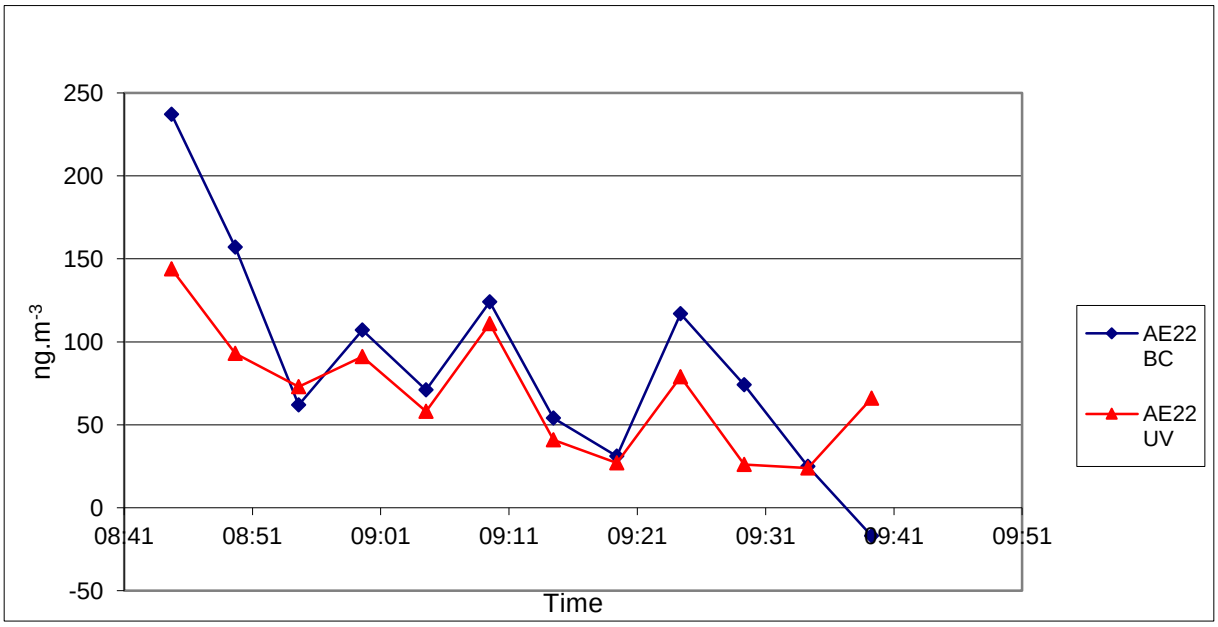


Figure 3 Strabane Aethalometer sampling HEPA filtered air

It should be noted that the concentrations normally reported by the Network are in $\mu g.m^{-3}$ and the above concentrations are in $ng.m^{-3}$. These concentrations during the zero noise tests are normally at or below the stated detection limit of the instrument, $0.1\mu g.m^{-3}$ ($100\ ng.m^{-3}$).

The zero noise is calculated as the standard deviation of the recorded concentrations multiplied by the student t-factor for the number of measurements. The results for each site are given in Table 5.

Site	**BC, $ng.m^{-3}$**	**UV Channel, $ng.m^{-3}$**
North Kensington	110	70
Birmingham Tyburn UB	334	177
Harwell	64	68
Birmingham Tyburn RS	N/A	N/A
Lisburn Kilmakee	238	136
Belfast Centre	271	357
Detling	121	146
Ballymena Ballykeel	209	70
Marylebone Road	358	184
Strabane	148	82
Glasgow Townhead	91	65
Auchencorth Moss	126	42

Table 5 Zero Noise of BC and UV component channels

There was a problem with the data collection during the HEPA filter test at the Birmingham Tyburn Roadside site audit which resulted in the test being invalid.

It should be noted that the UV Channel in Table 5 is not the UV component concentration, but the result taken from the UV channel. Section 1.3.1 gives a description of how the UV component is calculated.

The results in Table 5 are for measurements made with an Aethalometer time base of 5 minutes, these 5 minute readings are then averaged over 15 minutes before validation and ratification takes place. If the above 5 minute results are converted to a 15 minute noise result then the average Aethalometer noise recorded for the BC and UV channels is: 109 $ng.m^{-3}$ and 73 $ng.m^{-3}$ respectively. The shortest time period over which data is published is 1 hour, therefore the average noise on a 1 hour average concentration is expected to be 54 $ng.m^{-3}$ and 37 $ng.m^{-3}$, for BC and UV respectively. These figures are considered acceptable, being far less that the network mean Black Carbon concentration of 1.60 $\mu g.m^{-3}$ and the network mean UV component of 0.3 $\mu g.m^{-3}$.

QA/QC methods are continually being reviewed and improved for the network.

4.0 MEASUREMENT UNCERTAINTY

4.1 SAMPLE VOLUME

From measurements at the site audit the sample volume can be determined with an uncertainty of ±8.9%, 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 2014 audits was used. As leak rate is considered to be a rectangular distribution, its contribution to the standard uncertainty in sample volume is 3.1%.

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. Results from the HEPA filter zero noise tests show that the stability of the optical / electrical system is approximately ±0.05 $\mu g.m^{-3}$ for hourly means. Converting this into a standard uncertainty this represents a contribution of 3.1%, compared to the network mean of 1.60 $\mu g.m^{-3}$.

4.3 CORRECTION FOR SPOT DARKENING

The Virkkula[2] model was used to correct the measured concentrations to account for the nonlinearity of Aethalometer Black Carbon and UV component measurements 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 although this is decreased when hourly mean concentrations are calculated.

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

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

4.4 PRELIMINARY OVERALL MEASUREMENT UNCERTAINTY

When the contributions from sample volume and optical /electrical stability are combined, the overall measurement uncertainty for hourly Black Carbon concentrations is 15.4%, expressed with a level of confidence of 95%. The only source of uncertainty in the overall measurement uncertainty that reduces when producing longer term averages from the hourly data is the zero noise. The following is the overall measurement uncertainties for different averaging periods, expressed with a level of confidence of 95%:

Hourly	11.2%
Monthly	8.9%
Yearly	8.9%

Uncertainties year-on-year are consistent and compare well with the EU requirement of 25% for particulate mass concentration measurements.

This is an indicative measurement uncertainty for the Aethalometer method and is calculated from the results of the 2014 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 2014 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[2].

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 2014. The time resolution of the measurements is hourly. Data has been split into regions of the UK for presentation purposes. The maximum y-axis on these charts has been set to 45 μg.m^{-3} to enable easy comparison between charts, except for Figure 8 which shows concentrations measured at rural locations.

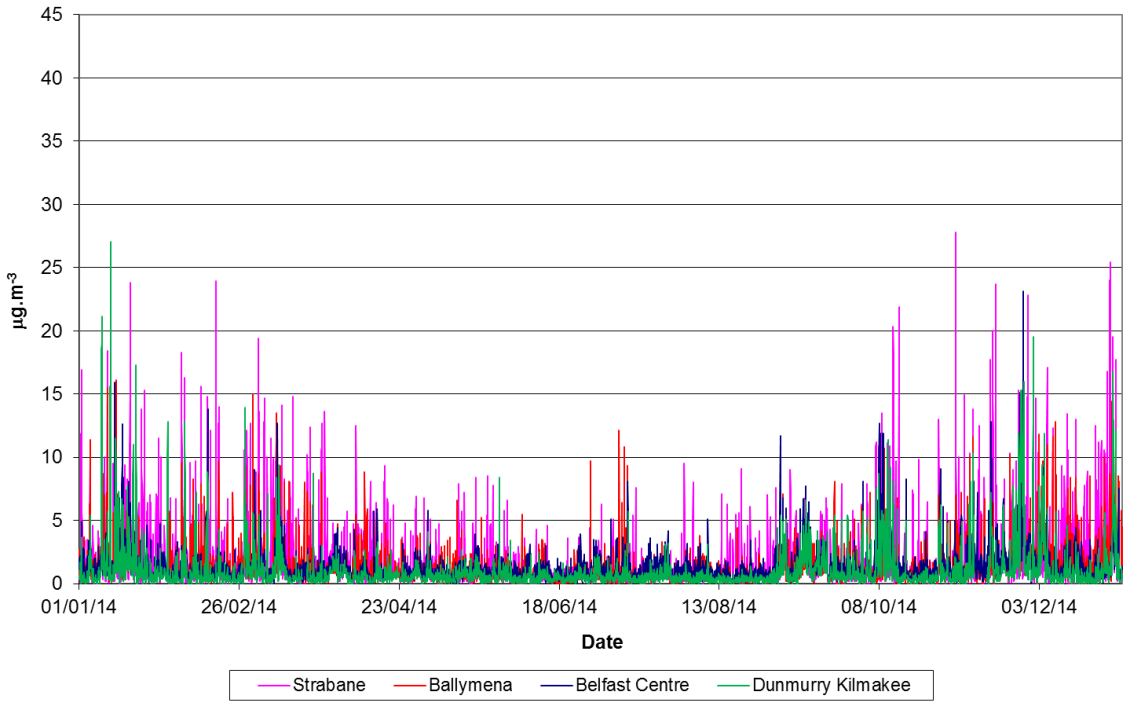


Figure 4 Black Carbon concentrations during 2014 in Northern Ireland

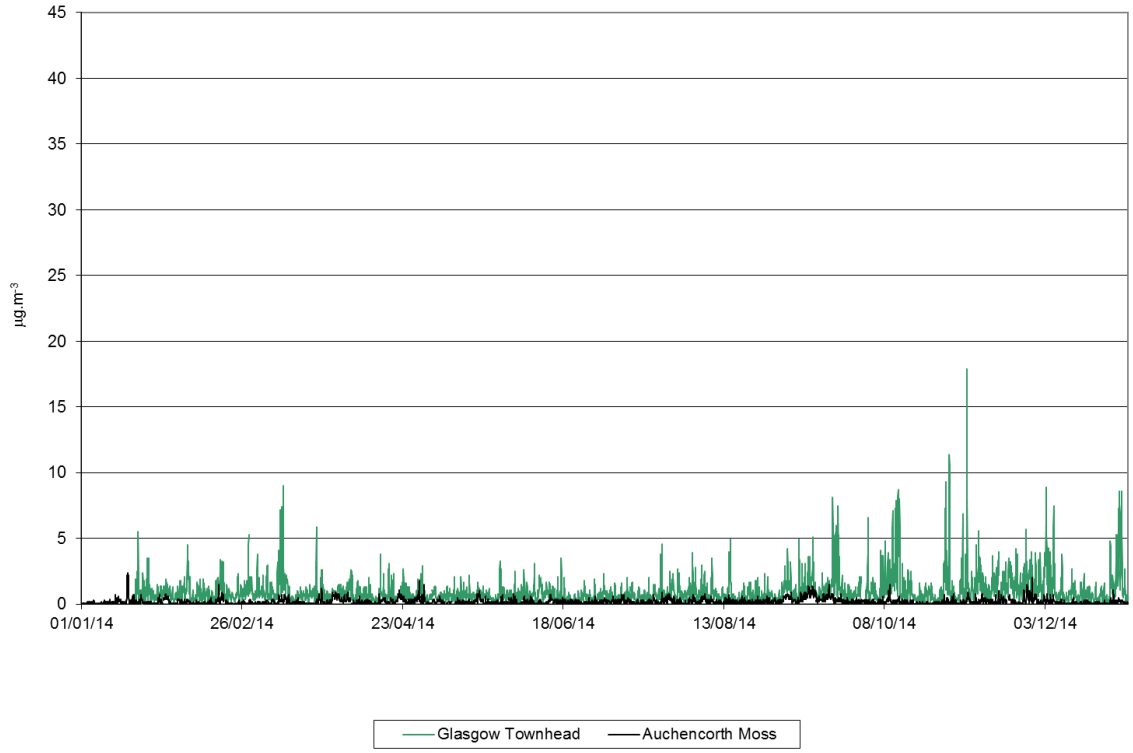


Figure 5 Black Carbon concentrations during 2014 in Scotland

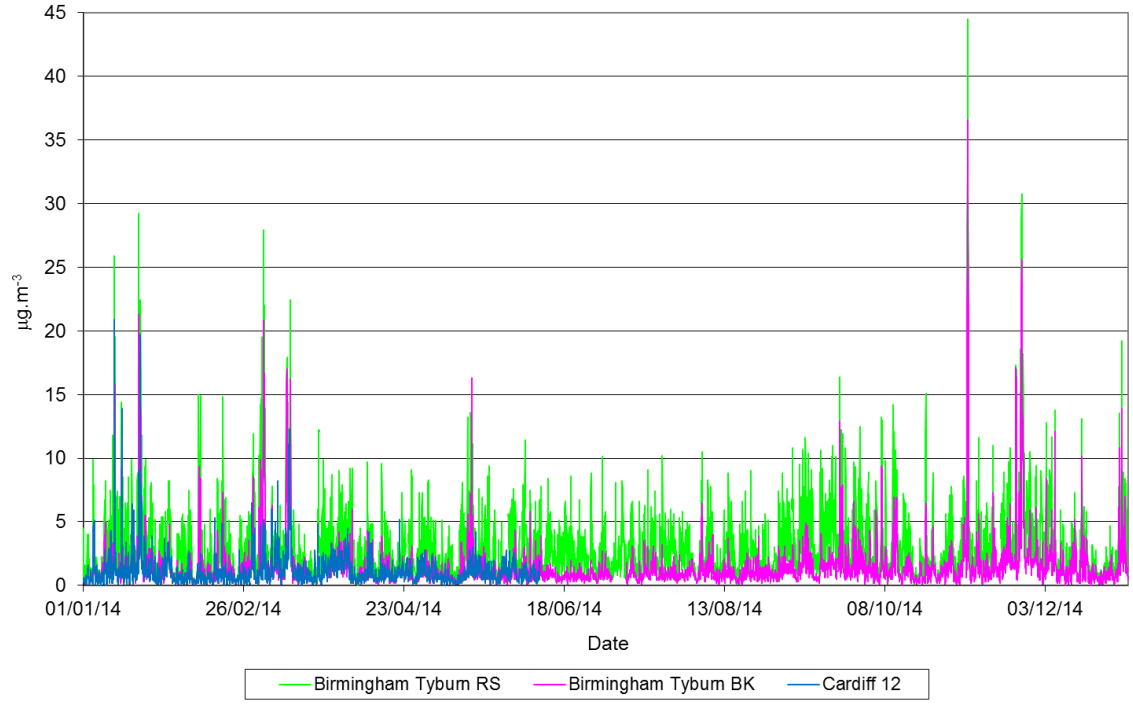


Figure 6 Black Carbon concentrations during 2014 in Wales and the Midlands

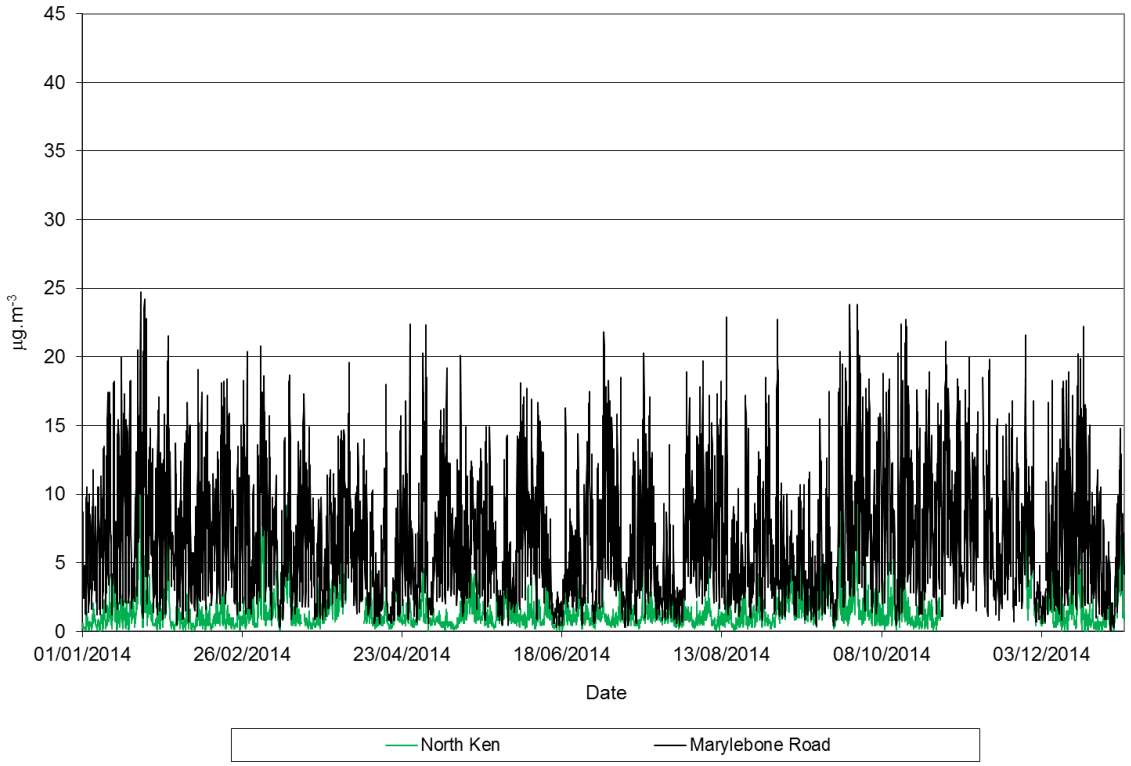


Figure 7 Black Carbon concentrations during 2014 in Southern and Eastern England

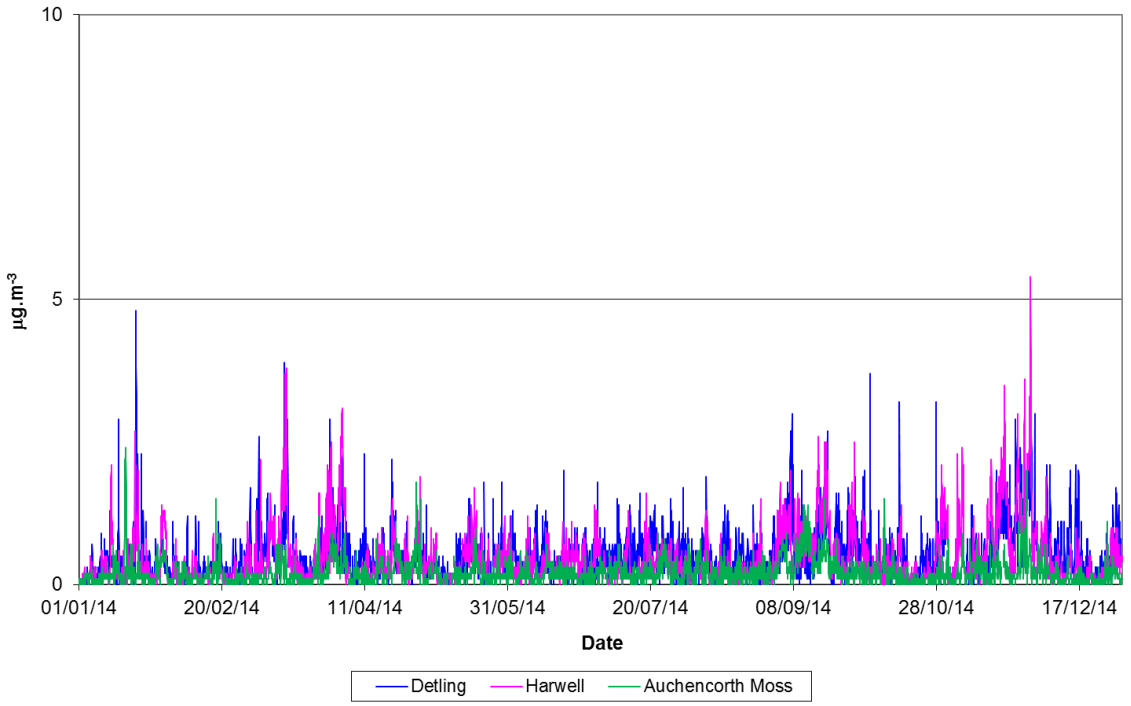


Figure 8 Black Carbon concentrations during 2014 at Rural Locations

Northern Irish sites measured increased concentrations during the cold months in January, February, March, October, November and December.

In previous years there has been is a noticeable drop in BC concentrations from late Christmas Eve at

all sites until the end of December, probably due to reduced road traffic across the country. However, in 2014 there was an increase in BC concentrations at all but the rural sites due to cold, still weather not dispersing local sources.

Elevated Black Carbon concentrations were also measured on the evening and 5th November at many sites across the UK, indicating emissions from celebrations associated with bonfire night. Especially high concentrations were recorded at Birmingham Tyburn Background and Roadside sites with concentrations reaching over 40 μg.m^{-3}.

5.1.2 UV component

The following charts show the UV component concentrations measured by the UK Black Carbon Network for 2014. 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 graphs have not been fixed to the same value for every chart, because the UV component is much more dependent on local site-specific conditions.

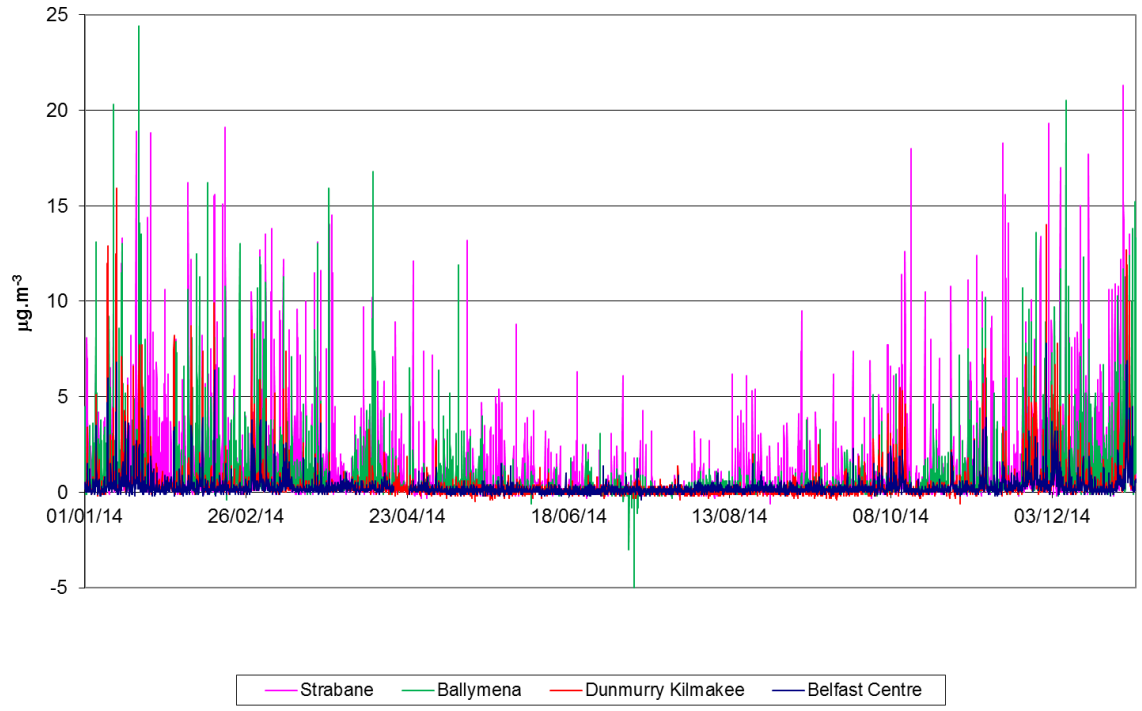


Figure 9 UV component concentrations during 2014 in Northern Ireland

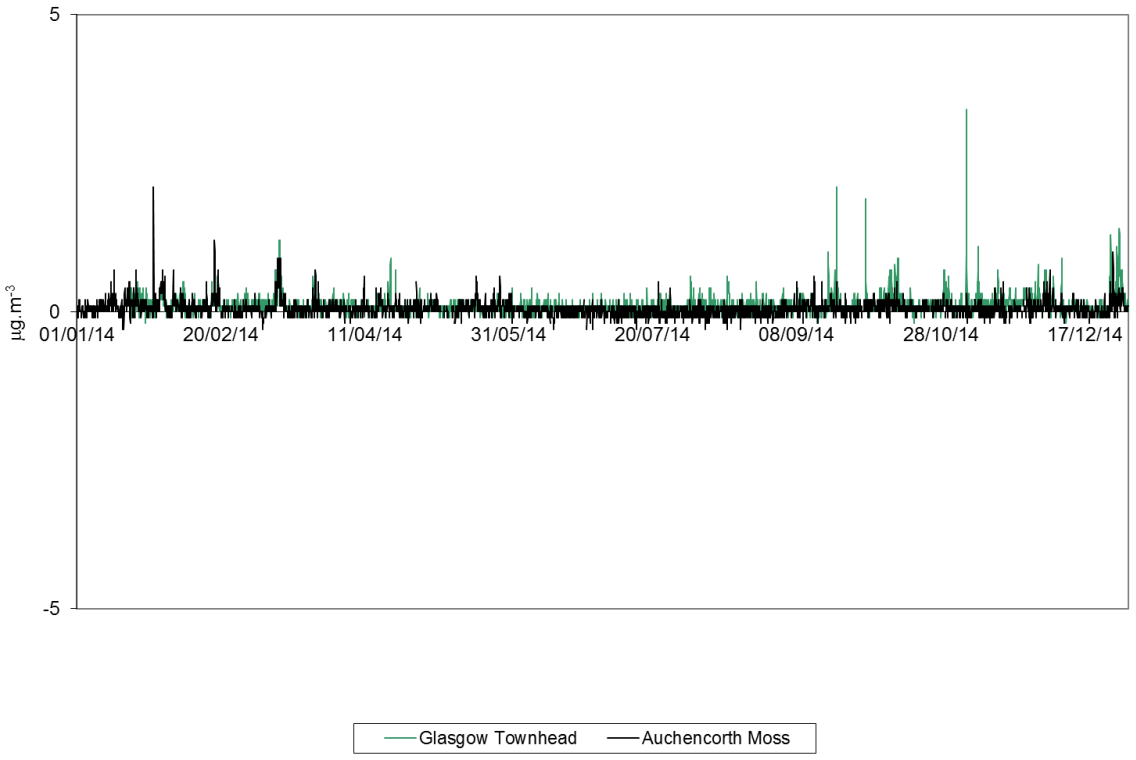


Figure 10 UV component concentrations during 2014 in Scotland

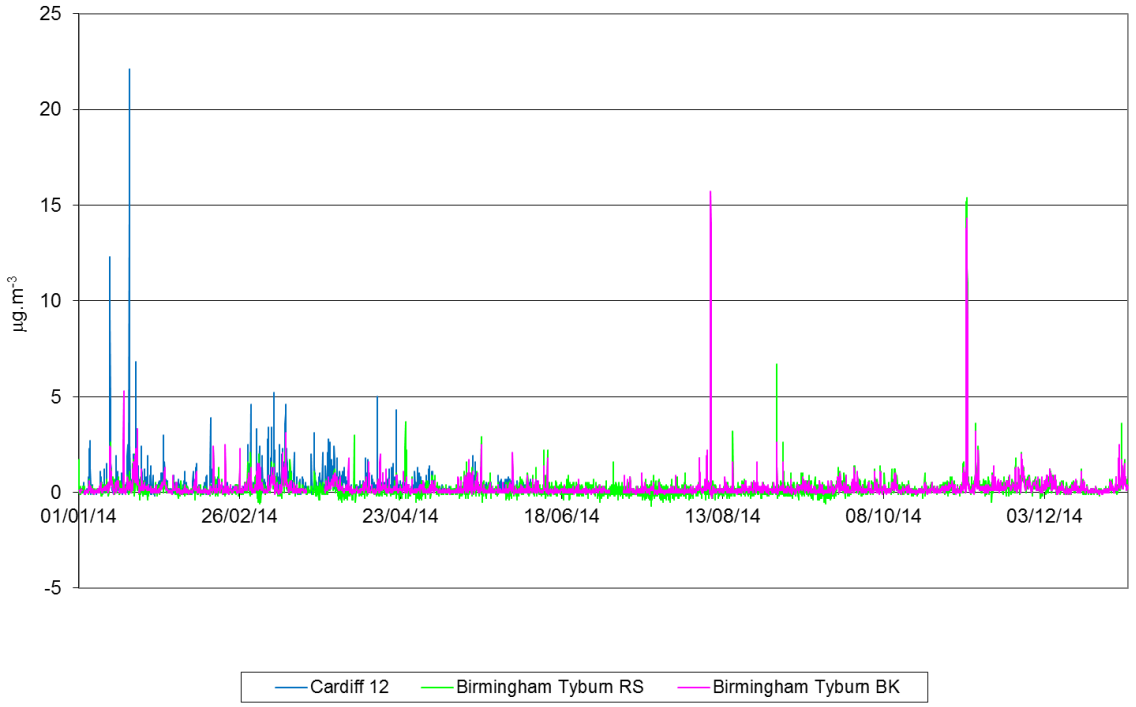


Figure 11 UV component concentrations during 2014 in Wales and the Midlands

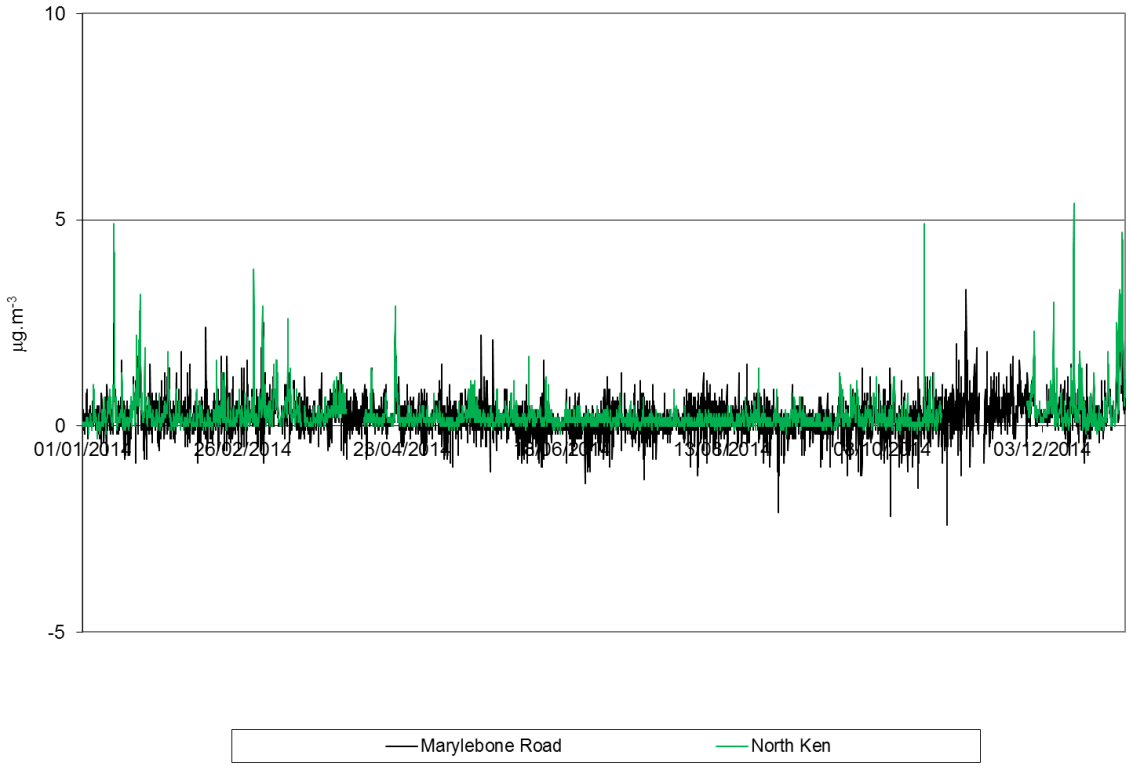


Figure 12 UV component concentrations during 2014 in Southern and Eastern England

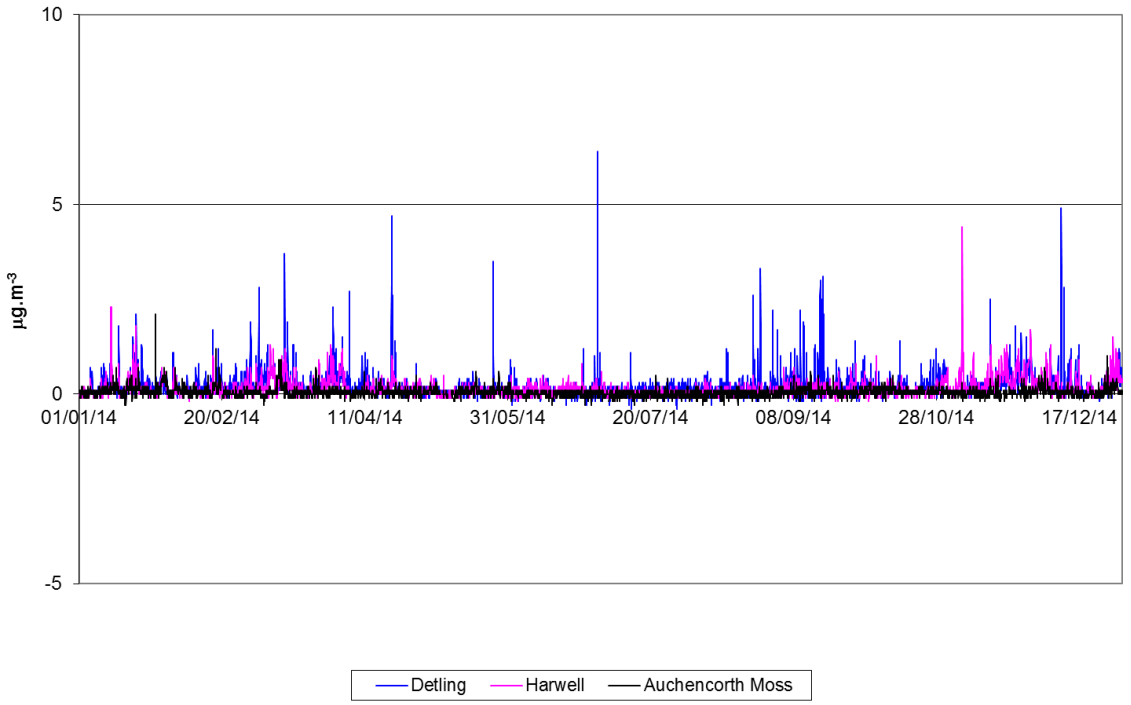


Figure 13 UV component concentrations during 2014 at Rural Locations

The Northern Irish sites measured increased UV component concentrations during the cold periods in January, February, March, October November and December. Evidence from the UV component concentrations for 2014 suggests that the heating season runs from January to mid-May in Strabane and Ballymena and from mid-September to the end of the year. Concentrations across 2014 were similar to

those measured in 2013, but with a slightly shorter heating season.

Elevated UV component concentrations were also measured on the evening of 5th November at many sites across the UK, indicating emissions from celebrations associated with bonfire night. Concentrations of approximately 15μg.m^{-3} were measured at both the Birmingham sites.

Several sites, especially London, have some days of high UV component in the last week of December. This is probably due to the settled weather conditions and also as an indicator that people were perhaps choosing to burn wood decoratively as families got together over the Christmas break.

The cause of the very short-term 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. 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 kerb, high traffic flow and predominantly diesel based exhaust signatures from HGVs, buses and taxis. A similar but smaller response is also found at Birmingham Tyburn Roadside, which still has high traffic flows but less diesel based exhaust emissions than Marylebone Road. This effect is not prevalent at Birmingham Tyburn Background which is approximately 60m away from the roadside site.

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 mean for each site for 2014.

Site	**Mean concentration μg.m^{-3}**
Auchencorth Moss	0.2
Ballymena	1.3
Belfast Centre	1.4
Birmingham Tyburn BK	1.4
Birmingham Tyburn RS	2.9
Cardiff 12	1.1
Detling	0.5
Dunmurry Kilmakee	1.0
Glasgow Townhead	1.0
Harwell	0.5
Marylebone Road	6.6
North Kensington	1.4
Strabane	1.6

Note: Cardiff 12 is not a full calendar year mean.

Table 6 Annual Mean Black Carbon Concentrations for 2014

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

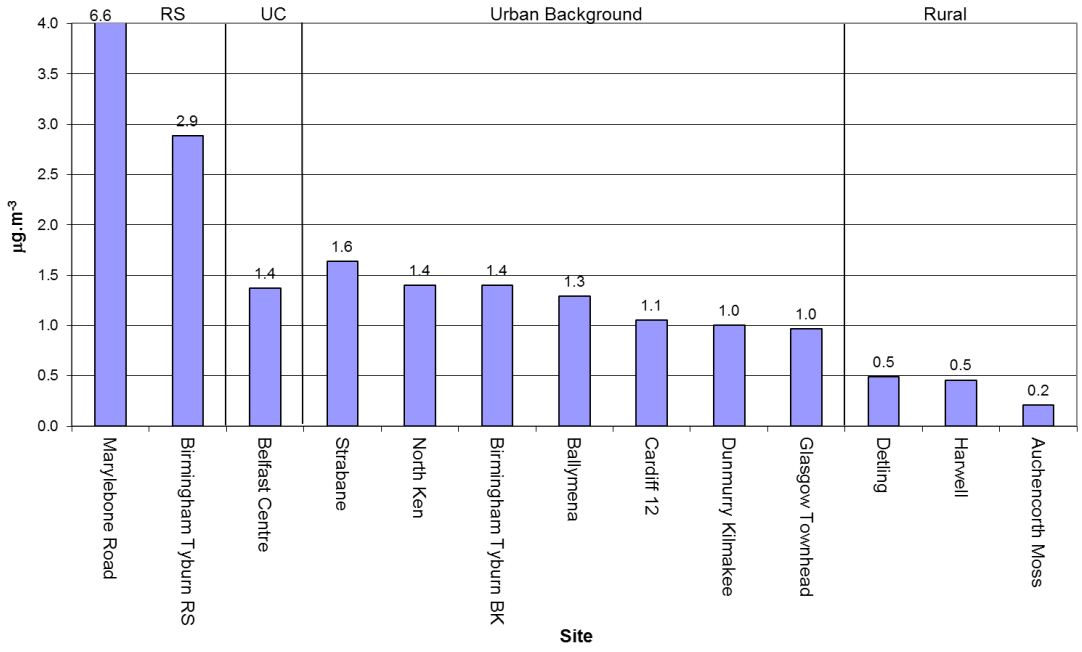


Figure 14 Annual Mean Black Carbon Concentrations for 2014

Black Carbon concentration increments between rural, urban background and roadside sites for London,

Birmingham and Scotland have been analysed from periods when all the sites were producing valid data, and are shown in Table 7. The figures for 2013 are given in Table 8 for comparison.

	Increment, $\mu g.m^{-3}$	
Conurbation	**Urban**	**Roadside**
London	1.0	5.1
Birmingham	0.9	1.5
Scotland	0.8	N/A

Table 7 Increments in Black Carbon concentrations between rural, background and roadside sites in 2014

	Increment, $\mu g.m^{-3}$	
Conurbation	**Urban**	**Roadside**
London	1.1	5.2
Birmingham	0.9	1.7
Scotland	0.8	N/A

Table 8 Increments in Black Carbon concentrations between rural, background and roadside sites in 2013

The urban and roadside increments for London are very similar to 2013, in contrast the roadside increment for London in 2013 was 2.0 $\mu g.m^{-3}$ (28%) less than that for 2012, while the 2013 and 2012 urban increments were similar. The increments at Birmingham and Scotland for both urban and roadside locations are very similar to those of 2013.

It can be seen that the urban increment for all three areas is similar, while the roadside increment for London is much larger than that for Birmingham. This is due to the much larger traffic flow and different vehicle profile of the Marylebone Road site compared to the Birmingham Tyburn roadside site. Highways Agency traffic count data for 2014 for the two roads passing the monitoring stations are given in Table 9.

Road (Count Point ID)	**Motor cycles**	**Cars Taxis**	**Buses Coaches**	**All HGVs**	**All Motor Vehicles**
Marylebone Road (27236)	4,789	56,394	3,074	3,574	79,528
Tyburn Road (56399)	145	24,772	251	1,657	31,893
Ratio	33	2.3	12.2	2.2	2.5

Table 9 2014 Average daily traffic count data for Marylebone and Tyburn Roads

The Marylebone Road roadside increment in Black Carbon concentration in 2014 was a factor of 3.4 higher than the Tyburn Road increment, somewhat higher than the ratio of numbers of cars / taxis and HGVs, between the sites at 2.3 and 2.2 respectively. However there are 12.2 times more buses and coaches and 33 times more motor cycles passing the Marylebone Road site compared to the Birmingham site, which would indicate that these are probably the predominant source of Black Carbon emissions at Marylebone Road. Changes in emissions from London buses and taxis are discussed in section 5.5.1.

5.2.2 UV component

Table 10 gives the annual average for each site for 2014.

Site	Mean concentration µg.m^{-3}
Auchencorth Moss	0.1
Ballymena	0.8
Belfast Centre	0.3
Birmingham Tyburn BK	0.2
Birmingham Tyburn RS	0.2
Cardiff 12	0.4
Detling	0.2
Dunmurry Kilmakee	0.4
Glasgow Townhead	0.1
Harwell	0.1
Marylebone Road	0.2
North Kensington	0.3
Strabane	1.1

Note: Cardiff12 is not a full calendar year mean.

Table 10 Annual Mean UV component Concentrations for 2014

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

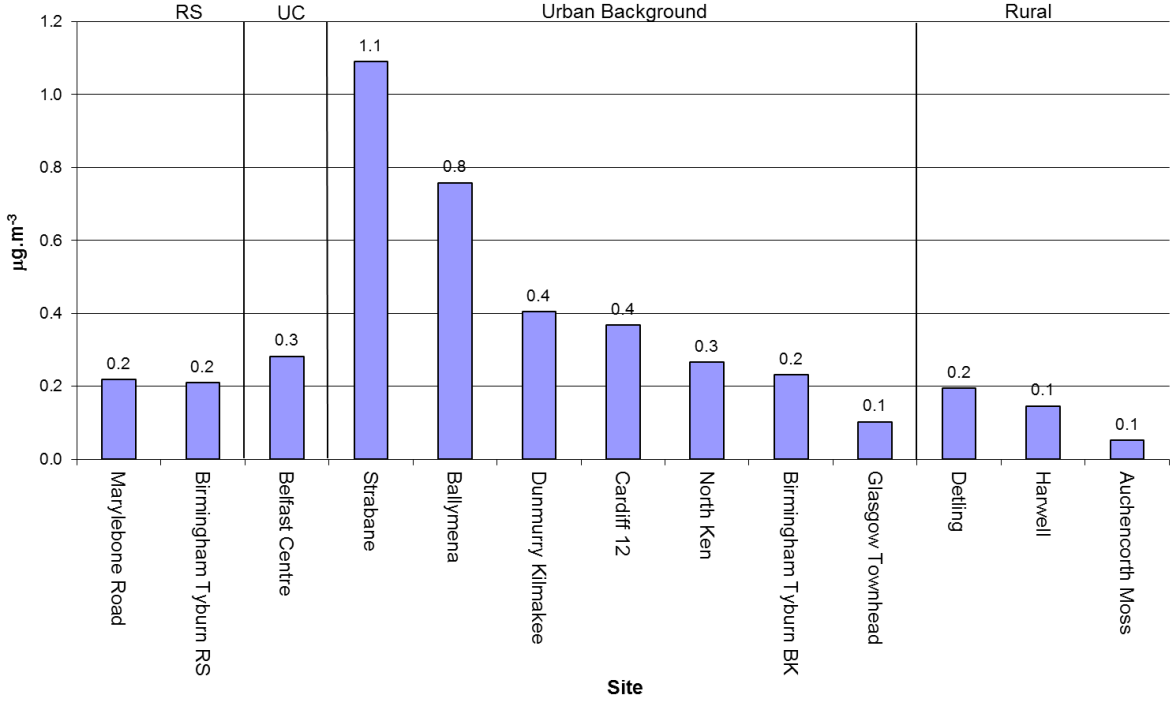


Figure 15 Annual Mean UV component Concentrations for 2014

UV component concentration increments between rural, urban background / centre and roadside sites for London, Birmingham and Scotland have been analysed from periods when all the sites were producing valid data, and are shown in Table 11.

	Increment, µg.m^{-3}	
Conurbation	**Urban**	**Roadside**
London	0.1	-0.1
Birmingham	0.1	0.0
Scotland	0.1	N/A

Table 11 Increments in UV component concentrations between rural, background and roadside sites in 2014

There is no significant difference in increments between 2012 and 2013.

It can be seen that the urban and roadside increments at all sites are similar, as domestic emissions in the three areas are of a similar magnitude due to similar fuel types and that road traffic is not a significant source for the UV component.

Using the same method, the urban increment in UV component concentration in Northern Ireland has been calculated relative to Belfast where gas heating has largely displaced oil and coal. The results are shown in Table 12.

Site	**Increment compared to Belfast, µg.m^{-3}**	**Increment compared to Belfast, %**
Dunmurry	0.1	44
Ballymena	0.5	169
Strabane	0.8	286

Table 12 Increment in UV component concentration in Northern Ireland

The increments at Dunmurry, Ballymena and Strabane are not surprising as domestic heating in Belfast is predominantly gas fired, while there is a history of solid fuel usage for secondary heating in Dunmurry, and a significant usage of non-smokeless fuel usage in Strabane. Ballymena is supplied by natural gas, but the benzo[a]pyrene (BaP) concentrations measured by the PAH Network are higher than might be expected. A similar increase in the UV component is also found here. Correlations between BaP and the UV component can be seen in Section 5.4.2. It can therefore be concluded that there is a significant emission source of both these components in the Ballymena area, probably from the use of non-smokeless fuel. The monitoring site is not within Ballymena's smoke control zone but is within its Air Quality Management Area for PM_{10}.

5.2.3 Data Capture

Table 13 gives the data capture for each site for 2014. Due to the Network changes during 2014 the time coverage for the complete calendar year for each site has also been given.

Site	Data Capture %	Time Coverage %
Auchencorth Moss	95	95
Ballymena	97	97
Belfast Centre	98	98
Birmingham Tyburn BK	96	96
Birmingham Tyburn RS	98	98
Cardiff 12	100	44
Detling	95	95
Dunmurry Kilmakee	96	96
Glasgow Townhead	94	94
Harwell	97	97
Marylebone Road	99	99
North Kensington	89	89
Strabane	97	97

Table 13 Data capture rates of the Aethalometers for 2014

The average data capture for the Network is 96% and there is only one site, North Kensington (89%), with a data capture of below 90%. The Aethalometer installed at North Kensington had one period where the inlet pipework was found to be disconnected from the inlet head and hence was sampling cabin air; there was also one major breakdown at North Kensington.

Cardiff Centre has annual time coverage of 44% due to its closure in mid-June.

The slightly low data capture at Glasgow Townhead (94%) was due to data storage and data collection problems at the start of January. Once this was resolved the data capture for the rest of the year was 99%.

5.3 TEMPORAL VARIATIONS

The following section presents analysis of the 2014 Black Carbon and UV component concentrations with respect to the hour of the day. Charts of variations over the day of the week and the month in the year are made using the data from 2009 – 2014, to avoid bias introduced by single year measurements. Y-axes vary by site.

All results have been grouped by site classification. The site order for the Roadside and Urban Centre sites is by decreasing Black Carbon concentration, while the site order for the Urban Background and Rural Background sites is by 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.

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.

The 2014 data are presented in Figures 14 to 17.

The 2009-2014 data is presented in Figures 18 to 23.

Chart Key

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

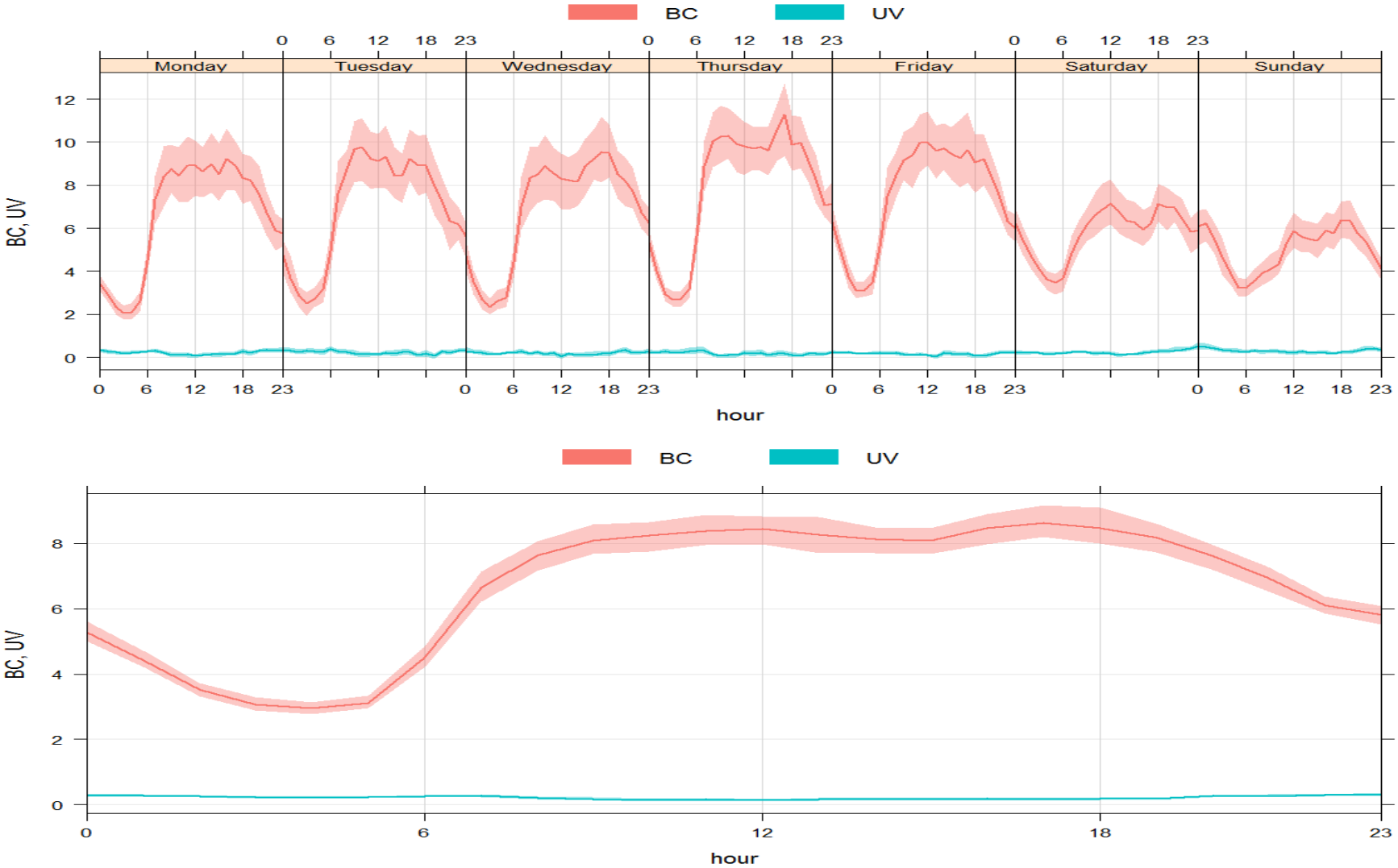
Acknowledgement

Figures 16 to 23 are generated using the Open-Air Tools run on the R software platform[3,4].

3 DC Carslaw and K Ropkins, (2012) OpenAir --- an R package for air quality data analysis, Environmental Modelling & Software. Volume 27-28, 52-61.

4 DC Carslaw and K Ropkins (2015). OpenAir: Open-source tools for the analysis of air pollution data, R package version 1.1-5

2014 Data



Marylebone Road

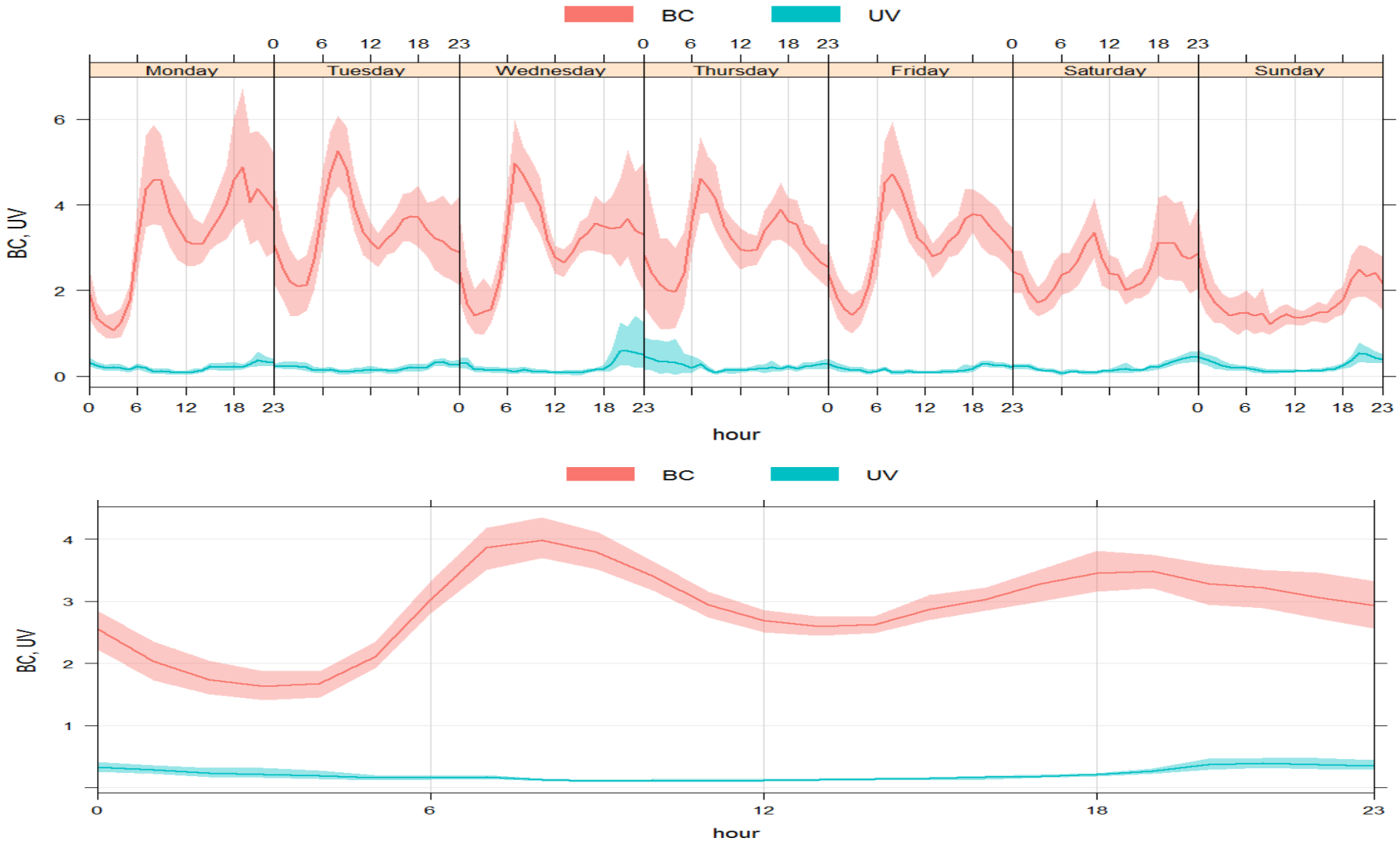


Figure 14 2014 Roadside sites

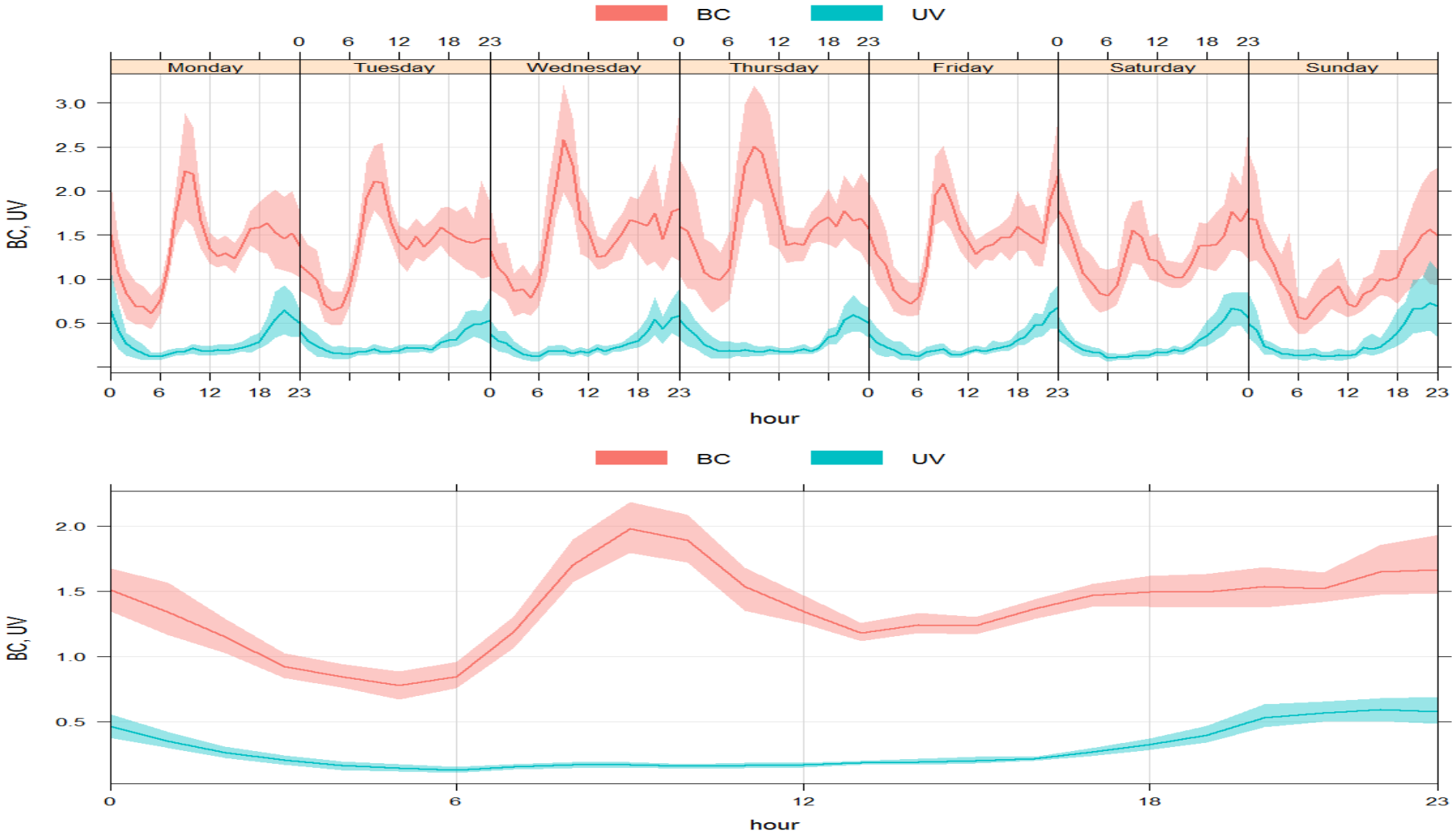
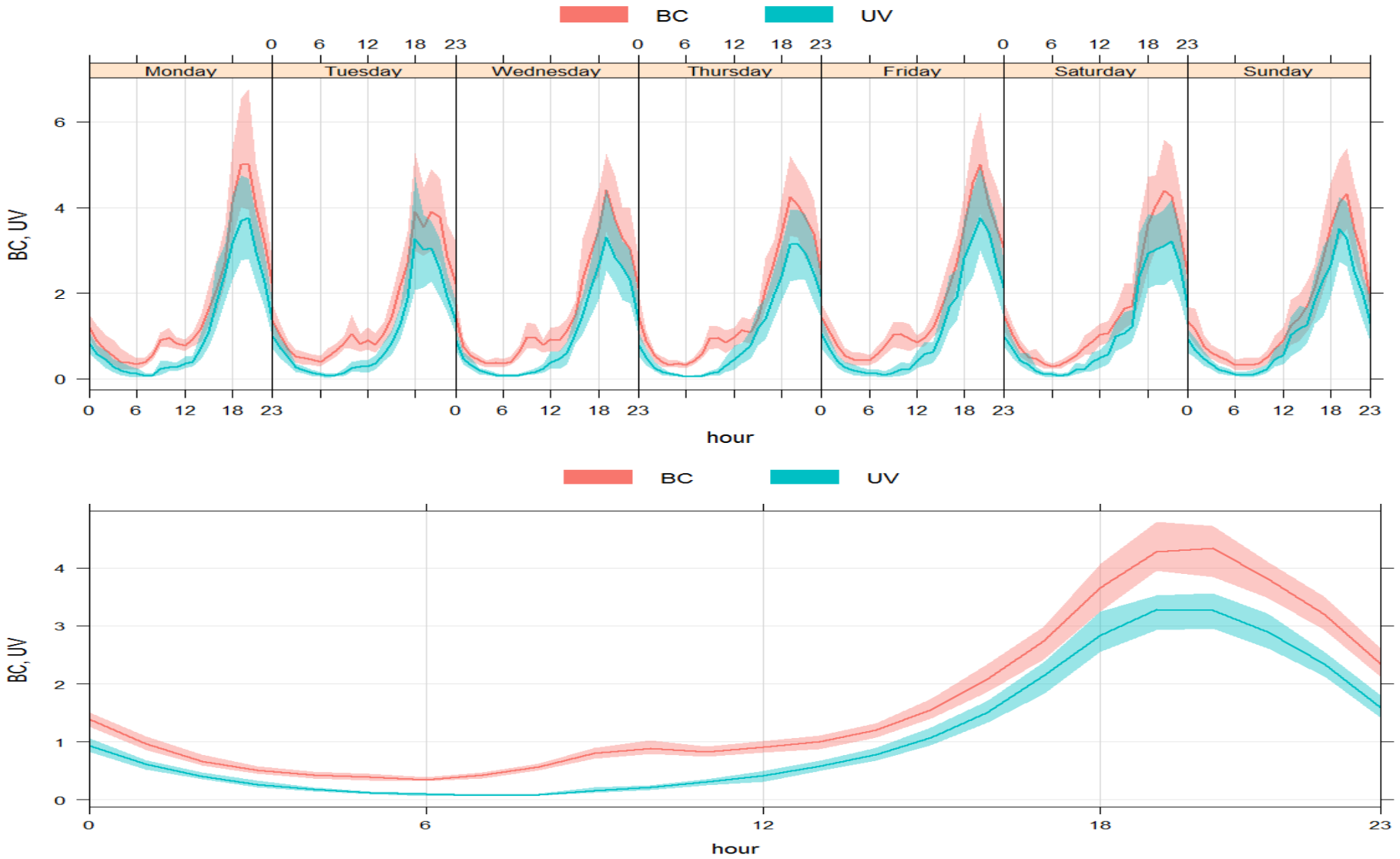
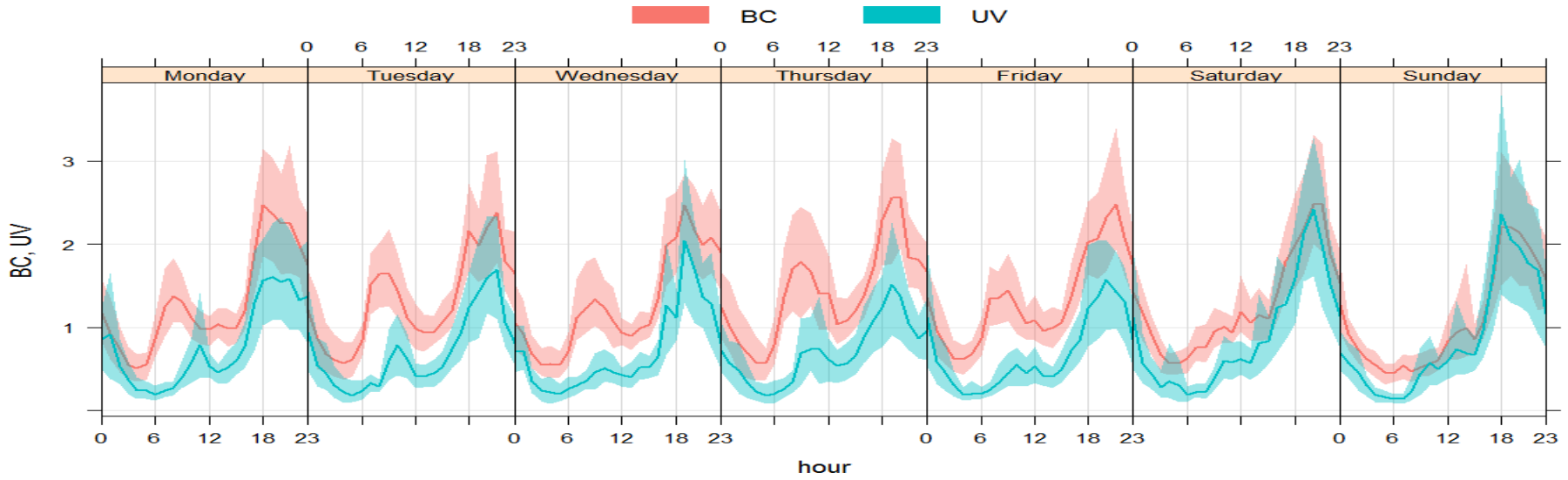
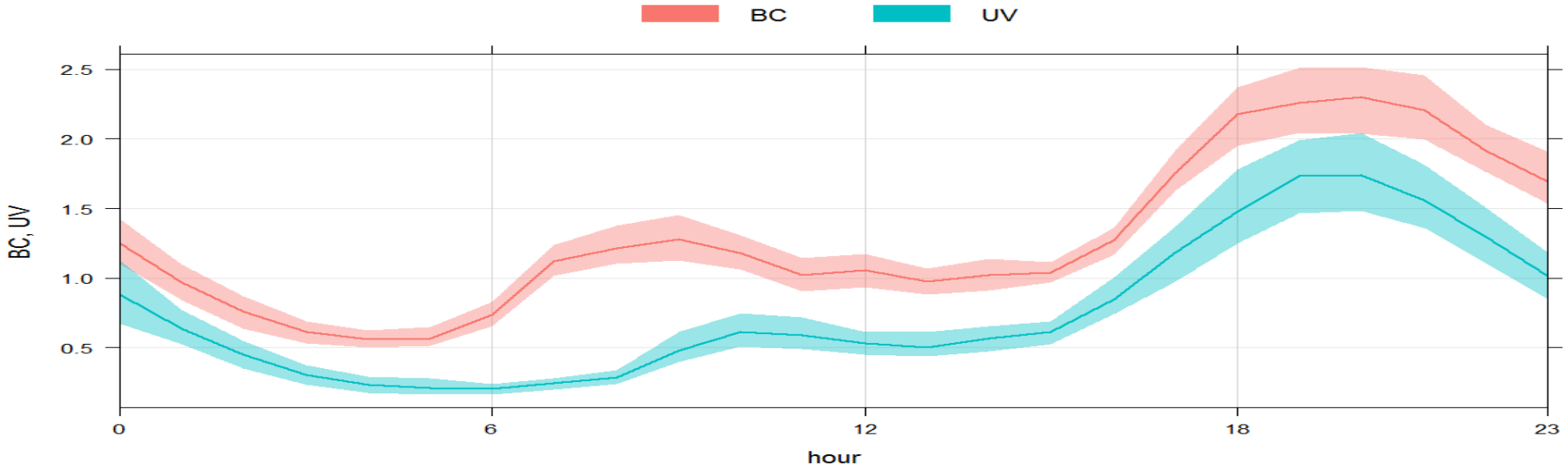


Figure 15 2014 Urban Centre sites

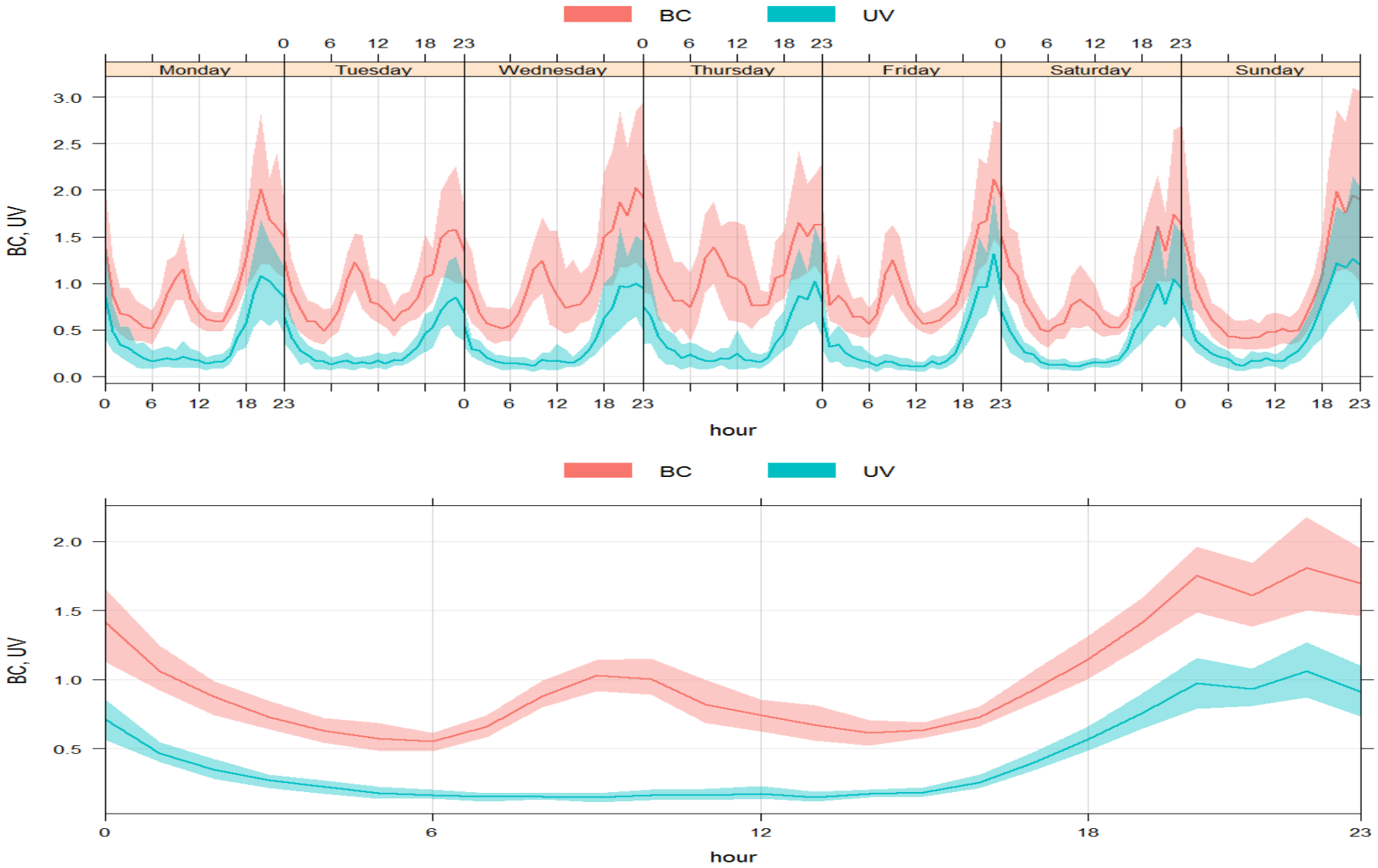

BC
UV
Monday
Tuesday
Wednesday
Thursday
Friday
Saturday
Sunday
BC, UV
hour
BC
UV
BC, UV
hour

Strabane

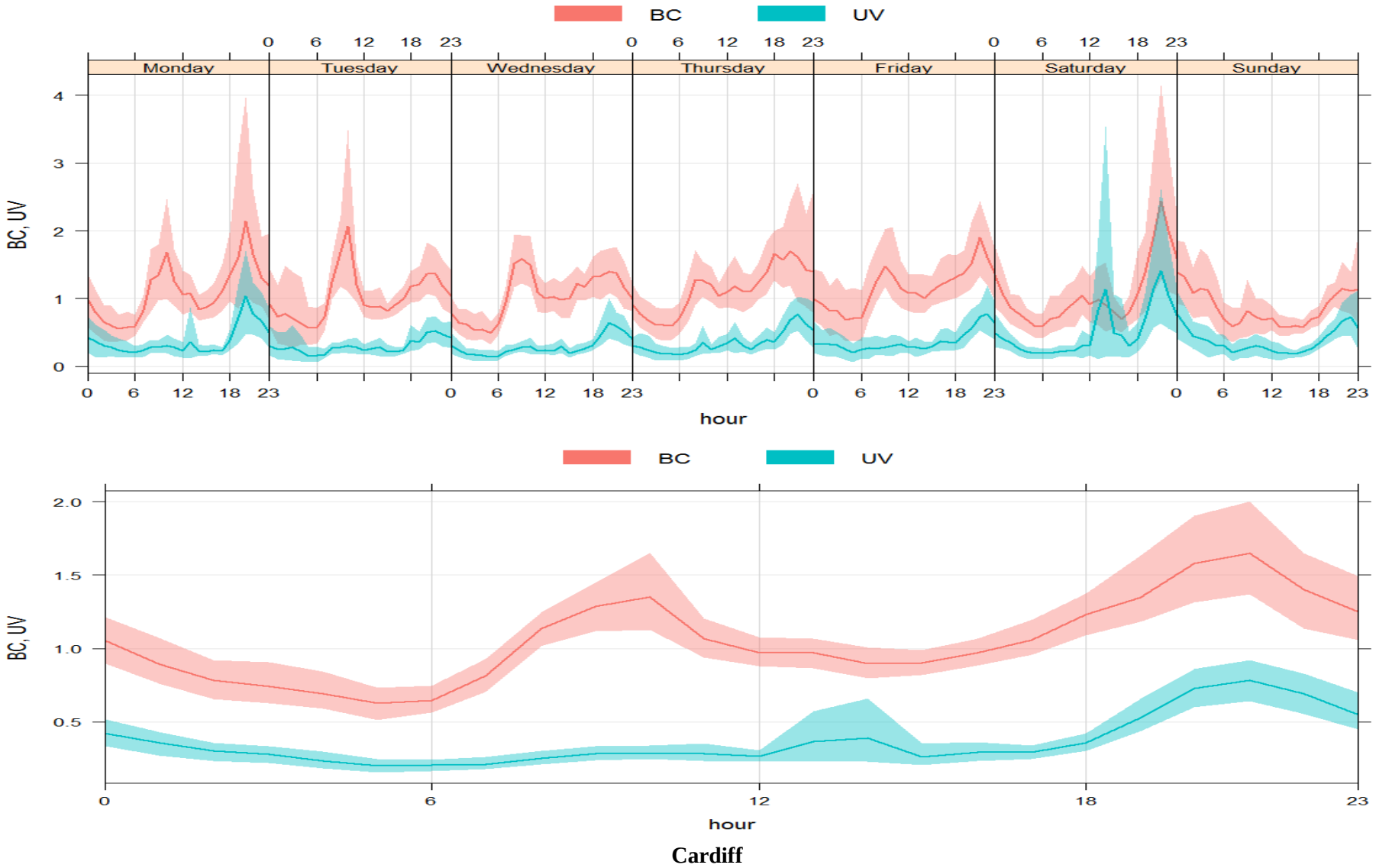

BC
UV
Monday
Tuesday
Wednesday
Thursday
Friday
Saturday
Sunday
BC, UV
hour


BC
UV
BC, UV
hour

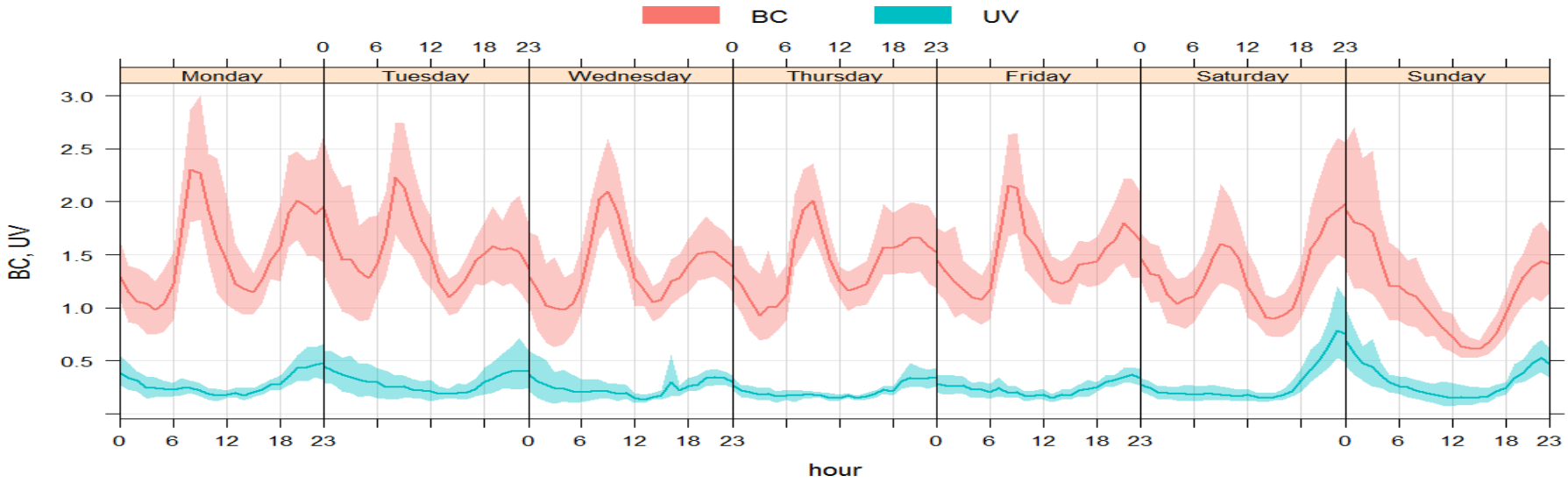
Ballymena

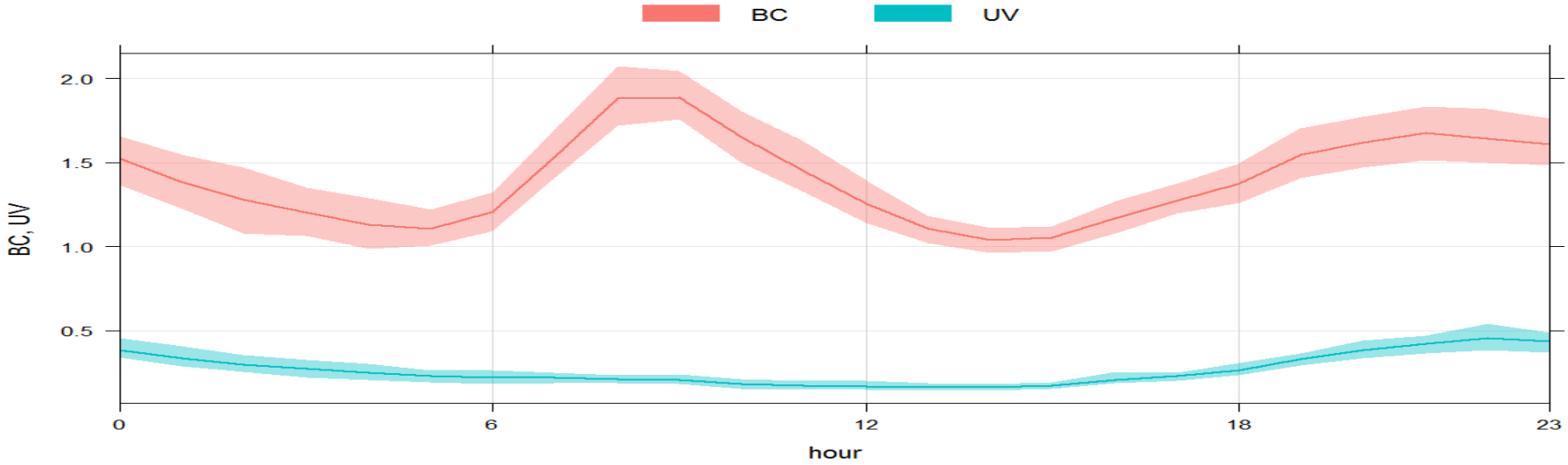


Dunmurry Kilmakee

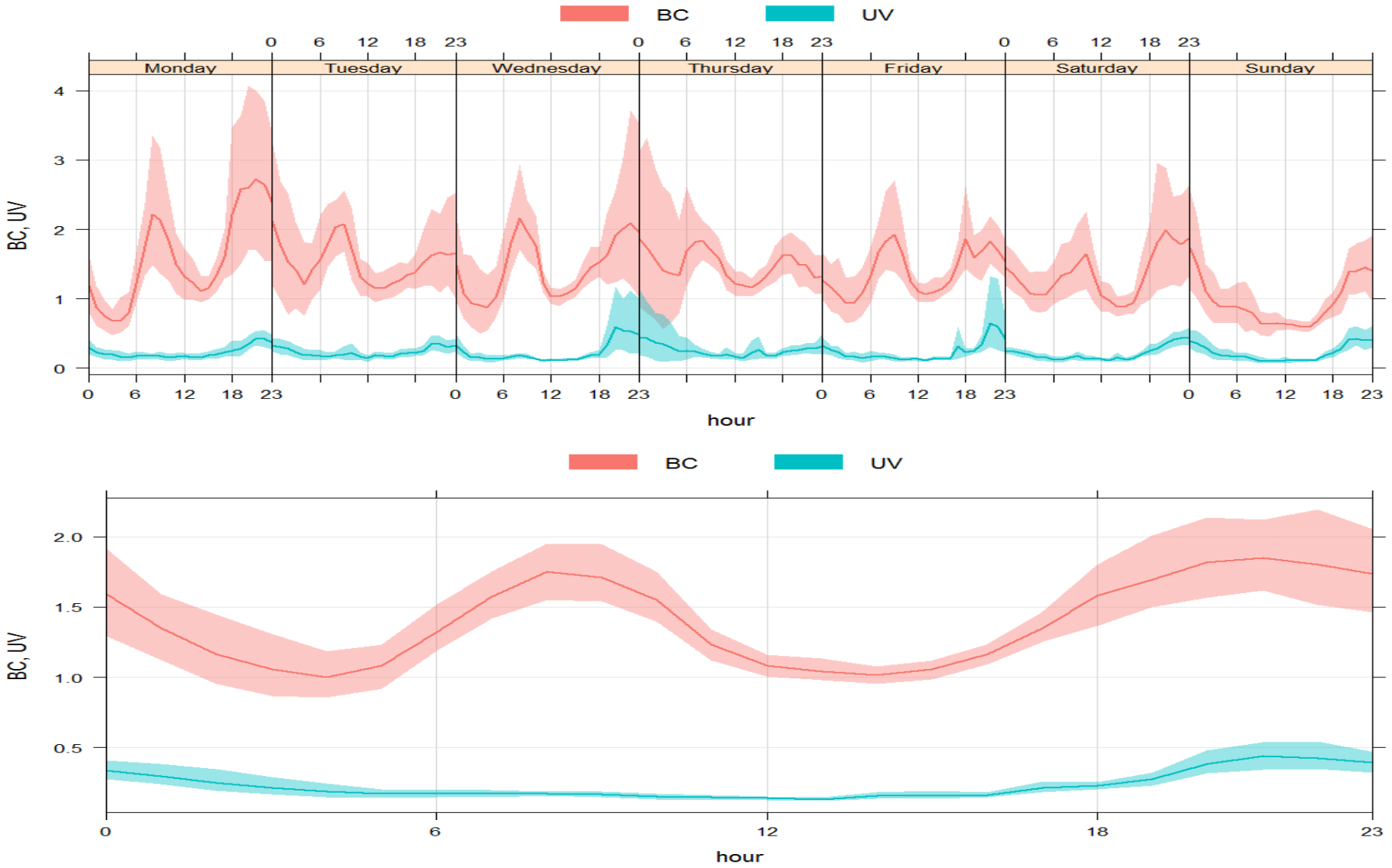

BC
UV
Monday
Tuesday
Wednesday
Thursday
Friday
Saturday
Sunday
BC, UV
hour
BC
UV
BC, UV
hour

Cardiff





North Kensington



Birmingham Tyburn Background

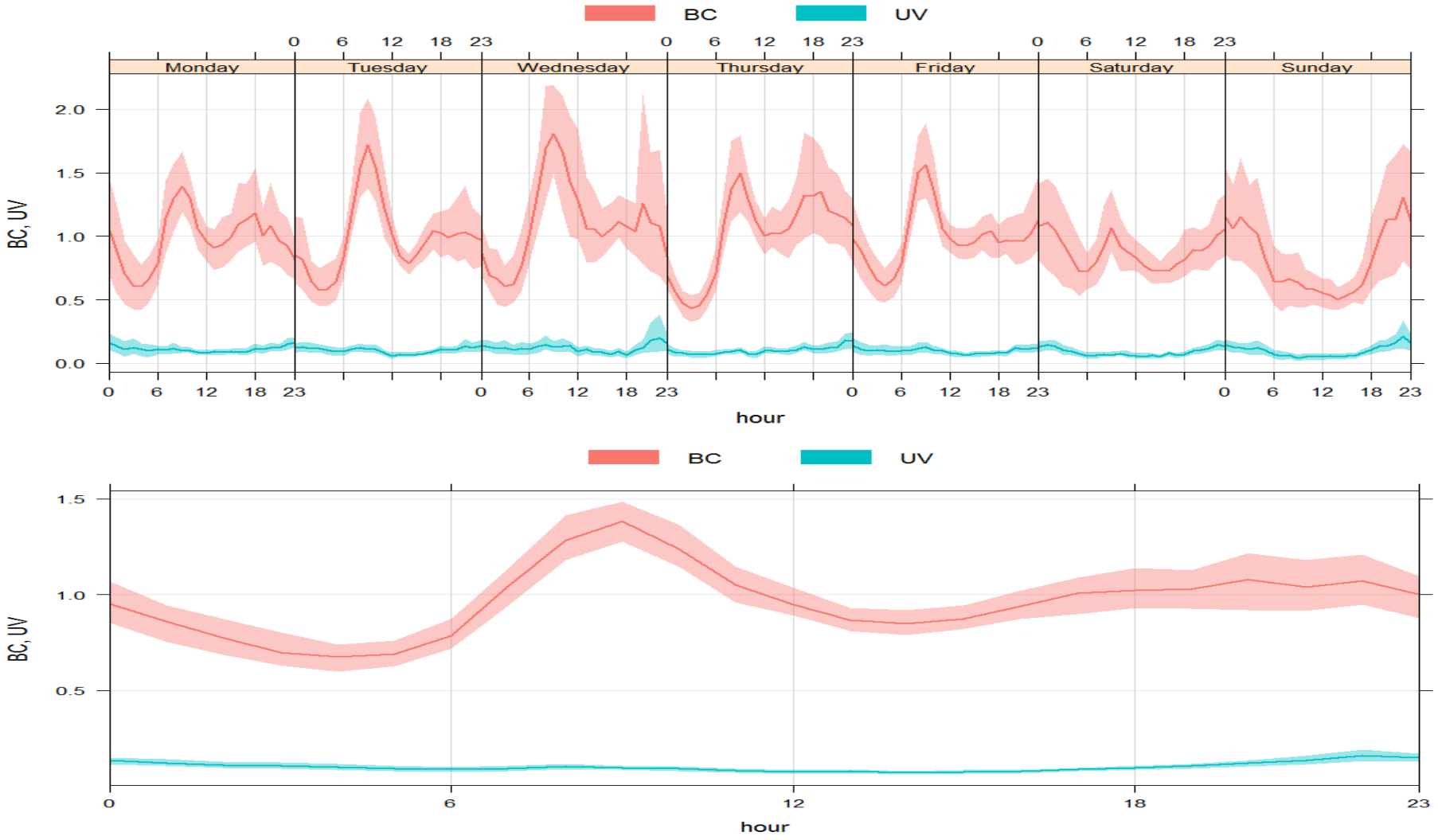
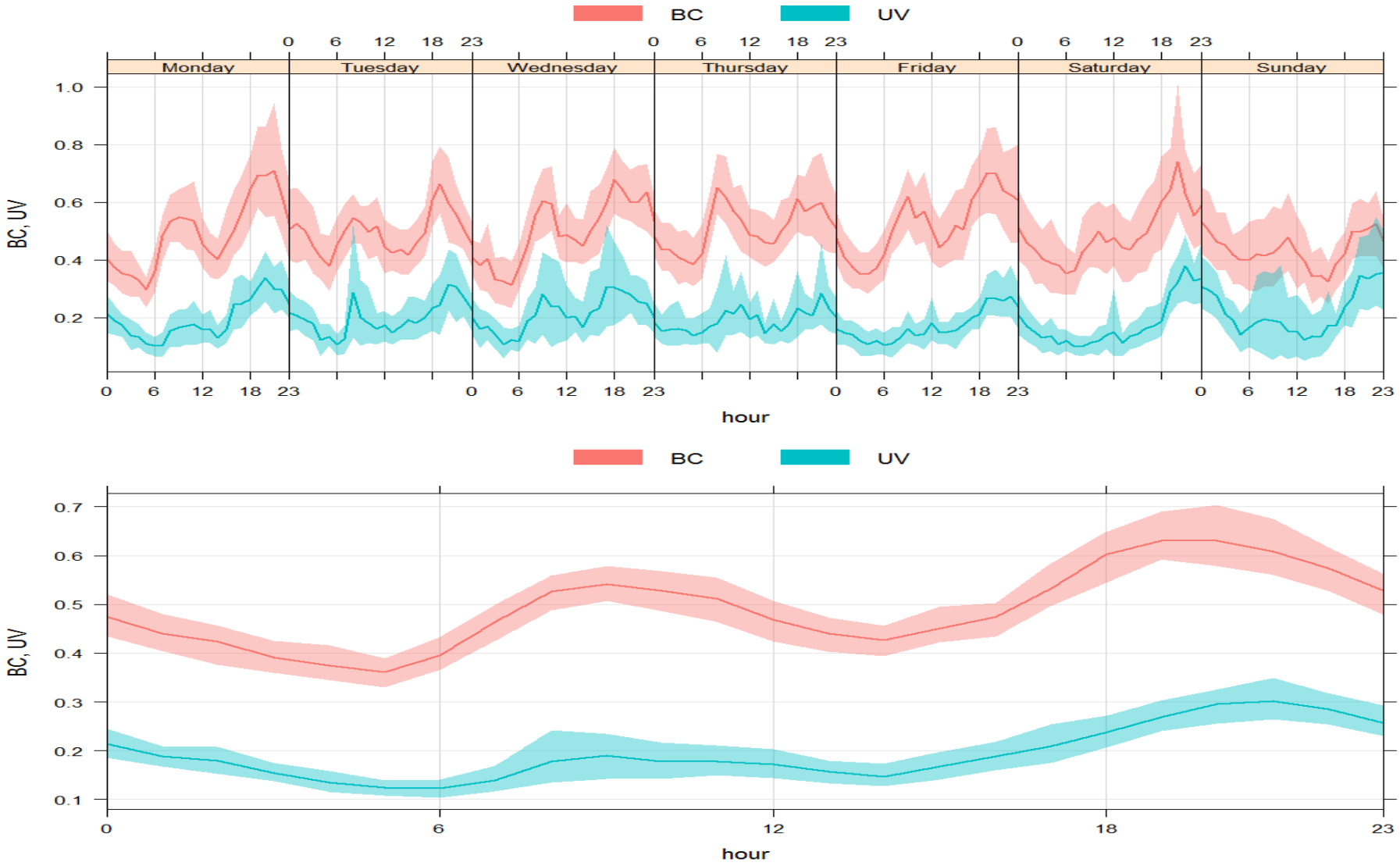
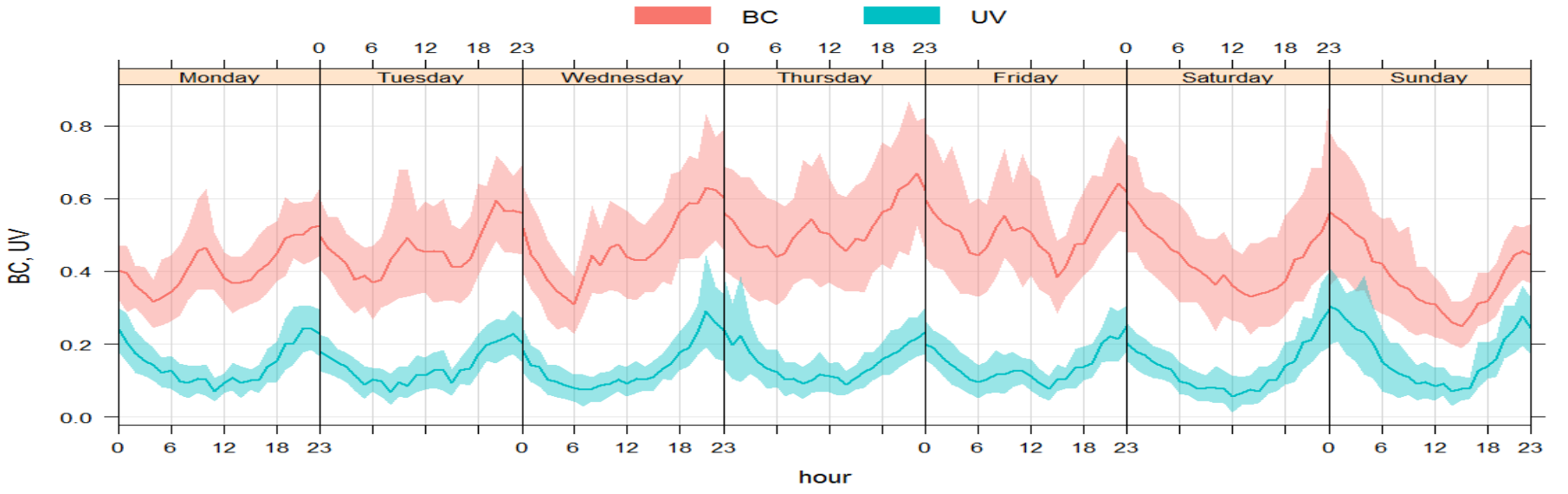
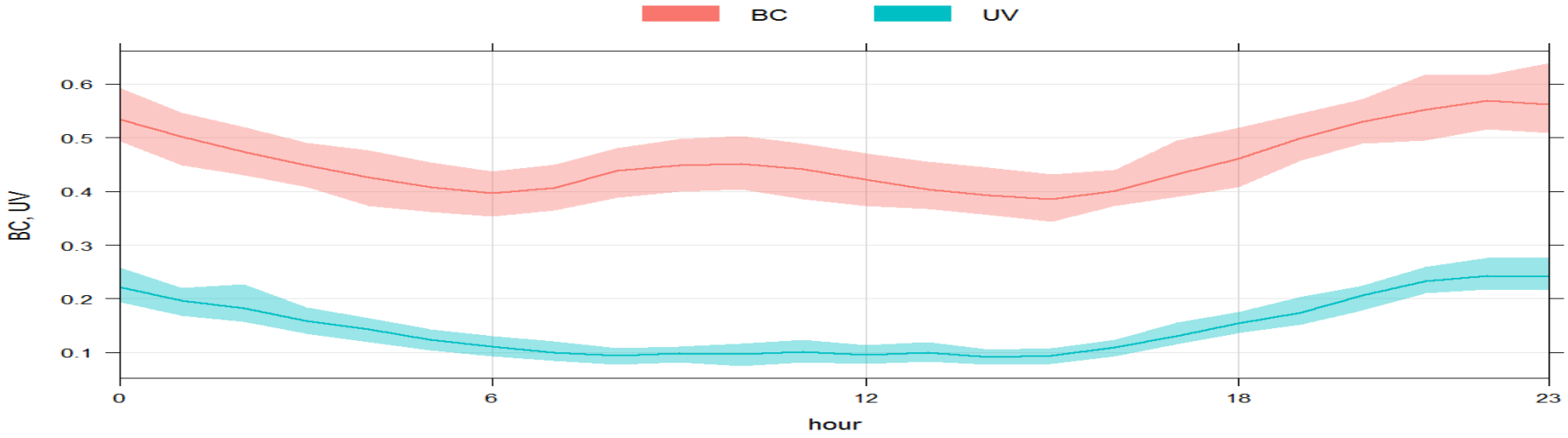


Figure16 2014 Urban Background sites


BC
UV
Monday
Tuesday
Wednesday
Thursday
Friday
Saturday
Sunday
BC, UV
hour
BC
UV
BC, UV
hour

Detling


BC
UV
Monday
Tuesday
Wednesday
Thursday
Friday
Saturday
Sunday
BC, UV
hour


BC
UV
BC, UV
hour

Harwell

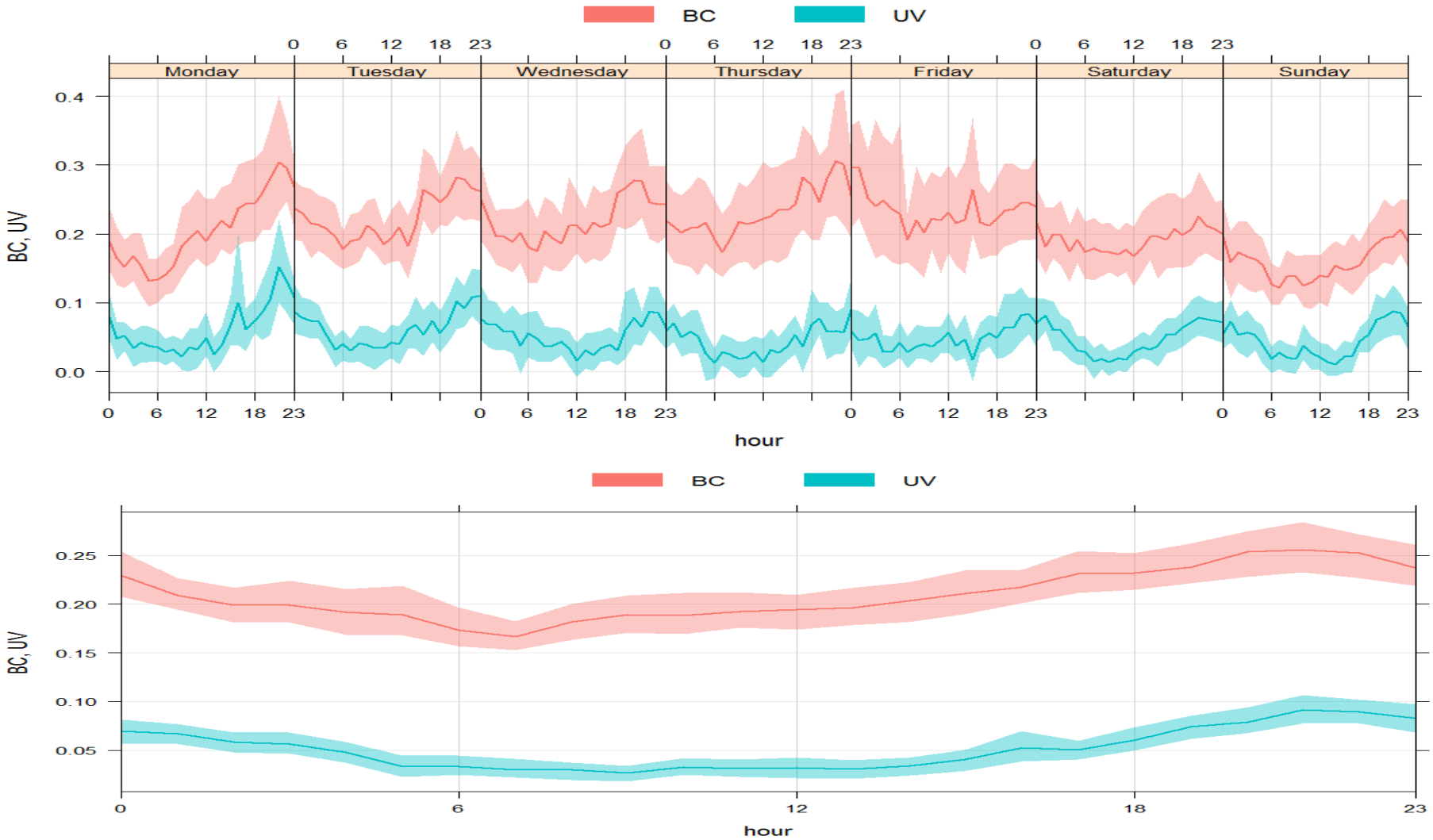
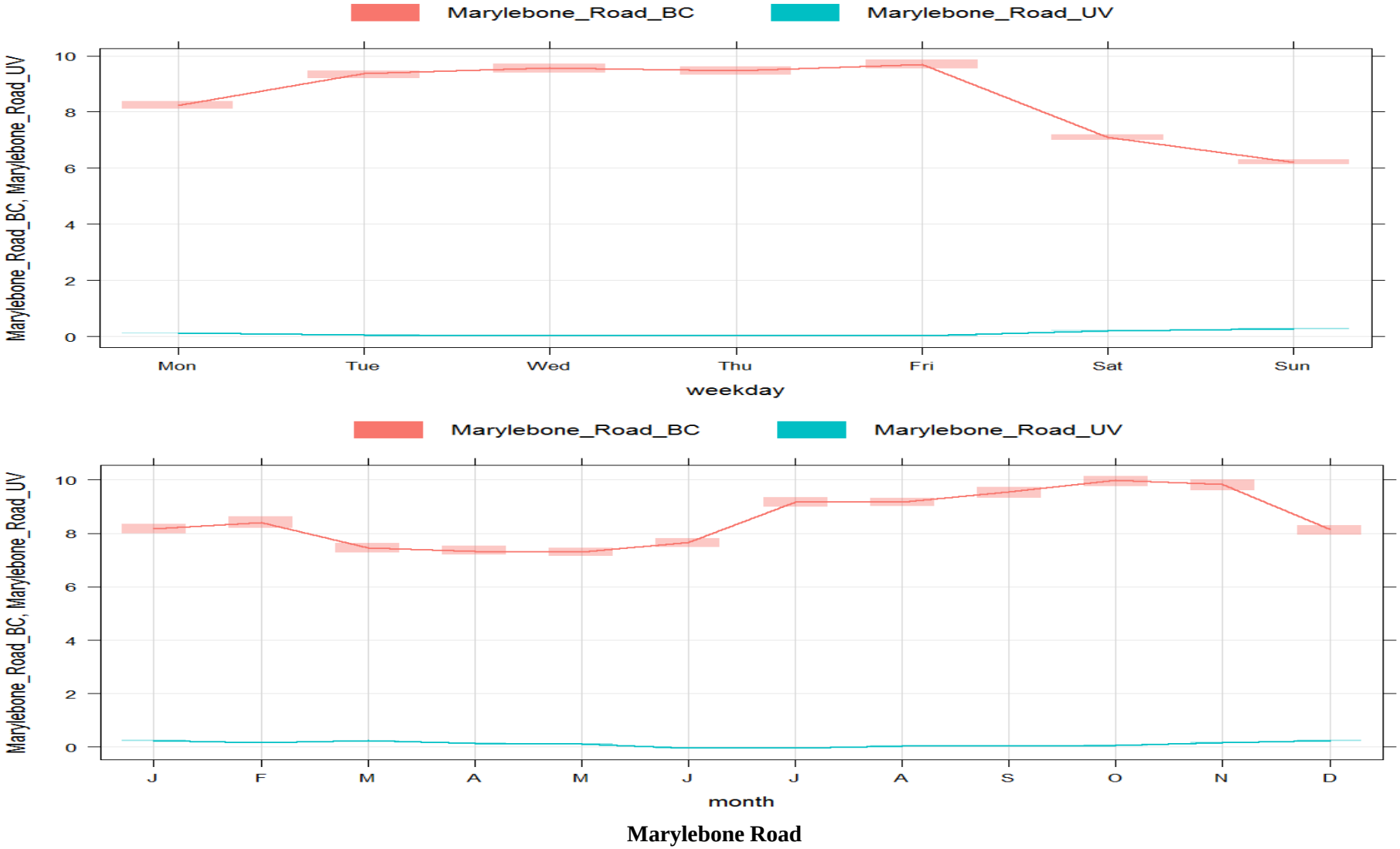


Figure 17 2014 Rural Background sites

2009 – 2014 Data



Marylebone Road

Figure 18 2009 – 2014 Roadside sites

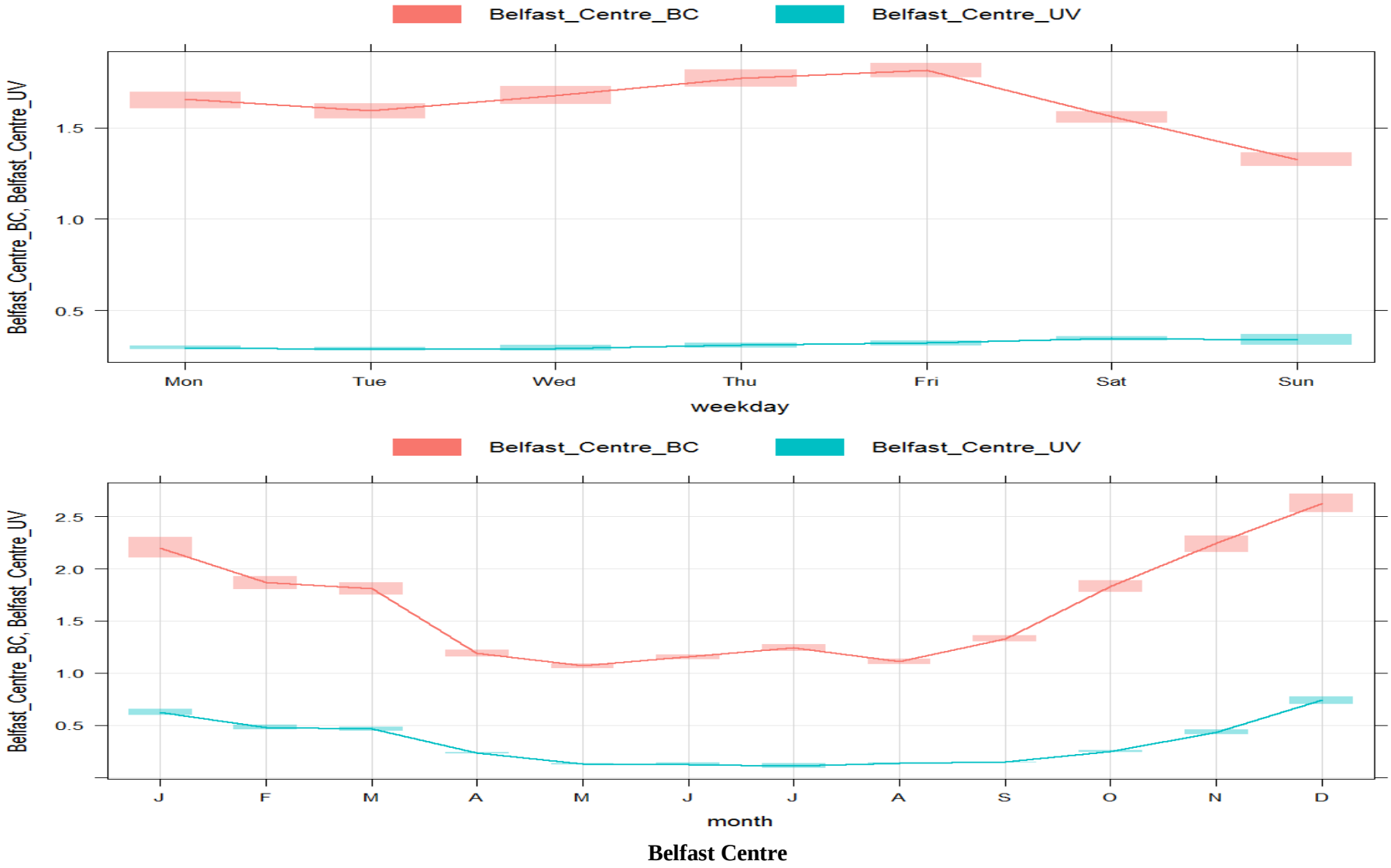
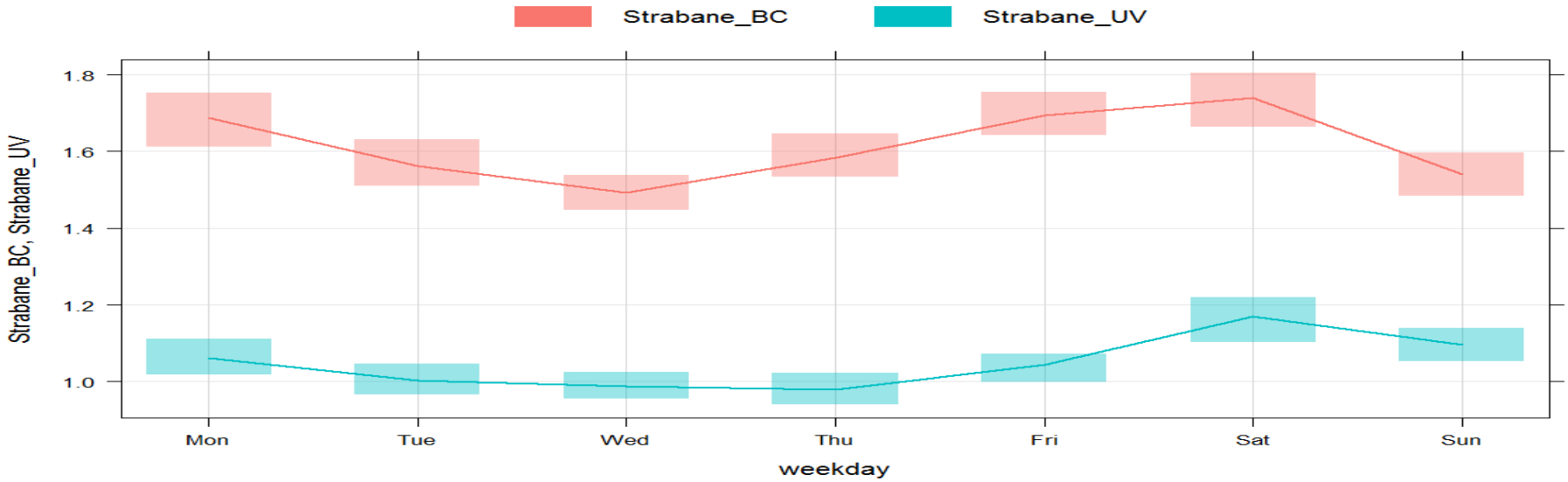
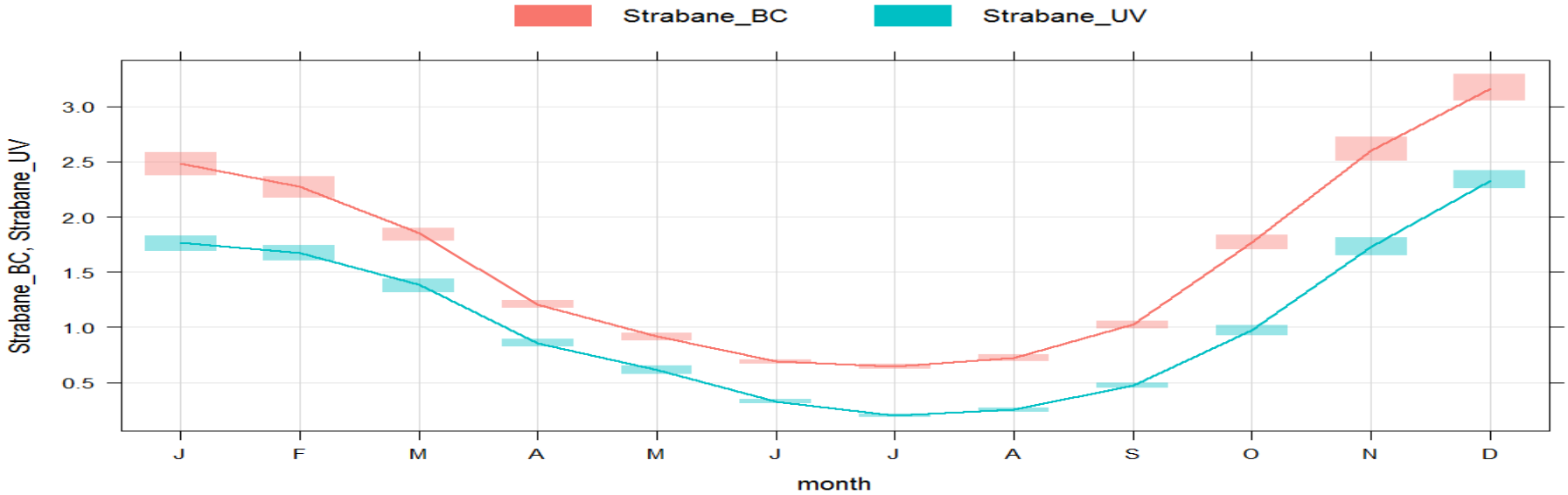
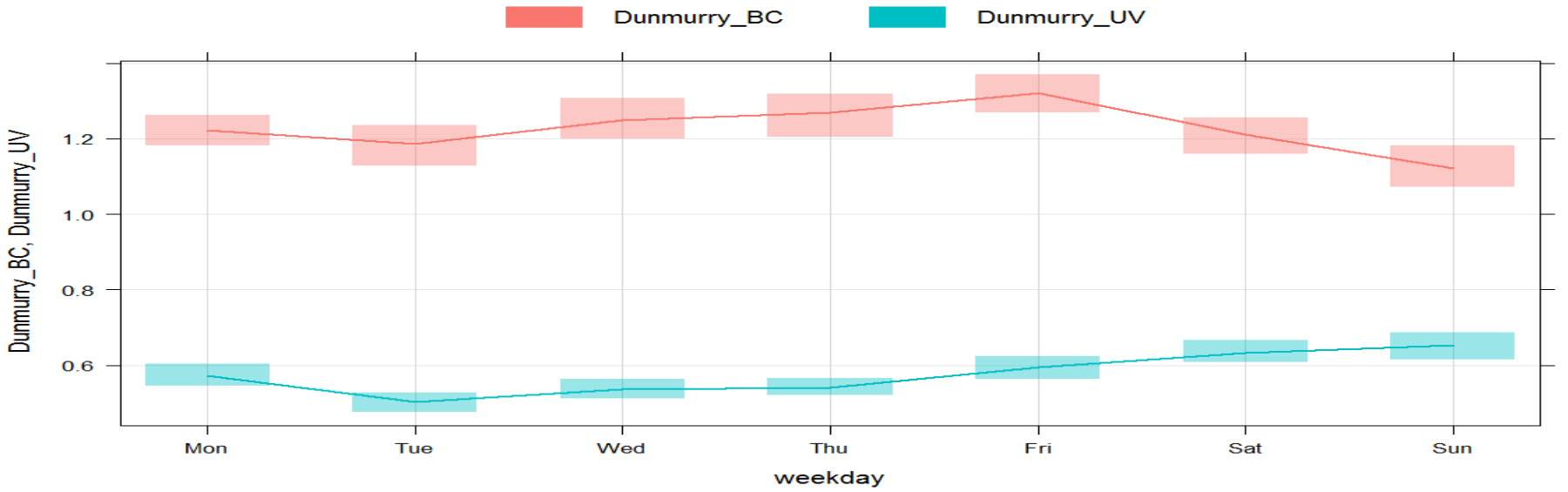


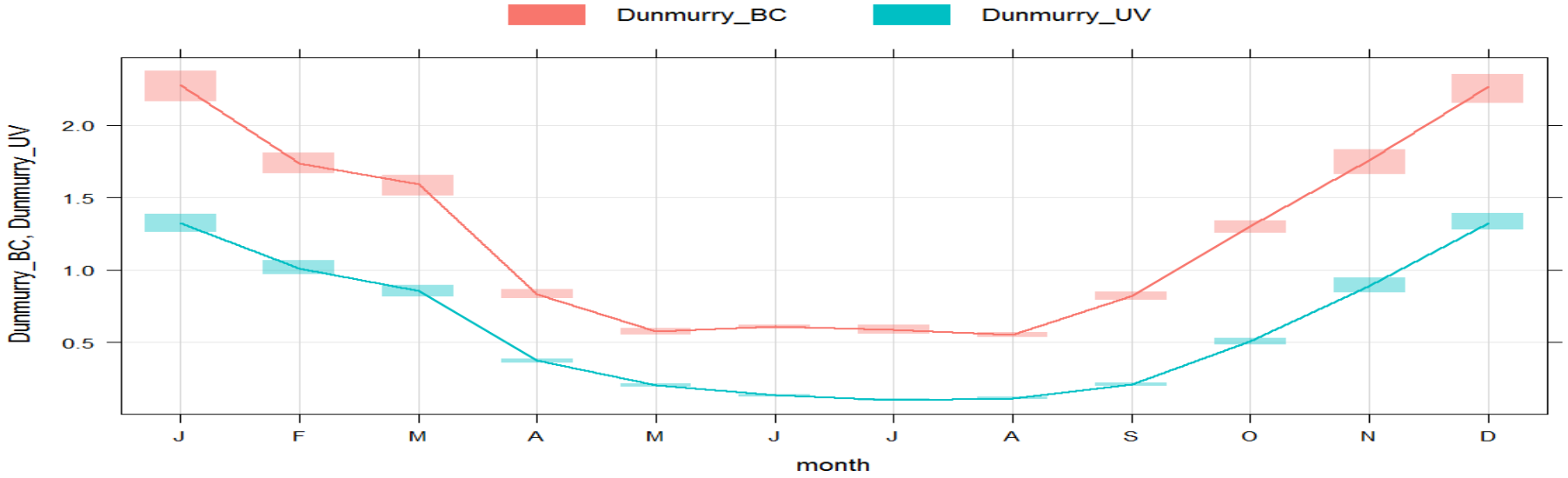
Figure 19 2009 – 2014 Urban Centre sites


Strabane_BC
Strabane_UV
Strabane_BC, Strabane_UV
1.8
1.6
1.4
1.2
1.0
Mon
Tue
Wed
Thu
Fri
Sat
Sun
weekday

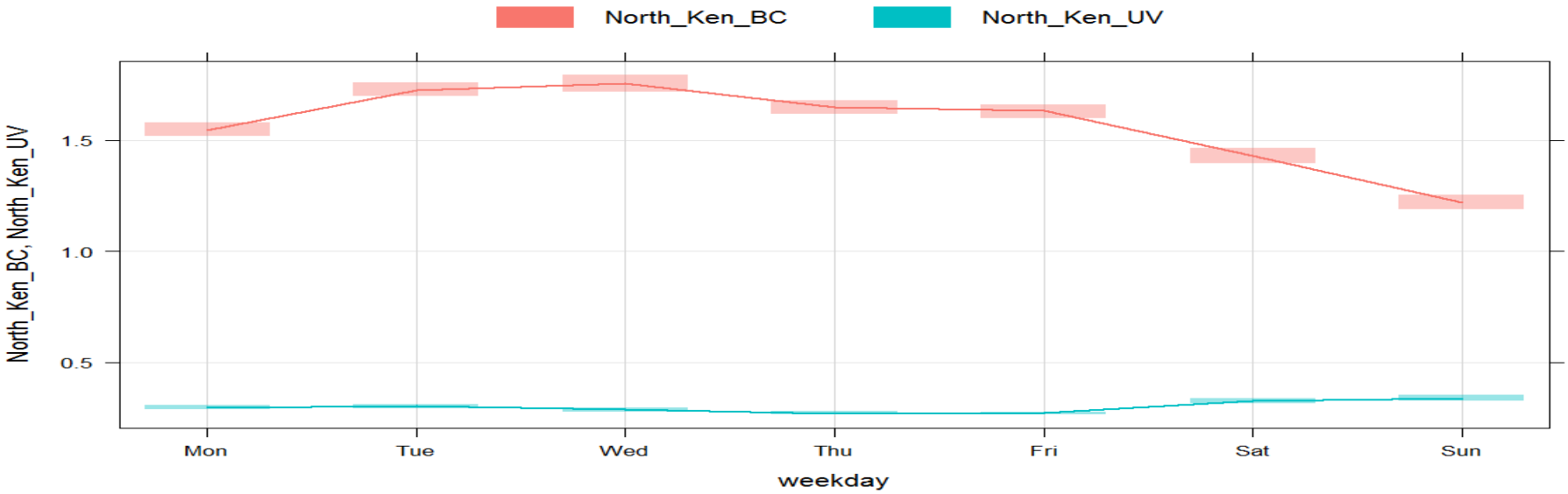

Strabane_BC
Strabane_UV
Strabane_BC, Strabane_UV
3.0
2.5
2.0
1.5
1.0
0.5
J
F
M
A
M
J
J
A
S
O
N
D
month

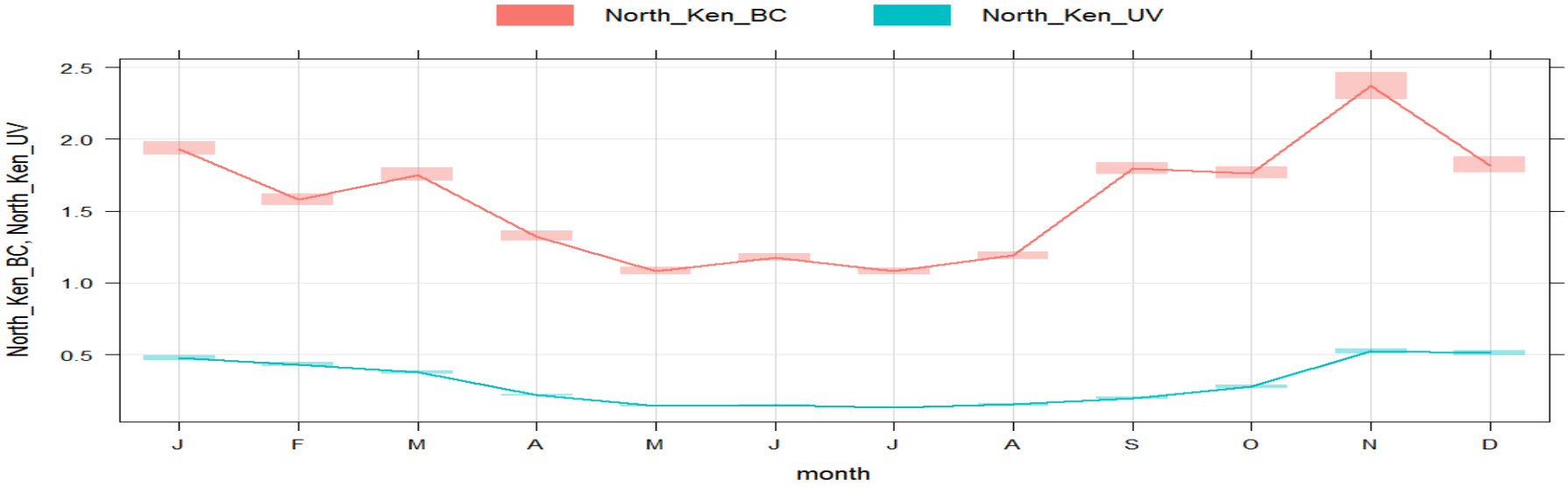
Strabane


Dunmurry_BC
Dunmurry_UV
Dunmurry_BC, Dunmurry_UV
1.2
1.0
0.8
0.6
Mon
Tue
Wed
Thu
Fri
Sat
Sun
weekday

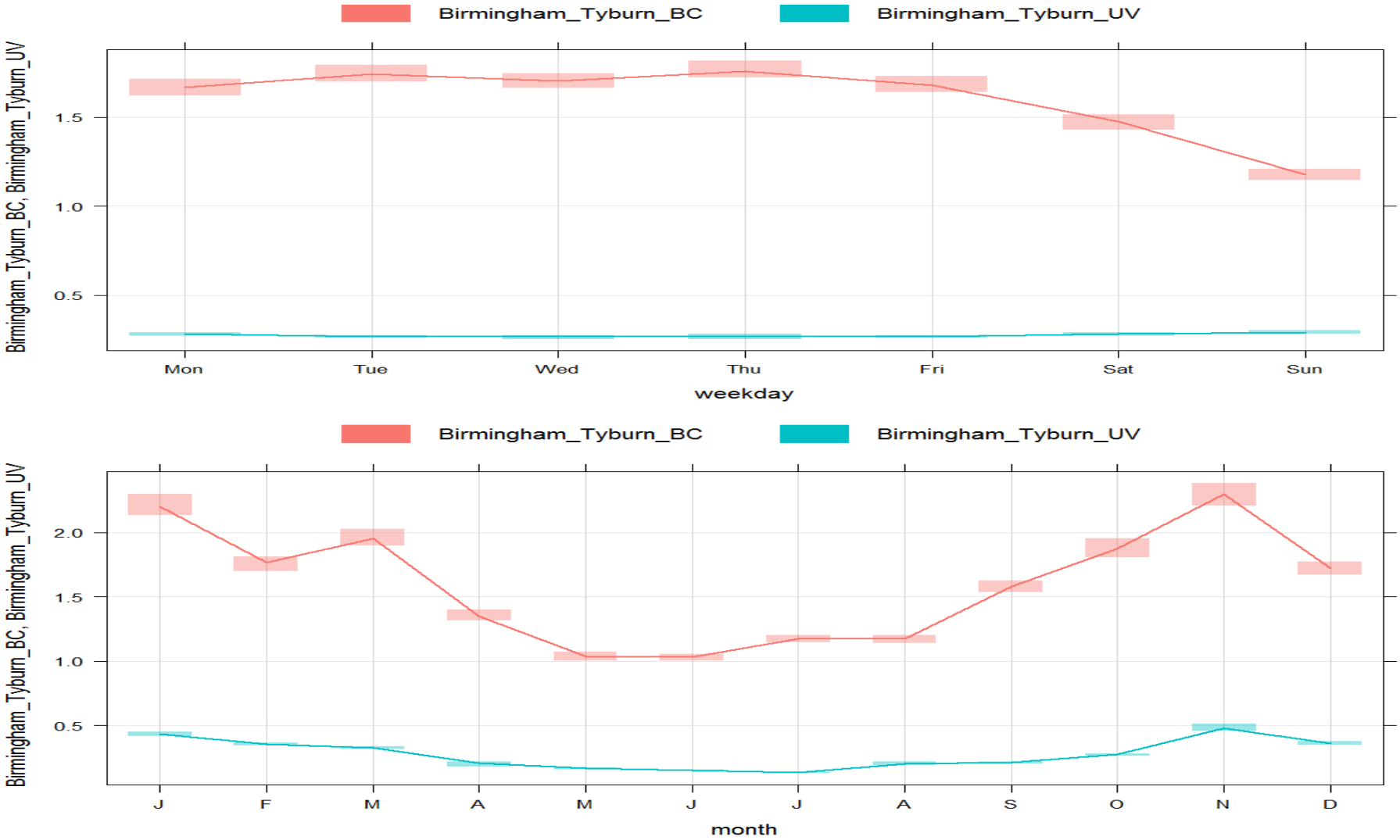

Dunmurry_BC
Dunmurry_UV
Dunmurry_BC, Dunmurry_UV
2.0
1.5
1.0
0.5
J
F
M
A
M
J
J
A
S
O
N
D
month

Dunmurry





North Kensington



Birmingham Tyburn Background

Figure 20 2009 – 2014 Urban Background sites

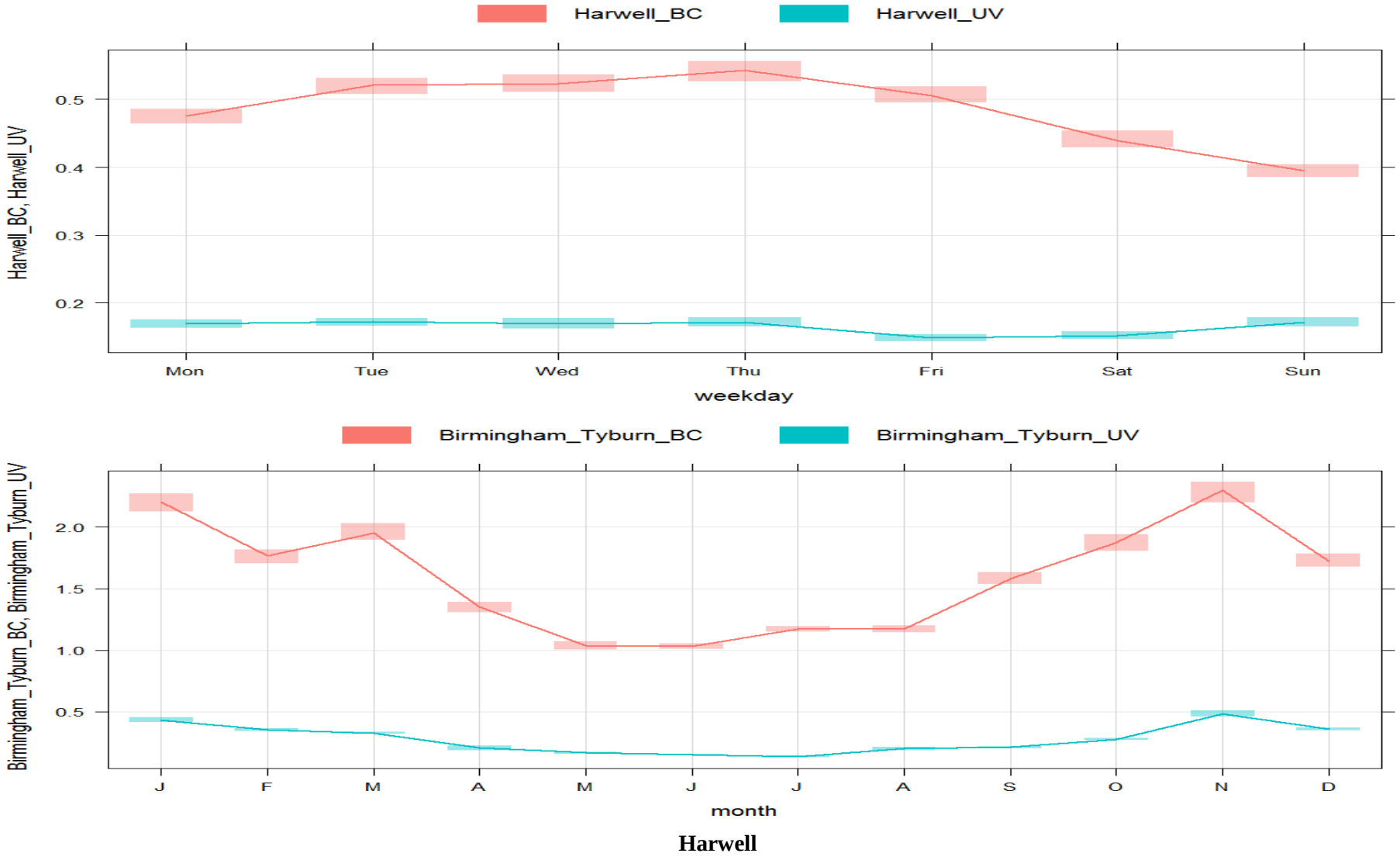


Figure 21 2009 -2014 Rural Background sites

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 decrease in Black Carbon concentrations at the weekend, when compared with weekdays, 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.

Birmingham Tyburn shows more of the traditional morning rush hour peak of Black Carbon in the morning, followed by a drop in concentrations during the day, with a smaller peak for the evening rush hour. Weekend concentrations are also a lot lower and relatively flat during the day. As with Marylebone Road there is little UV component signature, however Birmingham shows a slight increase in the evenings of the week end, indicating possible local solid fuel / wood burning secondary heating. The Wednesday evening peak is due to the large concentrations measured on the evening of 5th November. The same occurs in the urban background chart.

Marylebone Road shows no significant seasonal trend in either Black Carbon or UV component concentrations due to the consistent traffic flows being the dominant emission source of Black Carbon.

Urban Centre sites

Belfast centre also shows an increase in Black Carbon concentrations coinciding with the morning rush hour, but with concentrations remaining fairly constant from 17:00 hours until midnight. Black Carbon concentrations also show an increase late on Saturday evening / early Sunday morning, which can be assumed to be due to evening leisure journeys.

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

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. If it is assumed that the emissions from road transport are relatively consistent through the year then normalising the concentrations should reveal any monthly variability in either the Black Carbon or UV component emissions. This can be seen in Figure 22.

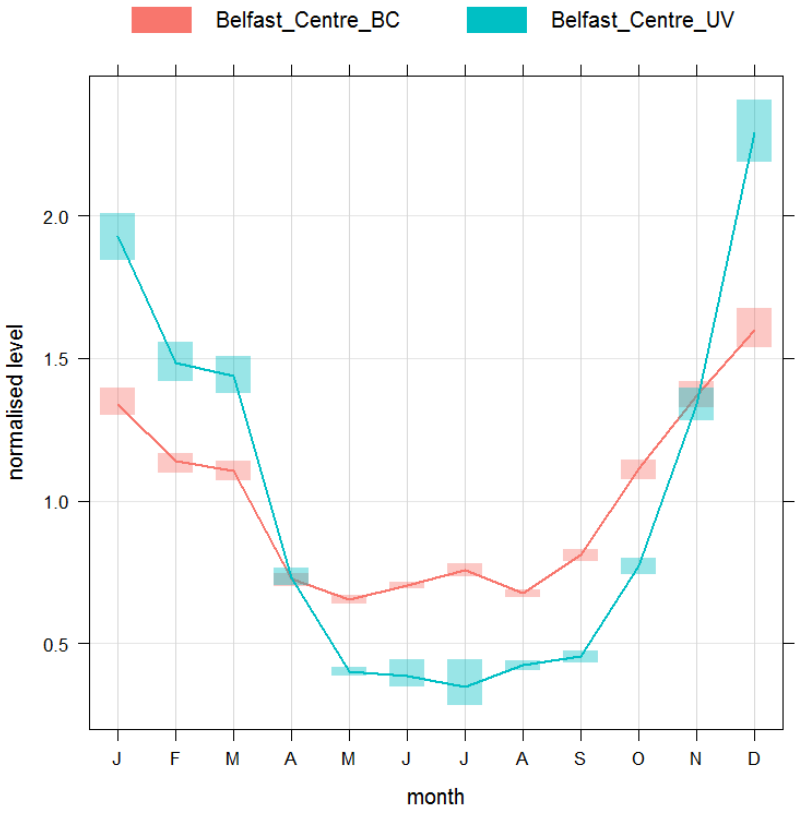


Figure 22 Normalised monthly variability at Belfast for the period 2009 - 2014

The increase in Black Carbon in July is due to localised burning around the period of 12 July as shown by Figure 23.

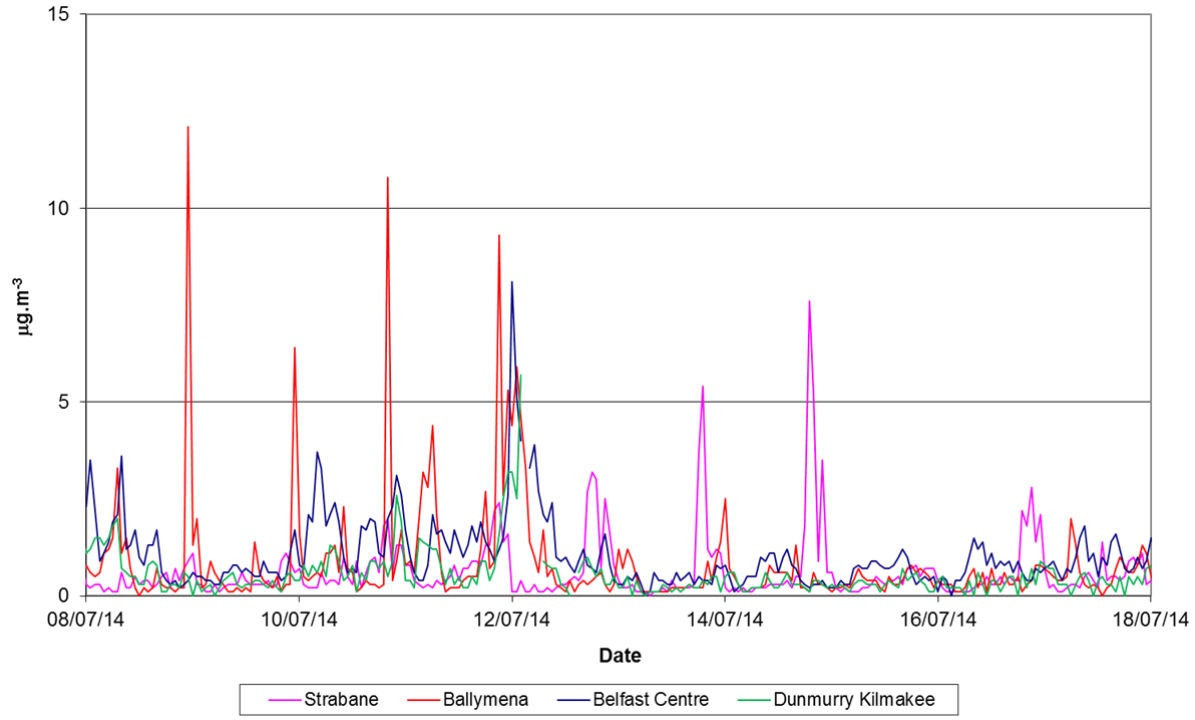


Figure 23 Black Carbon concentrations in Northern Ireland around the period of 12th July

Urban Background sites

Urban background sites can be split into three categories: those predominantly influenced by emissions from domestic heating, those away from main roads but still predominantly influenced by road traffic sources and those that are a combination of domestic and traffic sources.

Concentrations measured at Strabane, Ballymena and Dunmurry Kilmakee in Northern Ireland are dominated by emissions from domestic heating. UV component and Black Carbon concentrations follow similar hourly, daily and seasonal trends and have similar absolute concentrations. Strabane is not on the natural gas supply and domestic heating mainly comes from oil. Strabane is in a smokeless zone, however there is evidence that this is being ignored in some areas of the town and residents are burning smoky coal. Due to the large emission factors of PAHs from smoky coal[5] compared to oil and gas, it does not take many houses burning this coal to have a big influence on ambient concentrations. At Strabane there is little evidence of traffic emissions during the rush hour periods. Ballymena and Dunmurry are on the natural gas supply and this is the predominant source of domestic heating, however coal is often used as secondary heating in the evenings. Due to the difference in emission factor discussed above this can have a significant effect on ambient concentrations. At Ballymena and Dunmurry the morning rush hour is picked up in the Black Carbon concentrations, but the evening rush hour is masked by domestic emissions. Figure 24 gives the normalised monthly variability and Figure 25 gives the hourly variability

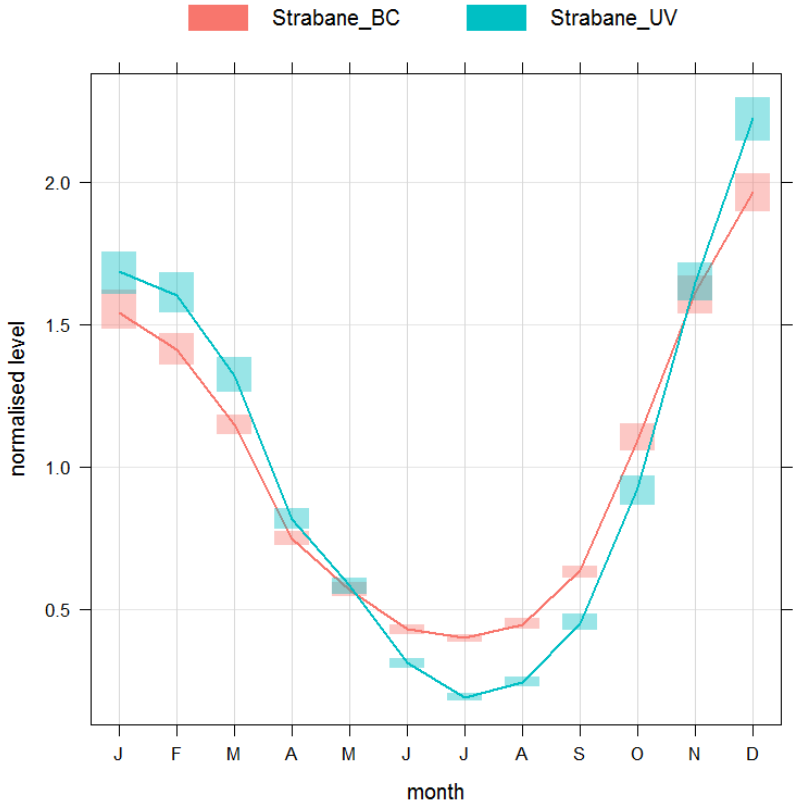


Figure 24 Normalised monthly variability at Strabane for the period 2009 - 2014

5 UK National Atmospheric Emissions Inventory

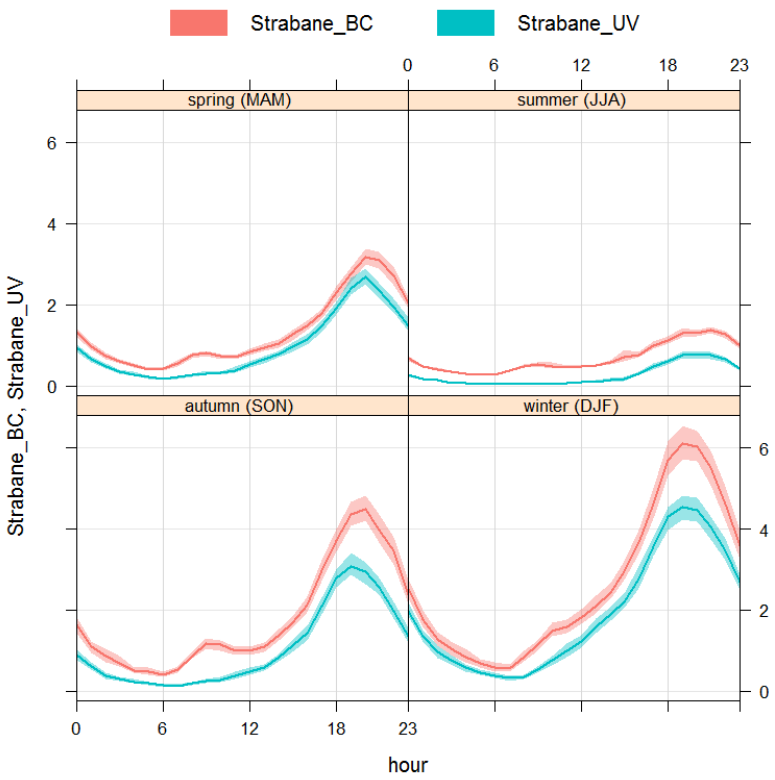


Figure 25 **Seasonal Black Carbon and UV component concentrations measured at Strabane in 2014**

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

Concentrations measured at Birmingham Tyburn and North Kensington are dominated by emissions from road traffic. The morning rush hour can be clearly seen in the Black Carbon concentrations, with the evening rush hour seen to a lesser extent. The peak in evening Black Carbon concentrations continues later into the evening than at roadside sites and could be linked to small scale emissions from domestic heating. This peak in the evening Black Carbon concentrations is also seen as a small peak in the UV component. Both sites have lower Black Carbon concentrations at the weekend and slightly elevated UV component concentrations over the same time scale. Also both sites show a seasonal component in Black Carbon and UV component concentrations. Both these phenomena point to the use of solid fuel (possibly wood burning) in the urban area.

Rural sites

The rural background site concentrations are lower than the other site classifications, as expected. The effect of local heating can also be seen in the concentrations at the Detling suburban site. All sites display the morning rush hour in the Black Carbon concentration to a small extent.

Over the longer dataset, Harwell shows some seasonality in the UV component concentration associated with domestic emissions, and reduced Black Carbon concentrations at weekends associated with lower local traffic flows.

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 three (different) sites.

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 Concentration and Number Network[6]. 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 26 to 28. The regression is calculated according to the Reduced Major Axis (RMA) method[7], which is based on minimising the product of the *x* and *y* deviations between the data values and "fitted values" instead of the least squares method, which minimises the sum of the squared deviations between the dependent variable (y) and the "fitted values". RMA is better suited to air quality measurements as pollutant concentrations are often dependent on each other, so there is no real separation into dependent and independent variables. Also deviations between fitted and observed data values will occur in both *x* and *y* directions due to random measurement uncertainties.

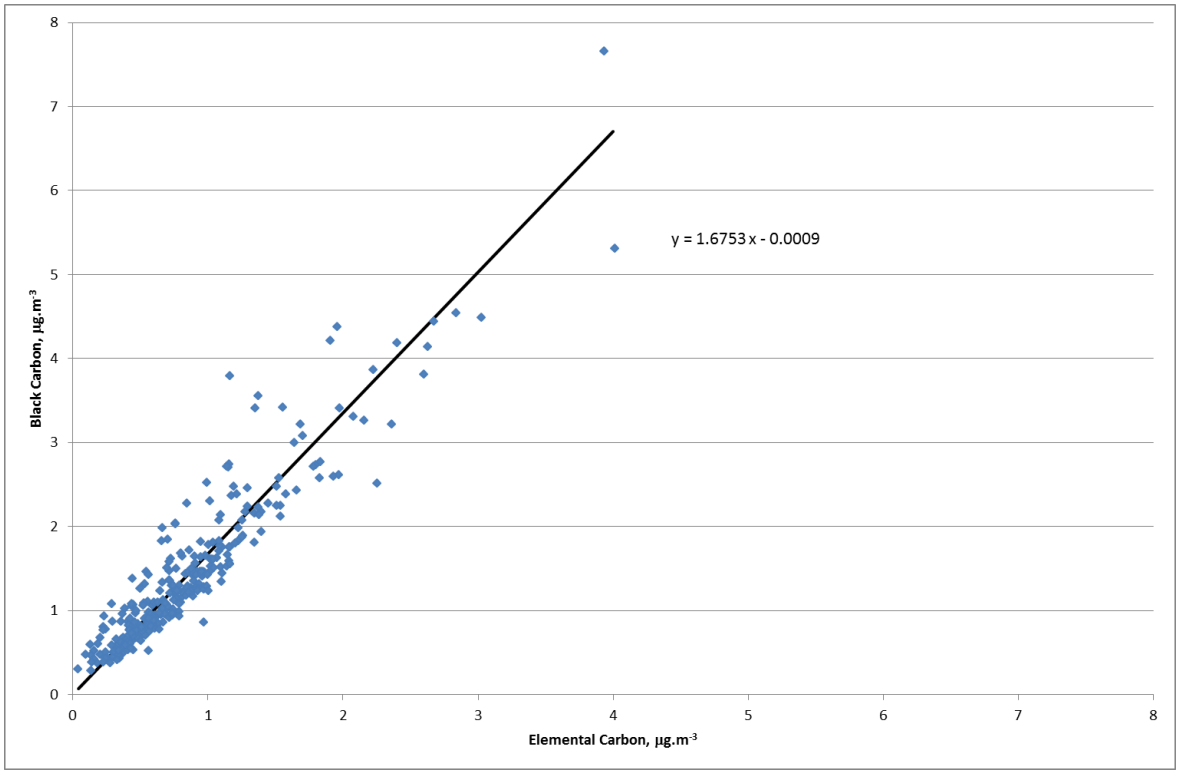


Figure 26 2014 EC and BC Measurements at North Kensington

6 S Beccaceci et al, Draft NPL REPORT, 2014 Annual Report for Airborne Particulate Concentrations and Numbers in the United Kingdom (phase 3), June 2014

7 G.P. Ayers, Comment on regression analysis of air quality data, Technical Note, Atmospheric Environment, 35 (2001) 2423 - 2425

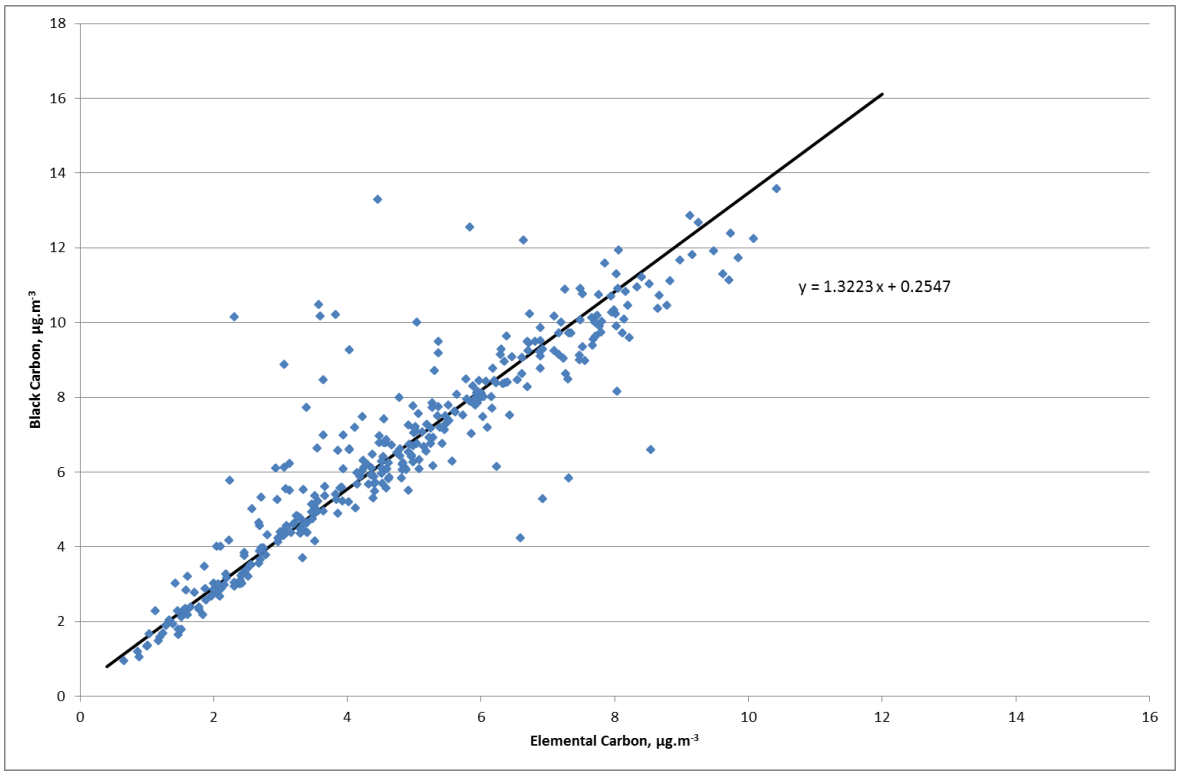


Figure 27 2014 EC and BC Measurements at Marylebone Road

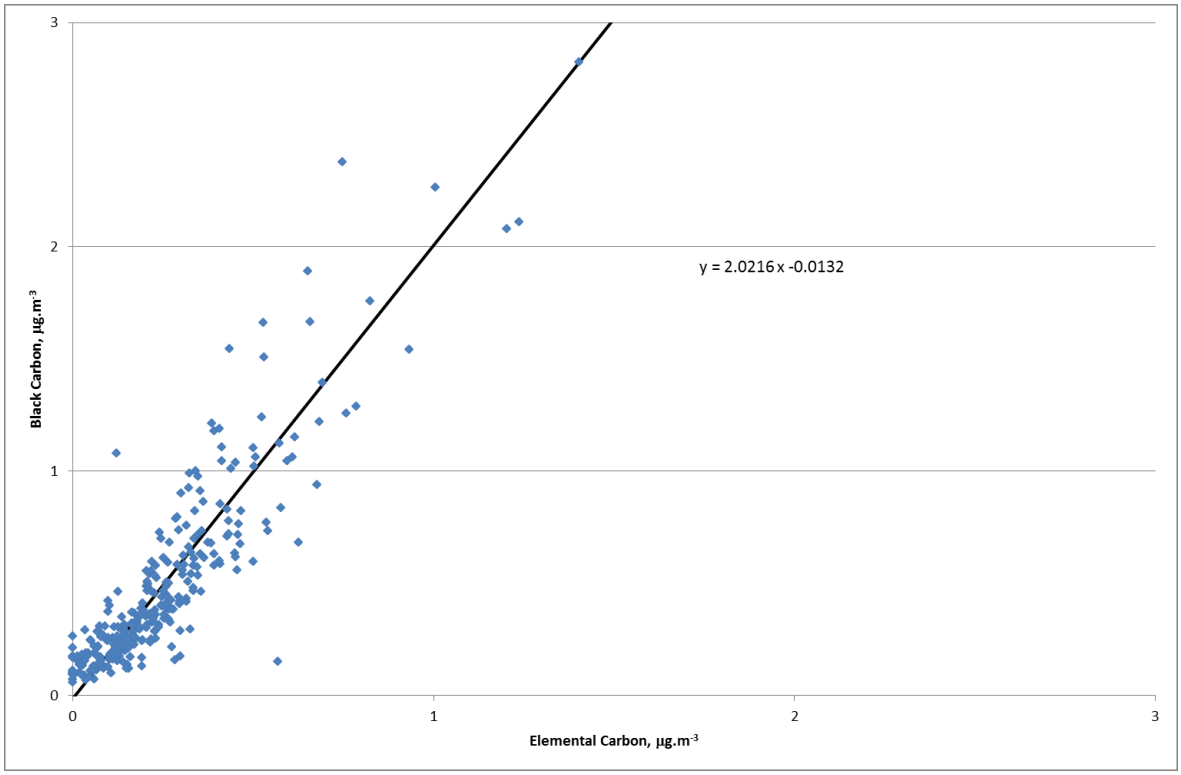


Figure 28 2014 EC and BC Measurements at Harwell

It can be seen that there are good linear relationships ($R^2 > 0.8$) between the Elemental Carbon and Black Carbon concentrations measured at all three sites. The relationship between Black Carbon and Elemental

Carbon is markedly different between sites, however, and this difference seems to have developed in recent years. The annual regression results (all RMA) are shown in Table 14.

	Harwell		North Kensington		Marylebone Road	
Year	**Relationship**	**R^2**	**Relationship**	**R^2**	**Relationship**	**R^2**
2009	N/A*	N/A	1.05 x + 0.20	0.858	1.36 x - 0.69	0.776
2010	1.32 x + 0.06	0.555	1.37 x – 0.32	0.734	1.28 x + 0.56	0.946
2011	1.52 x + 0.18	0.844	1.26 x + 0.07	0.810	1.50 x - 0.35	0.924
2012	1.84 x + 0.06	0.908	1.42 x + 0.17	0.906	1.43 x + 0.01	0.898
2013	1.74 x + 0.17	0.865	1.59 x + 0.33	0.871	1.47 x + 0.39	0.679
2014	2.02 x - 0.01	0.802	1.68 x - 0.00	0.872	1.32 x + 0.25	0.819

*There is not enough BC data collected at Harwell in 2009 to form a reliable relationship as the Aethalometer was only installed in November 2009.

Table 14 Relationships between Black Carbon and Elemental Carbon over the period 2009 – 2014

As the intercepts of the regression lines are all close to zero show that both analysis methods are measuring the same physical quantity, i.e. when there is no Elemental / Black Carbon present both methods read zero and that the sensitivity of the techniques to low concentrations is not affecting the comparison.

It can be seen that the slopes, i.e. the measured amounts of Black Carbon relative to Elemental Carbon, have been roughly constant at Marylebone Road, at 1.4 ± 0.1, but appear to have generally increased year on year at Harwell (from around 1.3 to 2.0) and North Kensington (from around 1.1 to 1.7).

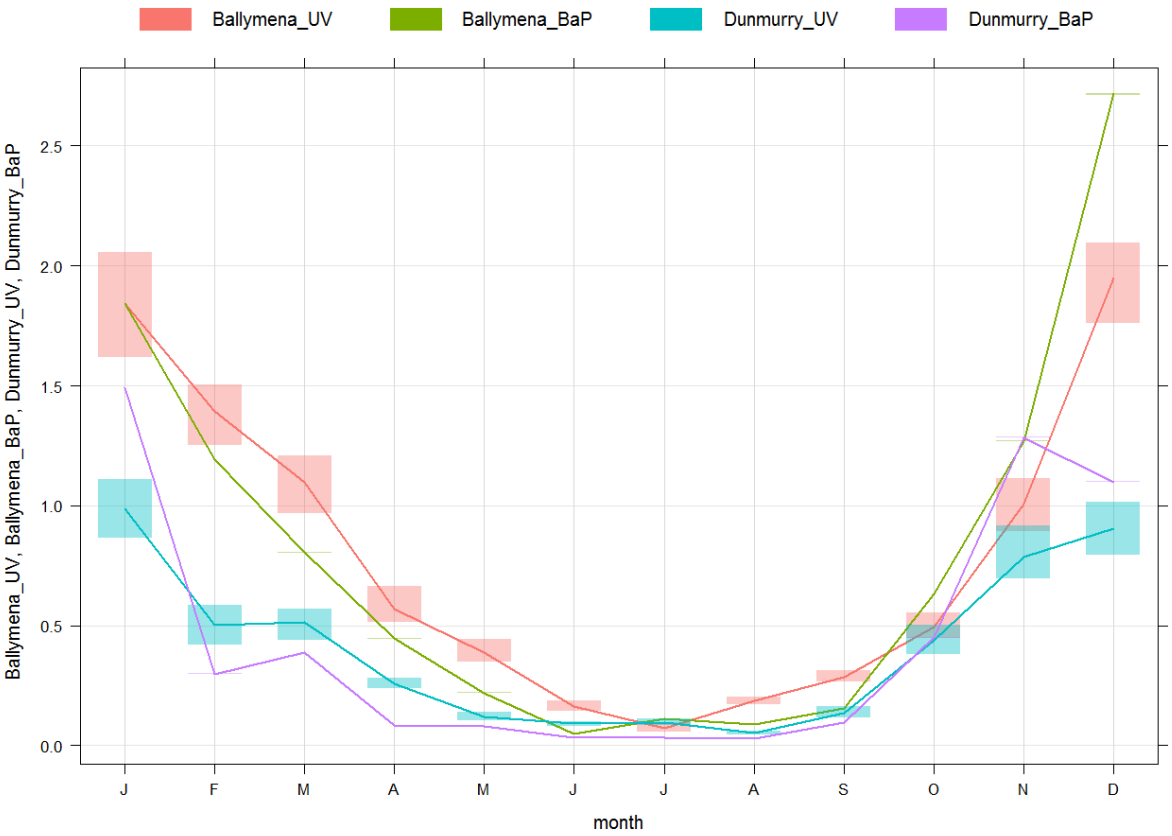
There are three possible general explanations for the increase in slope at these two sites, if it is real. (1) The method used for Black Carbon measurement has changed such that reported concentrations are now relatively higher than they used to be; (2) the method used for Elemental Carbon measurement has changed such that reported concentrations are now relatively lower than they used to be; and (3) the nature of the soot-like pollution has changed in a way that causes larger differences between the methods.

The Black Carbon method has not changed in any significant way over the years. The OCEC Sunset analyser was upgraded in early 2014 with a new optical system with a more powerful laser. This should have improved the determination of the OC / EC split point and improved the quality of the EC results. This seems to be apparent from the reduced scatter in the Marylebone Road data in 2014 compared to 2013, but the slope there did not change significantly, and this upgrade would not explain the increases in slope observed before the upgrade took place.

5.4.2 Polycyclic Aromatic Hydrocarbons (PAH)

Monthly concentrations of benzo[a]pyrene are measured at Dunmurry Kilmakee, Ballymena and Birmingham Tyburn Background under the UK PAH Network[8]. The concentrations at Birmingham are much lower than at the other two sites, and are not presented here graphically. Aethalometer concentrations (UV component) have been averaged into monthly measurements and plotted as a time series with the benzo[a]pyrene concentration for Dunmurry and Ballymena in Figure 29.

8 2014 Draft NPL 2014 Annual Report for UK PAH Network.



Note: The units are different for the two quantities, the PAH measurements are represented in ng.m^{-3} while the UV component is represented as µg.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.

Figure 29 UV component and Benzo[a]pyrene concentrations measured at Ballymena and Dunmurry in 2014

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.

Looking at data over the full period of Network operation, the move of the site from Dunmurry High School to Dunmurry Kilmakee has had an effect on the concentrations measured. Concentrations over the period 2009 – 2014 are shown in Table 15.

	BaP,ng.m^{-3}		UV component, μg.m^{-3}	
Year	**Dunmurry High School**	**Dunmurry Kilmakee**	**Dunmurry High School**	**Dunmurry Kilmakee**
2009	0.83		0.7	
2010	1.44		0.9	
2011	0.86		0.6	
2012	0.58	0.49	0.6	0.5
2013		0.46		0.4
2014		0.45		0.4

Table 15 Annual Mean BaP and UV component concentrations measured in Dunmurry over the period 2009 – 2014

The reduction in concentration of both pollutants may be due to different topography between the two sites or due to differences in local fuel use.

Table 16 compares the ratio of the BaP and UV component concentrations at Dunmurry, Ballymena and Birmingham Tyburn Background sites for the period 2011 to 2014.

	Dunmurry			**Ballymena**			**Birmingham Tyburn Background**		
Year	**UV Component, μg.m^{-3}**	**BaP, ng.m^{-3}**	**BaP / UV**	**UV Component, μg.m^{-3}**	**BaP, ng.m^{-3}**	**BaP / UV**	**UV Component, μg.m^{-3}**	**BaP, ng.m^{-3}**	**BaP / UV**
2011	0.60	0.86	1.438	N/A	N/A		0.30	0.199	0.663
2012	0.55	0.53	0.968	2.10	2.00	0.952	0.30	0.254	0.847
2013	0.40	0.46	1.150	0.80	0.82	1.025	0.20	0.200	1.000
2014	0.40	0.45	1.125	0.76	0.79	1.039	0.23	0.210	0.913

Table 16 UV component and BaP concentrations at Dunmurry, Ballymena and Birmingham Tyburn Background sites for the period 2011 – 2014.

The mean ratio of BaP/UV for the three sites is 1.011. This ratio can then be used at Strabane, where the Aethalometer shows a raised UV component concentration, to give an indication of the probable BaP concentration. Table 17 gives the predicted BaP concentrations at Strabane for the last 5 years.

Year	UV component concentration	Predicted BaP concentration ng.m^{-3}
2009	0.9	0.91
2010	1.3	1.31
2011	0.8	0.81
2012	1.1	1.11
2013	1.2	1.21
2014	1.1	1.10

Table 17 Predicted BaP concentrations from UV component concentration at Strabane for the period 2009 to 2014.

For 4 out of the last 6 five years the predicted BaP concentration is predicted to be above the 1.0ng.m^{-3} target value in the EC Directive 2004/107/EC[9] relating to ambient BaP concentrations. The average concentration over the last 6 years is predicted to be 1.08 ng.m^{-3}.

9 DIRECTIVE 2004/107/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL, relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, 15 December 2004.

A detailed analysis of PAH concentrations in Northern Ireland is contained in an NPL Report for the Department for the Environment Northern Ireland[10].

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. Two different types of instruments provide particulate mass concentrations across the Black Carbon Network: TEOM FDMS Model CB drier, 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 18.

Site	BC μg.m^{-3}	TEOM FDMS PM_{10} μg.m^{-3}	TEOM FDMS $PM_{2.5}$ μg.m^{-3}	MetOne BAM PM_{10} μg.m^{-3}	Percent BC PM_{10} %	Percent BC $PM_{2.5}$ %
Marylebone Road	6.6	26	18		25.4	36.7
Birmingham Tyburn Roadside	2.9	20	14		14.5	20.7
Birmingham Tyburn Background	1.4	19	13		7.4	10.8
North Kensington	1.4	N/A	16		N/A	8.8
Belfast Centre	1.4	16	11		8.8	12.7
Glasgow Townhead	1.0	13	7		7.7	14.3
Harwell	0.5	N/A	9		N/A	5.6
Auchencorth Moss	0.2	8	7		2.5	2.9
Detling*	0.5	25			2.0	
Strabane*	1.6			17.0	9.4	

Note: * Local Authority run site, may not have identical QAQC procedures to AURN datasets. MetOne data is taken from the Air Quality Northern Ireland web site where it is stated to be Reference Equivalent.

Grey shaded cells indicate no measurements were made.

Table 18 Comparison of Annual Black Carbon and Particulate Mass Concentrations

Data capture for the North Kensington and Harwell PM10 TEOM-FDMS systems was below the 75% required for a valid annual average. 2014 data capture for both of these 2 sites was 74%.

The particulate mass measurements made by the bottom two 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.

It can be seen that the PM_{10} and $PM_{2.5}$ mass concentration measured at Marylebone Road and Birmingham Tyburn roadside sites have a much higher percentage of Black Carbon than the other sites. Black Carbon represents a significant proportion of the total particulate mass at sites influenced by road

10 D Butterfield, R Brown, NPL REPORT AS66, Polycyclic Aromatic Hydrocarbons in Northern Ireland, February 2012.

traffic emissions. Any significant reduction in Black Carbon emissions from road traffic should lead to a measurable reduction in PM_{10} and $PM_{2.5}$ mass concentrations.

The same comparison cannot be done for the UV component as this 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.

5.5 TRENDS

Short and long-term trends in Black Carbon and UV component concentrations are given below.

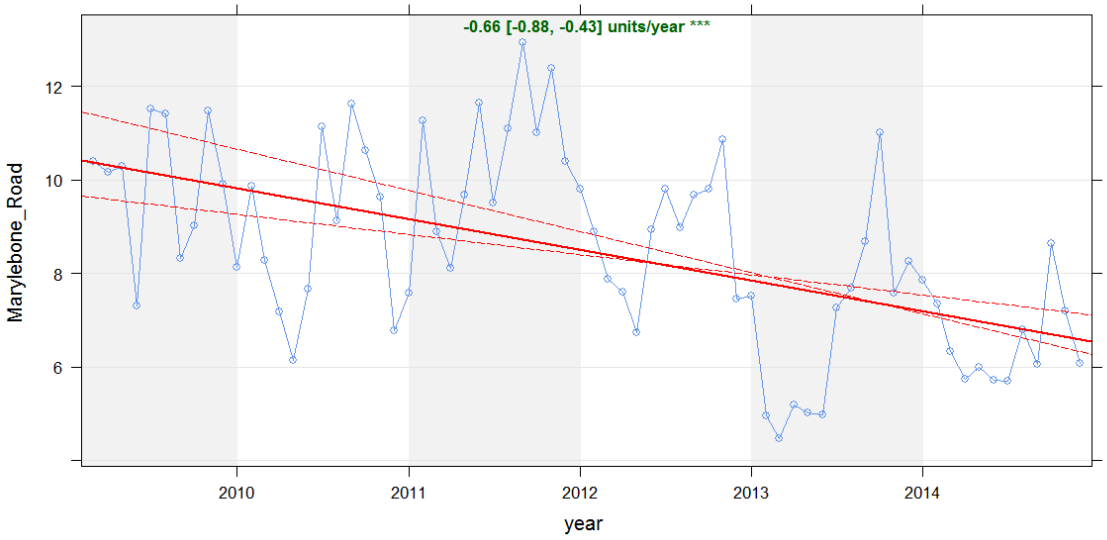
5.5.1 Short-Term Trends by Site

Figures 30 to 39 show the trend in Black Carbon and UV component concentrations as monthly averages over the full calendar years 2009 to 2014. The Theil-Sen method in OpenAir[4,5] was used to calculate the regression parameters including slope and uncertainty in the slope.

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

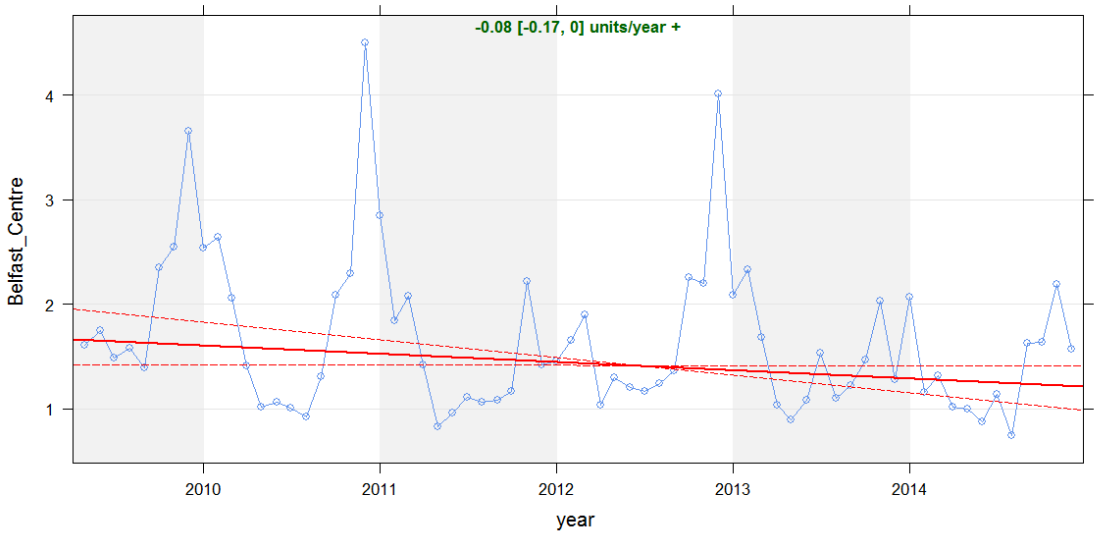
Bootstrap resampling provides the confidence interval for the regression slope. For these analyses the 2.5^{th} and 97.5^{th} percentile slopes are taken from all possible slopes.

5.5.1.1 Black Carbon



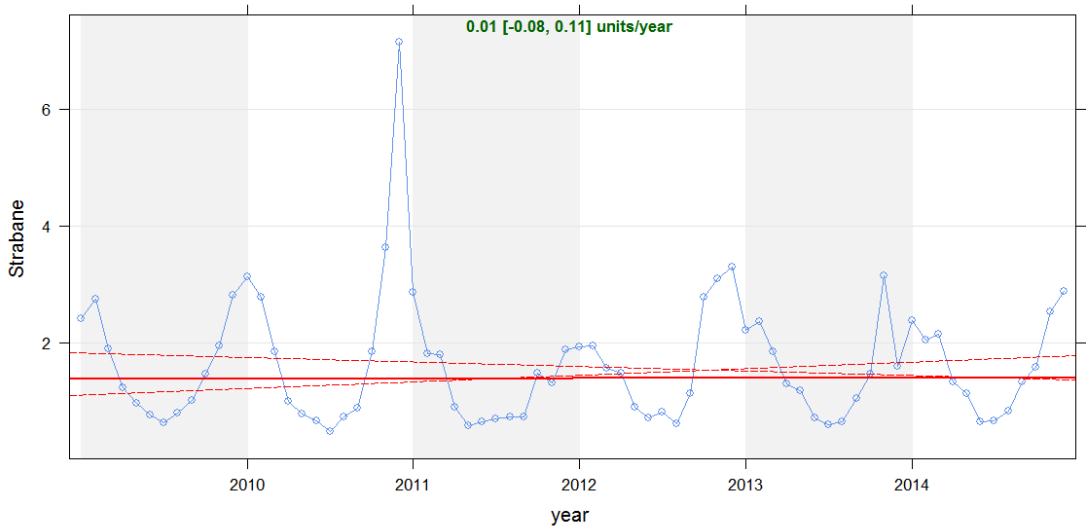
Marylebone Road

Figure 30 Black Carbon concentrations measured at roadside sites, 2009 – 2014

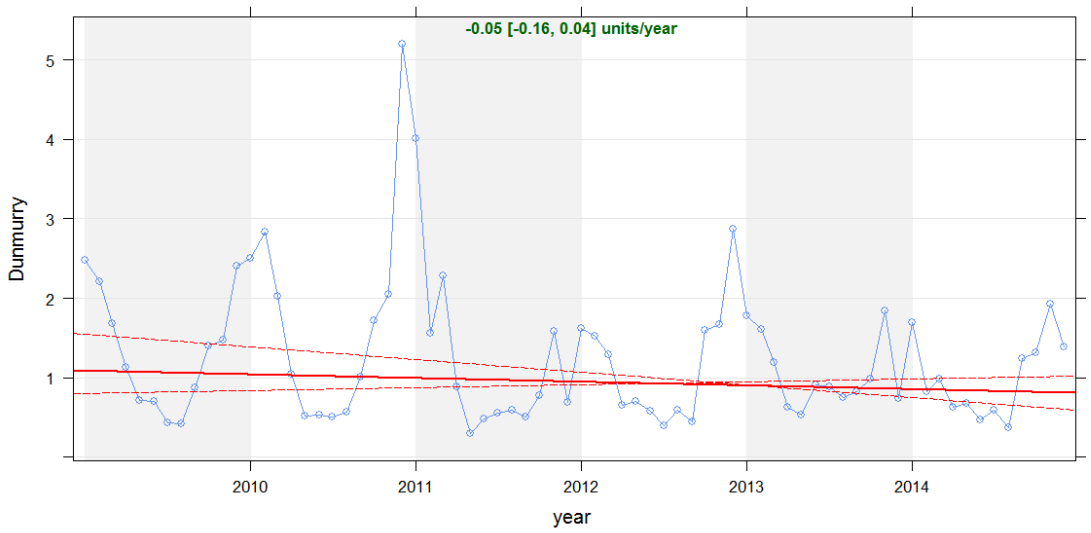


Belfast Centre

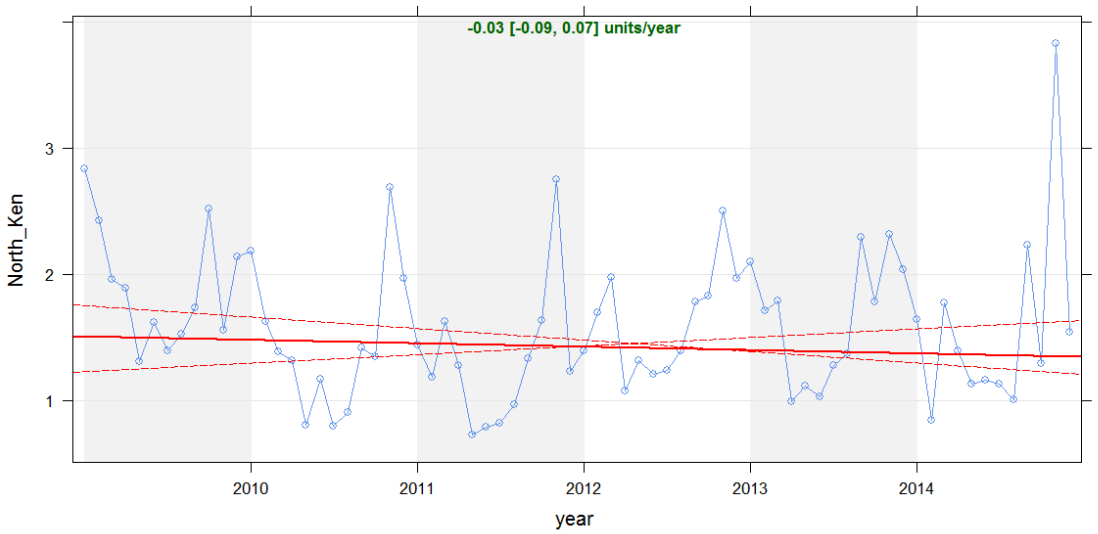
Figure 31 Black Carbon concentrations measured at urban centre sites, 2009 – 2014



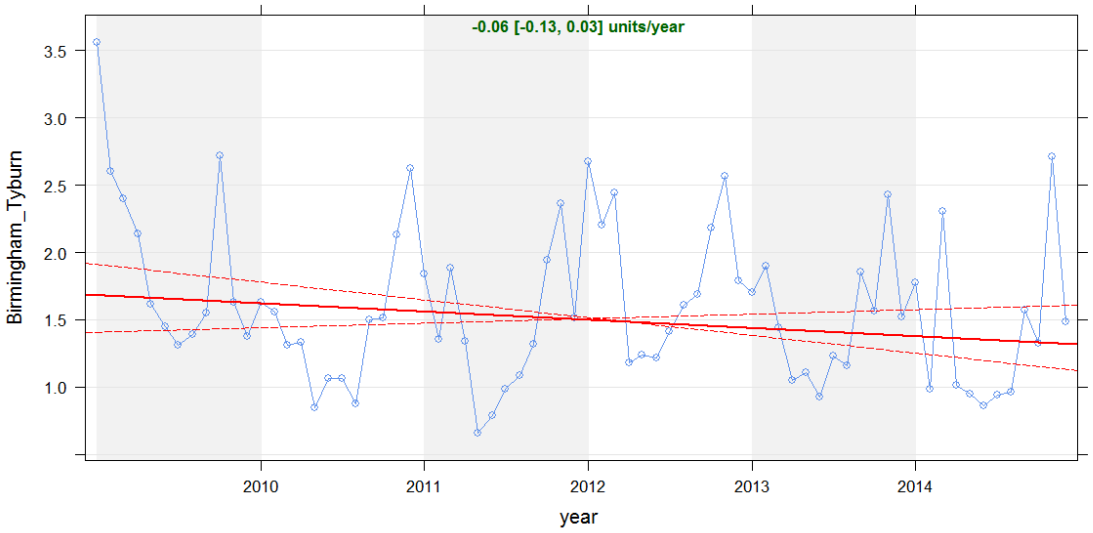
Strabane



Dunmurry

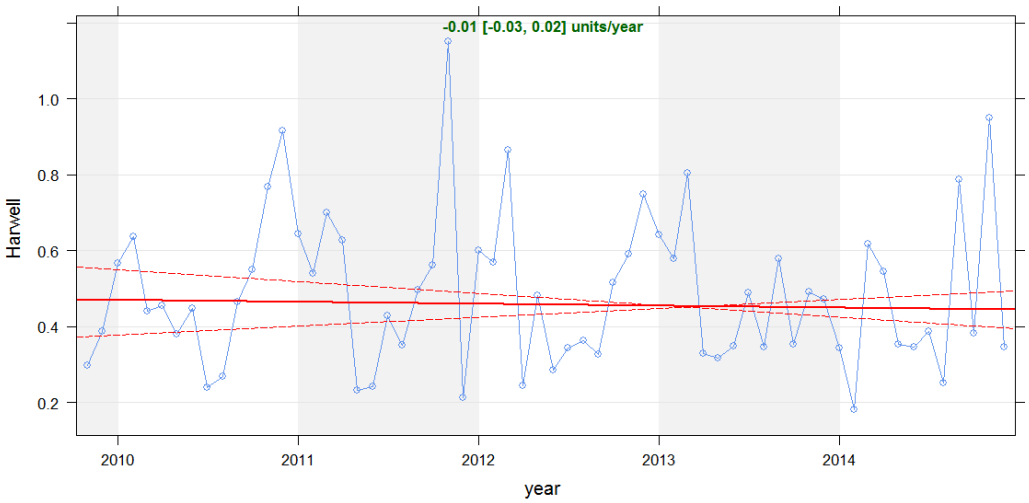


North Kensington



Birmingham Tyburn

Figure 32 Black Carbon concentrations measured at urban background sites, 2009 – 2014



Harwell

Figure 33 Black Carbon concentrations measured at rural background sites, 2009 – 2014

Site	Slope	Lower limit	Upper limit	Slope significant
Roadside				
Marylebone Road	-0.66	-0.88	-0.43	Y
Urban Centre				
Belfast Centre	-0.08	-0.17	0.00	N
Urban Background				
North Kensington	-0.03	-0.09	0.07	N
Birmingham Tyburn	-0.06	-0.13	0.03	N
Dunmurry	-0.05	-0.16	0.04	N
Strabane	0.01	-0.08	0.11	N
Rural				
Harwell	-0.01	-0.03	0.02	N

Table 19 Summary of Black Carbon trends

Over the period 2009 - 2014 the only site that has a significant slope in Black Carbon concentration is Marylebone Road. This should be treated with caution as it may be unduly influenced by the lower than normal concentrations in February to June 2013, but 2014 concentrations are in general lower than 2012. This early 2013 drop in concentration is real, as it is also seen in the oxides of nitrogen (NOx) concentrations (Figure 35). NOx concentrations are a good tracer for changes in the local primary emissions. Not all $PM_{2.5}$ is due to local primary emissions whereas NOx is more dominant

Figure 34 shows the 2009-2014 time series for Marylebone Road, with data averaged into monthly values to remove daily fluctuations in concentration. The peaks in the March 2013 and 2014 $PM_{2.5}$ concentrations could be due to secondary aerosol formation during a long-range transport episode. These particles will contain little Black Carbon compared to their mass.

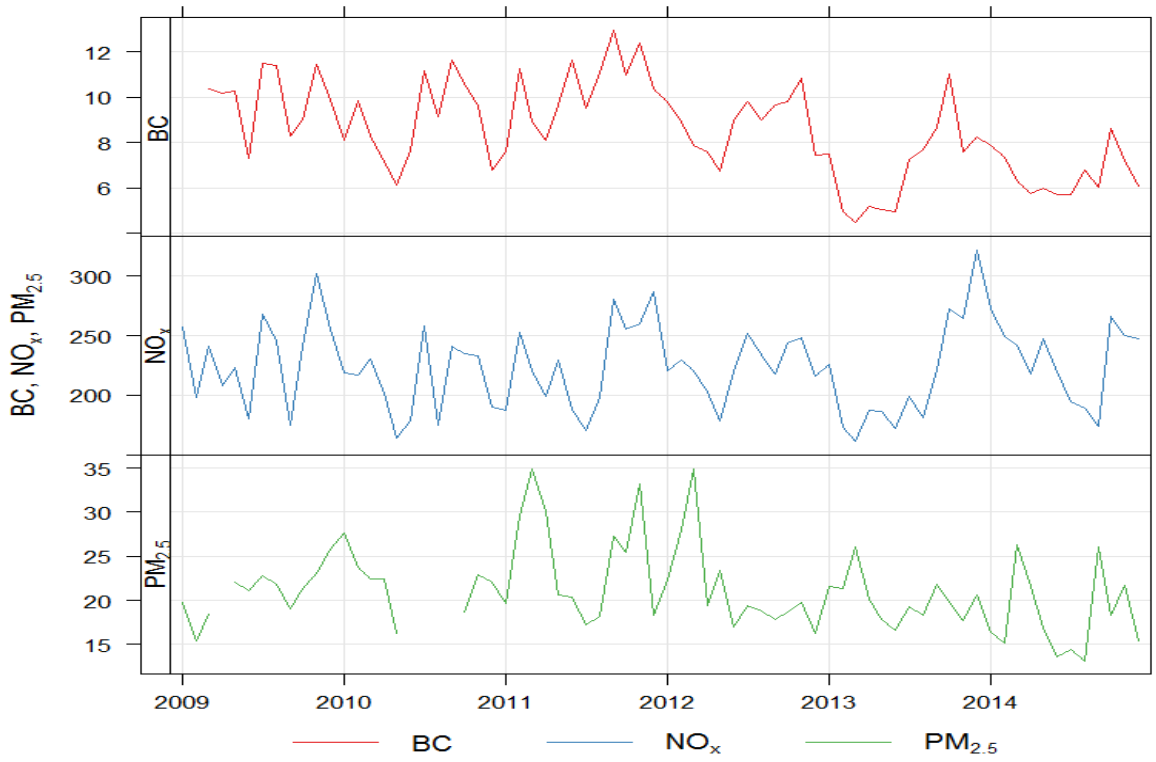


Figure 34 **Monthly averages of Black Carbon, $PM_{2.5}$ and Oxides of Nitrogen (NOx) at Marylebone Road over the period 2009 - 2014**

In addition to correlations with other pollutants, daily average traffic flow at Marylebone Road have been compared to Black Carbon and Elemental Carbon concentrations over the period 2009 – 2014, as shown in Figure 35.

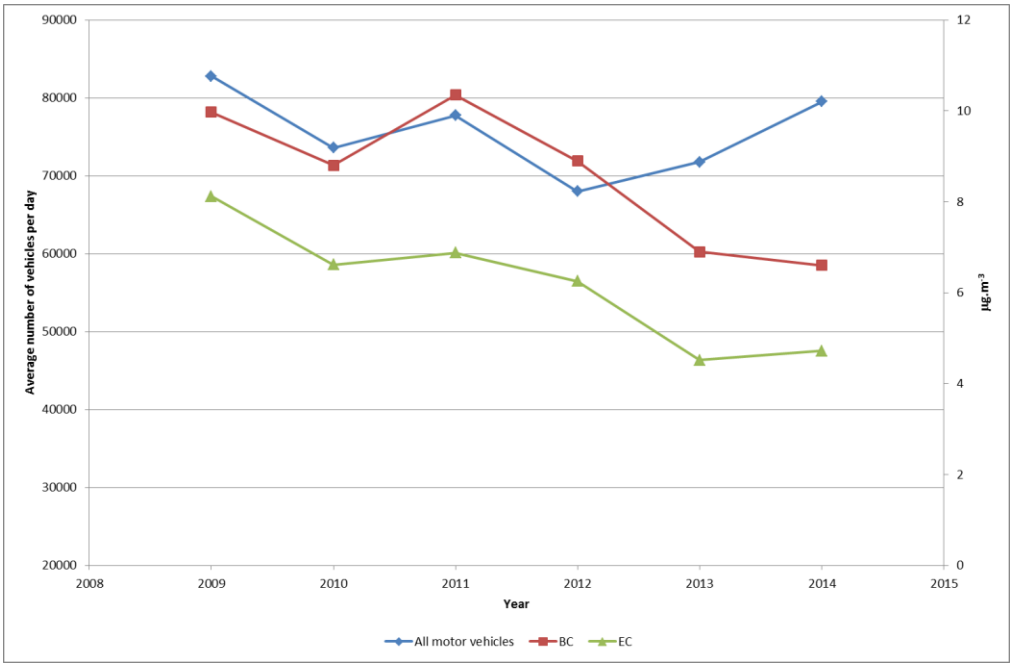


Figure 35 **Annual Average Black Carbon, Elemental Carbon and Motor Vehicles per Day at Marylebone Road for the period 2009 – 2014**

It can be seen that the changes in Black Carbon and Elemental Carbon concentrations follow changes in the total traffic flow for the years 2009 to 2012, but not for 2013 & 2014, which would indicate that Black Carbon emissions per vehicle have reduced over the last 2 years. The drop in emissions per vehicle type may be linked to the increased proportion of low emission buses (hybrid and fuel cell / hybrid) in the London bus fleet[11] . Table 20 shows the composition of the London bus fleet over the period 2010 to 2014. The bottom row of the table shows the percentage of low emission buses, which is a combination of the hybrid and fuel cell / hybrid bus numbers.

		Number of buses				
Bus Type	**Drive train type**	**2010**	**2011**	**2012**	**2013**	**2014**
New Routemaster	Hybrid	0	0	5	8	168
Routemaster	Diesel	18	18	19	20	19
Artic	Diesel	320	260	0	0	0
Single deck	Diesel	2,676	2,670	2,661	2,608	2,606
	Fuel Cell/Hybrid	0	5	5	5	8
	Hybrid	27	27	33	28	23
	Electric	0	0	0	0	2
Double deck	Diesel	5,554	5,487	5,787	5,696	5,296
	Hybrid	29	79	233	352	643
TOTAL		8,624	8,546	8,743	8,717	8,765
% low emission		0.65	1.30	3.16	4.51	9.63

Table 20 Composition of London bus fleet, 2010 to 2014

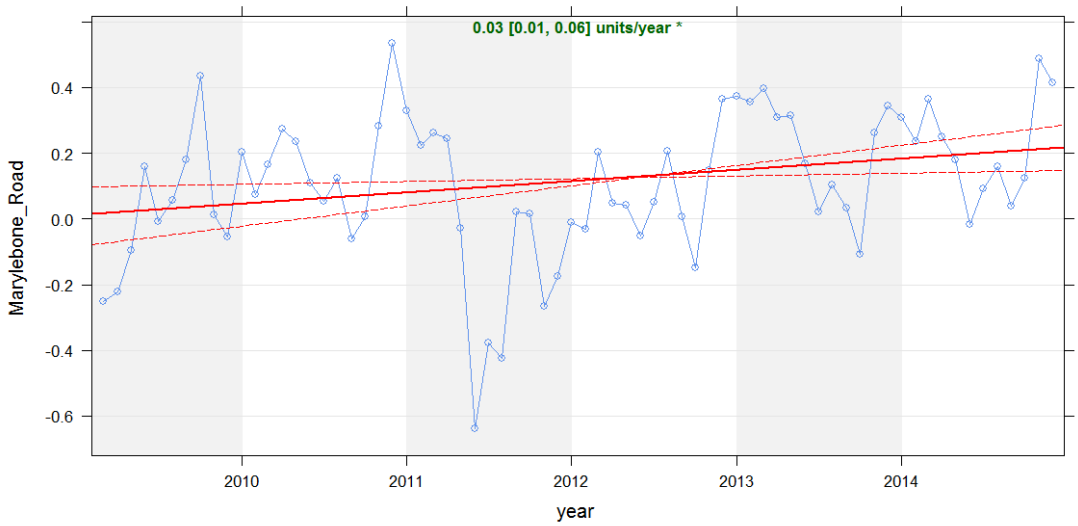
In addition all of London's Euro II and III diesel busses were retro-fitted with engine exhaust particulate filters by the end of 2011, which would have also reduced Black Carbon emissions.

Also in 2012 the vehicles types affected by the London Low Emission Zone (LEZ) was increased to include: large vans, minibuses and other specialist diesel vehicles. Vehicles entering the LEZ must be Euro III or higher to be compliant with the requirements. In addition the requirements for Lorries, buses, coaches, licensed private hire and specialist heavy vehicles changed from Euro III to Euro IV. These changes may have also reduced Black Carbon emissions from road transport.

11 Number of Buses by Type of Bus in London, tfl-buses-type.xls, London Datastore, https://londondatastore-upload.s3.amazonaws.com/tfl-buses-type.xls

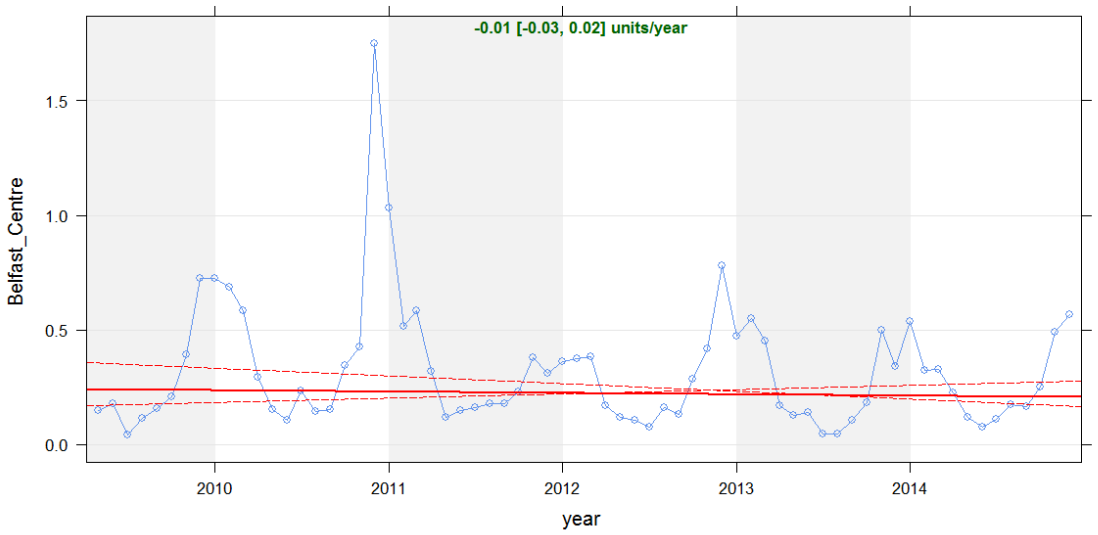
5.5.1.2 UV Component

Figures 36 to 39 show the UV component trends.



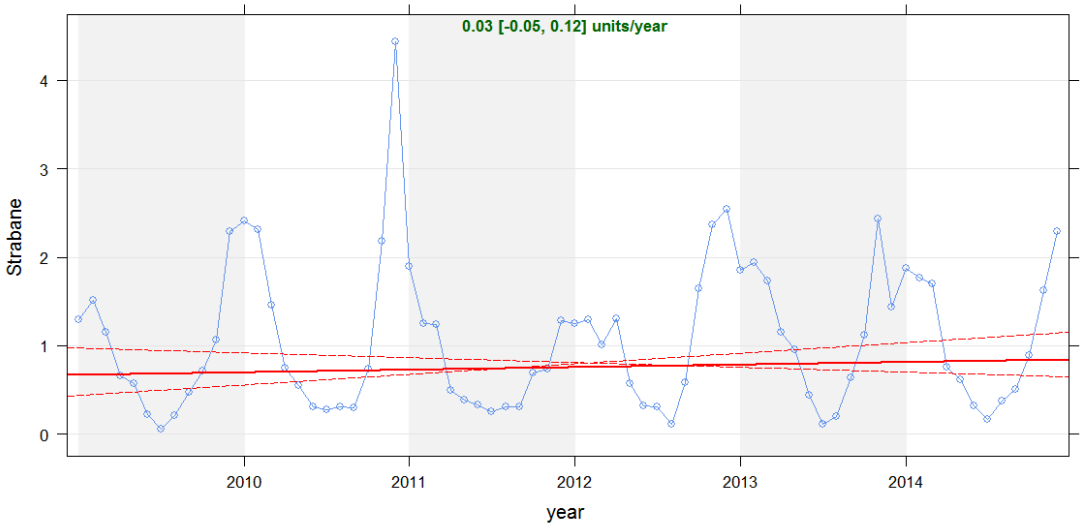
Marylebone Road

Figure 36 UV component concentrations measured at roadside sites, 2009 – 2014

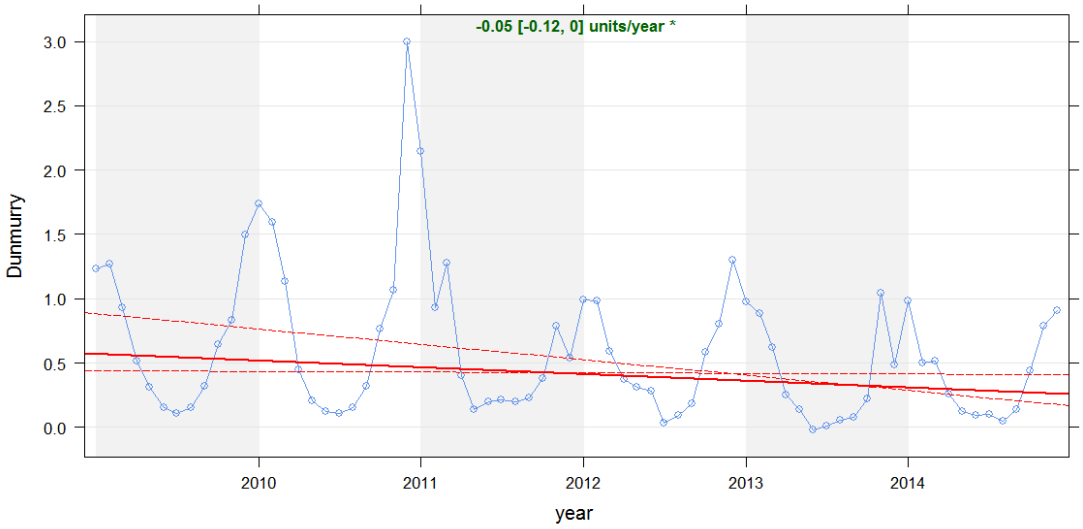


Belfast Centre

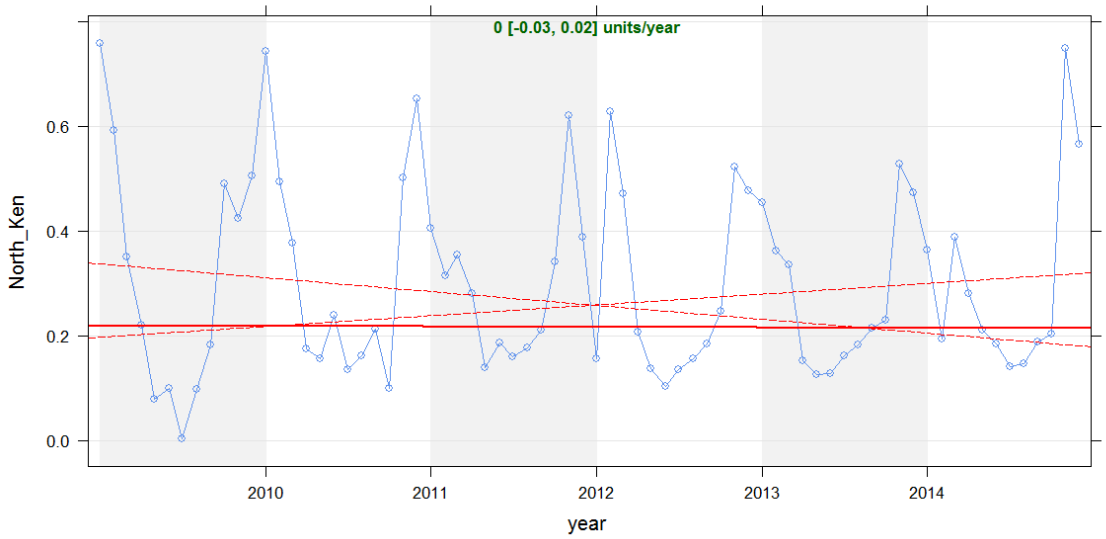
Figure 37 UV component concentrations measured at urban centre sites, 2009 – 2014



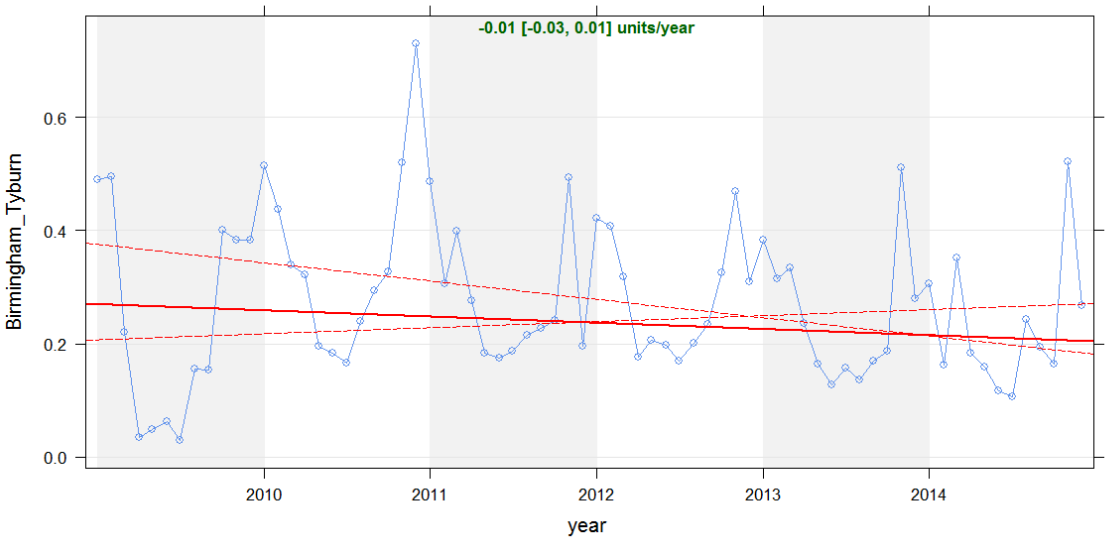
Strabane



Dunmurry

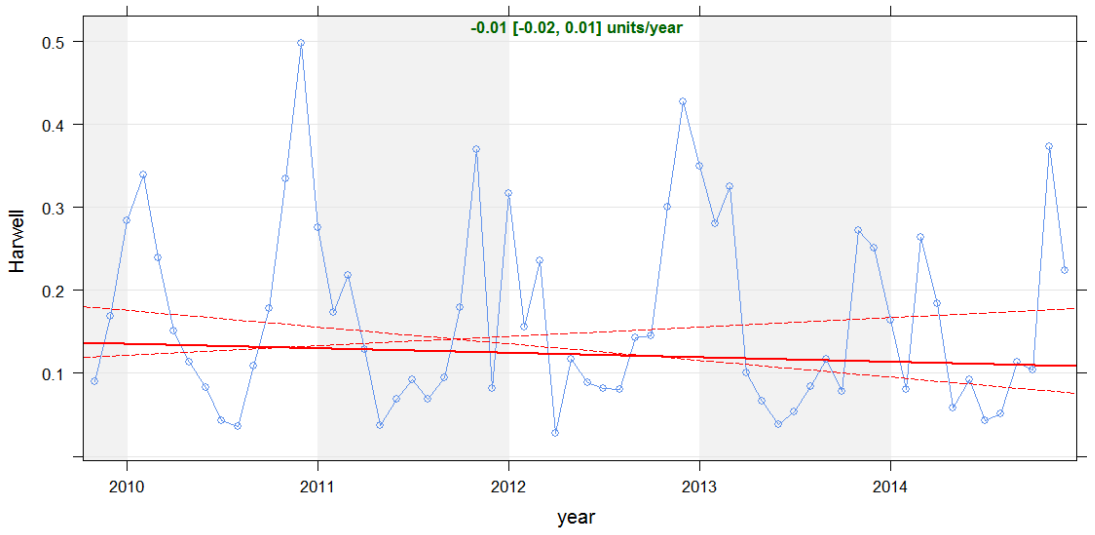


North Kensington



Birmingham Tyburn

Figure 38 UV component concentrations measured at urban background sites, 2009 – 2014



Harwell

Figure 39 UV component concentrations measured at rural background sites, 2009 – 2014

Site	Slope	Lower limit	Upper limit	Slope significant
Roadside				
Marylebone Road	0.03	0.01	0.06	Y
Urban Centre				
Belfast Centre	-0.01	-0.03	0.02	N
Urban Background				
North Kensington	0.00	-0.03	0.02	N
Birmingham Tyburn	-0.01	-0.03	0.01	N
Dunmurry	-0.05	-0.12	0.00	N
Strabane	0.03	-0.05	0.12	N
Rural				
Harwell	-0.01	-0.02	0.01	N

Table 21 Summary of UV component trends

The only site showing a significant trend in UV component concentration between 2009 and 2014 is Marylebone Road and this should be treated with caution due to the very low concentrations.

To show how pollutant concentrations can depend strongly on the weather, the 2009-2014 UV component concentrations at Strabane, which are strongly affected by domestic solid fuel use, are plotted in Figure 40, along with average temperature for same period. Temperature measurements from Armagh have been used as this is the nearest Met Office site with a long time series.

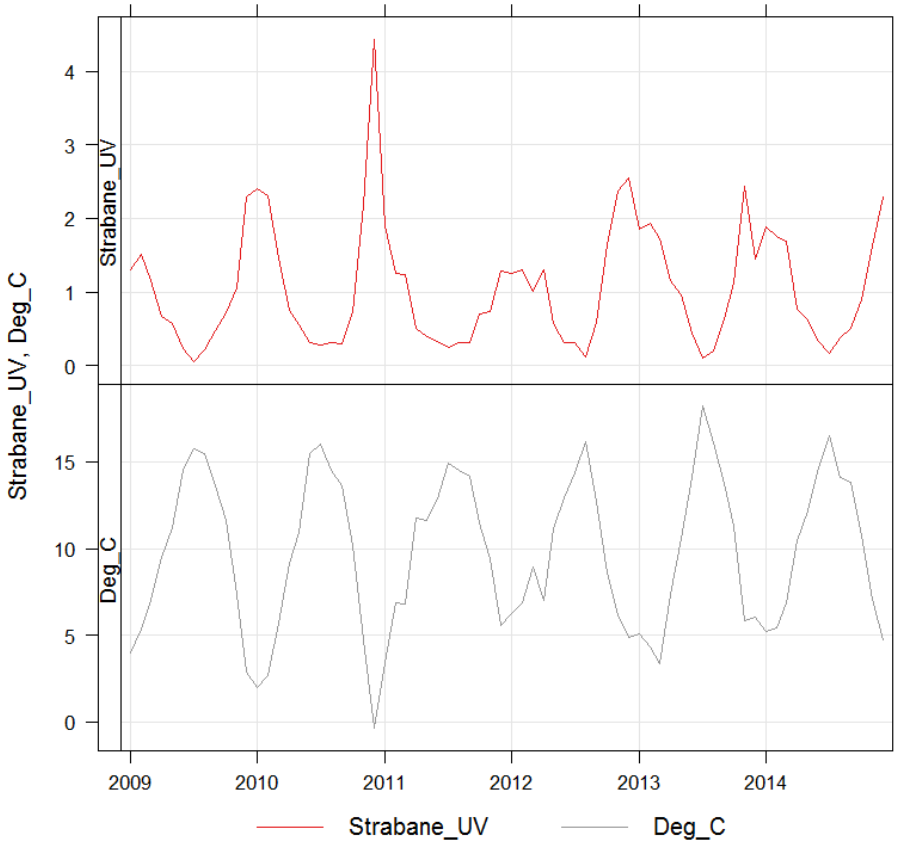


Figure 40 Strabane monthly UV component concentration and average ambient temperature for 2009 – 2014

It can be seen that the UV component concentration is inversely proportional to the average ambient temperature. This is due to the main source of UV component emissions being local domestic heating in Strabane. This relationship is also shown in Figure 41 as a scatter plot.

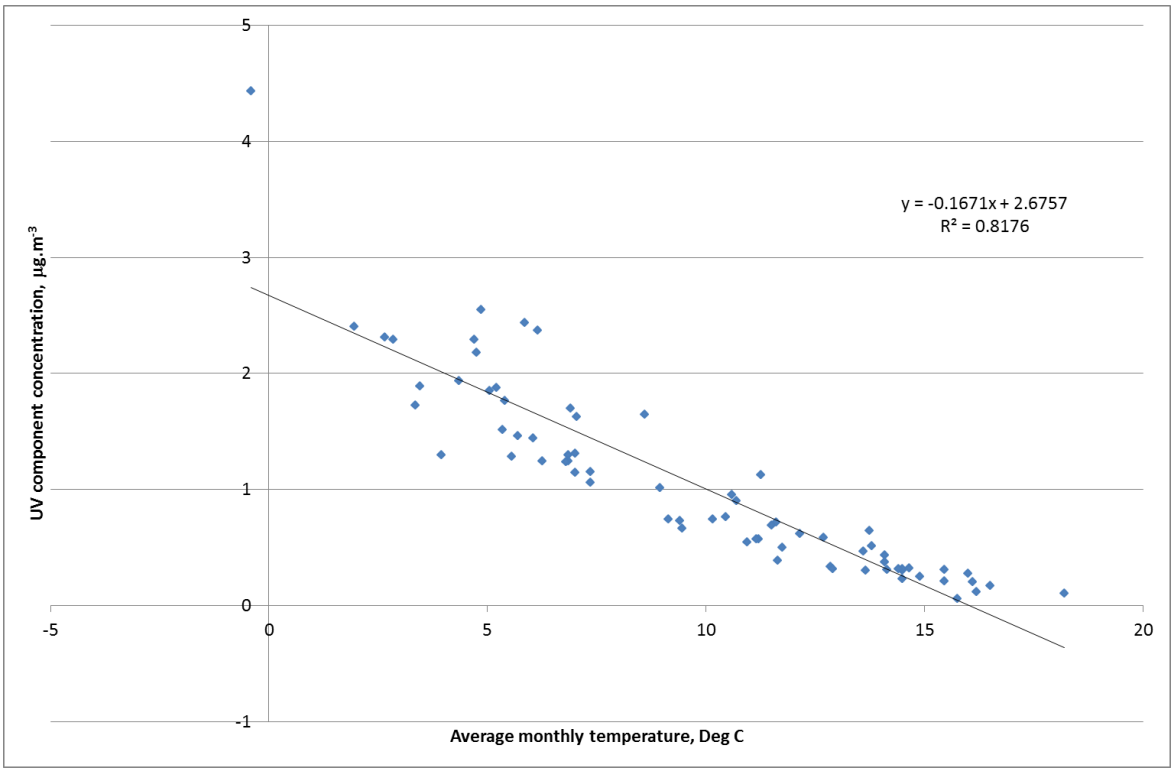


Figure 41 Scatter plot of monthly UV component concentration versus ambient temperature at Strabane over the period 2009 -20013

It can be seen that there is a clear linear relationship between increased UV component concentrations with a drop in ambient temperature, due to the increase in fuel usage in cold weather periods. It can be seen that there is a significant UV source when temperatures are below 15ºC, linking the UV component to fuels used for domestic heating systems.

5.5.2 Network Short-Term Trends

Figures 42 and 43 show the Network annual mean and median concentrations for Black Carbon and UV component for the subset of sites that have been continuously running since 2009 (Belfast Centre, Birmingham Tyburn UB, Dunmurry, Harwell, Marylebone Road, North Kensington and Strabane). The median concentration is shown to remove the influence of large changes in a single site that would skew the overall result for the Network.

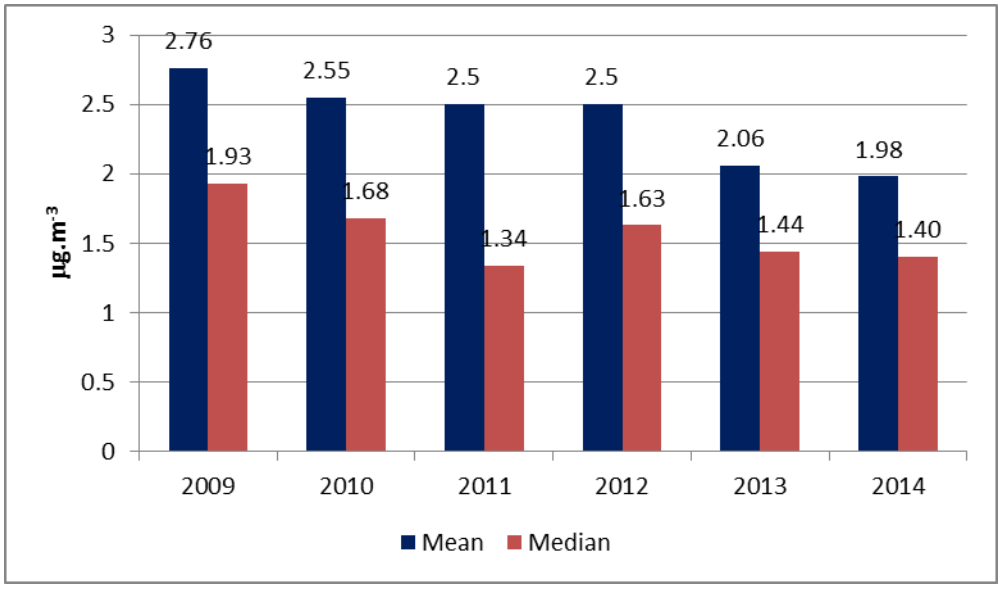


Figure 42 Network annual average Black Carbon concentrations

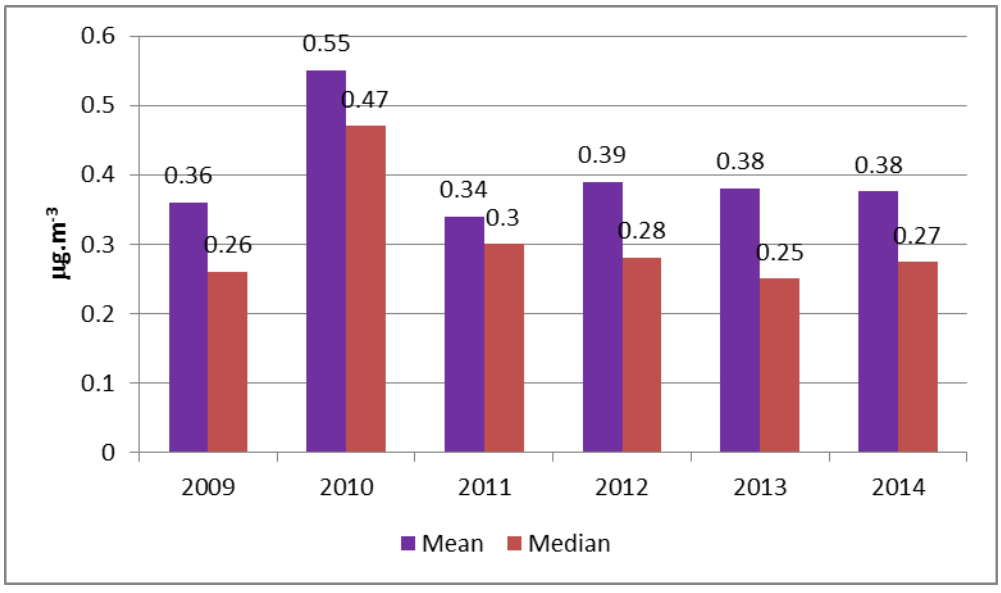


Figure 43 Network annual average UV component concentrations

It can be seen that there has been a considerable drop in the Network Annual mean for Black Carbon in 2013, with a similar concentration in 2014, while the median concentration is similar to previous years. The drop in average concentration is mainly driven by the drop in concentrations at Marylebone Road. Concentrations for previous years are relatively similar. The drop in the median concentration in 2011 is due, with the exception of Marylebone Road, to most sites showing lower than average concentrations.

Both the annual average and median UV component concentrations vary from year to year with maximum concentrations in 2010. 2010 had very cold and snowy periods at the start and end of the year, especially in Northern Ireland, as shown in Figure 40, so elevated concentrations are probably due to domestic emissions.

5.5.3 Long term Black Carbon concentrations

Trends in annual average Aethalometer concentrations over the period 2009 to 2014 are given along with the long-term trend in Black Carbon concentrations by converting historical Black Smoke concentrations into Black Carbon concentrations. The relationship, described by Equation 1 below[12], was used to convert Black Smoke Index measured between 2000 and 2008 into Black Carbon concentrations. For the two still continuing into 2014, these Black Carbon concentrations are given in Figure 44.

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

where:

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

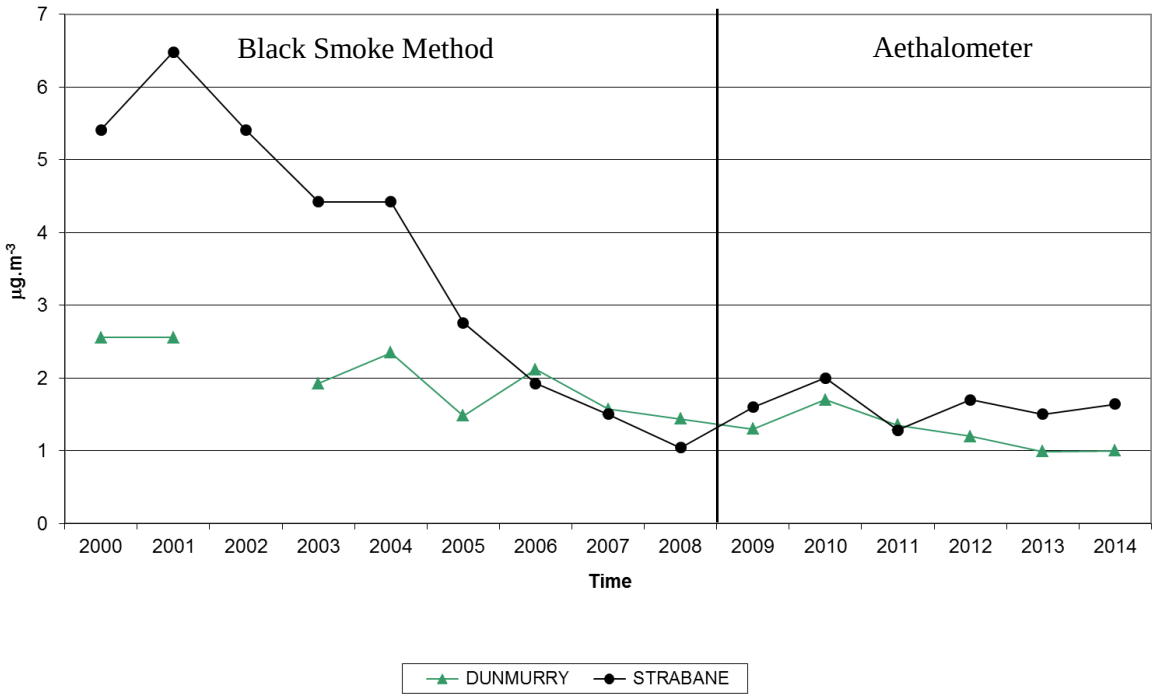


Figure 44 Trends in Black Carbon Concentrations 2000 to 2014

It can be seen that there is no significant discontinuity in results between the two methods. The drop in concentrations at Strabane between 200 and 2006 was due to tighter air quality controls by Strabane

12 P Quincey, D Butterfield, D Green, G Fuller, Black Smoke and Black Carbon: further investigation of the relationship between these ambient air metrics. Atmospheric Environment, 2011, 45, (21), 3528-3534

Council and the 2004 replacement of central heating systems in the local Council-controlled housing from coal to oil.

6.0 EUROPEAN STANDARDISATION

The European standardisation body CEN is formulating a European Standard on the measurement of Elemental Carbon and Organic Carbon deposited on filters. Technical Report EN/TR 16243 has been published[13]. The standardisation working group are now performing validation work on the procedures and requirements laid out in this technical report. The work packages being performed are:

- WP1: Literature review
- WP2: Lab tests
- WP3: Field tests
- WP4: Statistical evaluation

The current progress is as follows:

WP1 The final draft of the literature review has been approved by the working group and publication is imminent.

WP2 Two inter-laboratory comparisons have been performed. The first demonstrated the requirement to perform regular instrument calibrations to ensure satisfactory performance from the thermal / optical method. The second intercomparison showed good agreement between the 4 laboratories.

WP3 Sampling has been performed at 6 field locations along with parallel sampling using automatic analysers. The automatic analysers being used are the Magee AE33 dual spot, 7-wavelength Aethalometer, and a Thermo Scientific Multi Angle Absorption Photometer (MAAP). The AE33 differs from the AE22 Aethalometer used on the Network in 2 ways. Firstly the AE22 is a 2 wavelength analyser, while the AE33 uses 7 wavelengths. Secondly the AE33 does an internal correction for tape loading, while for the AE22 this has to be performed post sampling in the ratification process. Part of the remit of the working group is to comment on the comparability between the proposed reference method and automatic analyser methods.

WP4 The first interim report on the working group's progress has been approved by the working group and sent to CEN. The statistical analysis of the filed data has been completed and reported to CEN.

It is likely that the EUSAAR2 thermal protocol with transmission OCEC split point determination will be adopted as the standard analysis protocol for OCEC $PM_{2.5}$ particulate matter collected on filters. Currently the Network uses the NIOSH transmission protocol. In 2012 NPL analysed filters using both the EUSAAR2 transmission and NIOSH transmission protocols[14] and found no significant difference could be identified in TC – a reassuring check of the analysis system. As expected, Quartz gives somewhat lower EC values than EUSAAR II (with correspondingly higher OC values). These differences are of the order of 20% for EC and 5% for OC.

Protocols that have a lower maximum temperature during the inert-gas heating phase, such as the EUSAAR II protocol with a maximum of 650°C, tend to record significantly higher EC values than protocols such as Quartz, with a maximum of 870°C, with correspondingly less OC, such that the sum of EC and OC is the same in both cases. More charring of organic material will occur in the Quartz case,

13 CEN/TR 16243: Ambient air quality - Guide for the measurement of elemental carbon (EC) and organic carbon (OC) deposited on filters, August 2011.
14 Airborne Particulate Concentrations and Numbers in the United Kingdom (phase 3) Annual report 2012, NPL Report AS 83, December 2013.

which may be inadequately accounted for by the optical correction. Alternatively, the EUSAAR II protocol may not be removing all material that should be classified as OC. Ultimately the difference is because EC and OC are not objectively defined, but rather defined by the method used.

The final draft of the proposed standard was finalised in May 2015 and will be circulated for CEN enquiry in October 2015.

Assuming that the EUSAAR2 transmission protocol is adopted, NPL propose to use this protocol on filters sampled in 2016 onwards.

7.0 CONCLUSIONS

Black Carbon concentrations measured at most sites in 2014 were similar to those in previous years, with the 2013 drop in Marylebone Road concentrations maintained through 2014. UV component concentrations in 2014 were very similar to previous years. The Network mean Black Carbon concentration in 2014 was 1.6 $\mu g.m^{-3}$ the same as that in 2013. These years are not totally comparable as the sites making up the Network were different. From looking at the trend in Black Carbon concentrations for only those sites that have been open from 2009 – 2014, the concentration was stable from 2009 to 2012, with a significant drop in average concentration from 2.51 $\mu g.m^{-3}$ in 2012 to 2.06 $\mu g.m^{-3}$ in 2013 (22%), and 1.98 $\mu g.m^{-3}$ in 2014, while the median concentration has dropped from 1.63 $\mu g.m^{-3}$ to 1.43 $\mu g.m^{-3}$ in 2013 (12%) and 1.40 $\mu g.m^{-3}$ in 2014.. The median concentration is much less susceptible to changes at one site. The 2014 UV component concentration was 0.3 $\mu g.m^{-3}$, which is the same as 2012 and 2013. The range of concentrations between roadside and rural background were also similar.

At individual sites, short term trends in Black Carbon concentrations measured by the Aethalometer (2009 – 2014) are insignificant at all stations except Marylebone Road. Black Carbon concentrations at this site have dropped over the last 2 years due to the increased use of hybrid buses and stricter emission controls on London taxis (Euro III to Euro IV).

There are no significant trends in UV component concentration at any of the sites, or in the annual average or median concentration across the history of the Network.

The new network design implemented in early 2012 allows urban increments in Black Carbon and UV component concentrations to be determined for London, Birmingham and Glasgow, and roadside increments for London and Birmingham. The urban increment for Black Carbon was similar for all locations while the roadside increment was roughly proportional to road traffic volumes. There was no significant urban or roadside increment in UV component concentration.

Diurnal average concentrations of Black Carbon show that the dominant emission sources are road traffic and domestic heating using non-smokeless fuel. The diurnal average concentrations of the UV component show that its main source is domestic heating with solid fuels with little influence from traffic.