

**2011 Annual Report for the UK Black Carbon Network**

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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 2011. 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 Bradford was closed after Defra reviewed its monitoring requirements.

The 2011 data capture for Aethalometer measurements was 98%. This is a remarkably high figure for an automatic monitoring network and shows the effectiveness of daily on-line surveillance of the equipment.

Measured annual average Black Carbon concentrations on the Network ranged from 0.7 (0.8)  $\mu\text{g.m}^{-3}$  at Norwich Lakenfields to 10.3 (8.8)  $\mu\text{g.m}^{-3}$  at Marylebone Road. Harwell (rural background) reported an average concentration of 0.5 (0.5)  $\mu\text{g.m}^{-3}$ . The network mean for Black Carbon concentration was 1.8 (1.9)  $\mu\text{g.m}^{-3}$ . The figures in brackets are the corresponding concentrations for 2010.

Measured annual average UV component concentrations ranged from -0.1 (0.2)  $\mu\text{g.m}^{-3}$  measured at Marylebone Road to 0.8 (1.3)  $\mu\text{g.m}^{-3}$  measured at Strabane. Roadside sites show a lot of negative spikes in the UV component concentration mainly due to 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 0.3 (0.4)  $\mu\text{g.m}^{-3}$ . The figures in brackets are the corresponding concentrations for 2010.

As with Black Smoke in previous years, Black Carbon concentrations show reasonable agreement between sites located in similar regions of the country showing similar source behaviour and similar meteorological conditions.

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

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

Comparisons between Black Carbon concentrations and Elemental Carbon concentrations showed good agreement ( $R^2$  values between 0.84 and 0.92) between the measurements at all the sites where these measurements are collocated (North Kensington, Marylebone Road and Harwell).

Comparisons between particulate mass concentrations and Black Carbon concentrations showed that Black Carbon makes up a significant proportion of the particulate mass concentration at roadside sites. At Marylebone Road the Black Carbon concentration makes up 27% of the  $\text{PM}_{10}$  concentration and 42% of the  $\text{PM}_{2.5}$  concentration.

Monthly averages of Black Carbon concentrations were examined over the period 2009 to 2011. These trends indicate that Black Carbon has increased at roadside sites over this period, but uncertainties in the slope encompass stable or slightly negative slopes. At urban centre sites concentrations are generally decreasing over the same period with some slopes being statistically significant (Glasgow, Stoke and Nottingham). At urban background sites concentrations are generally decreasing over the same period with some slopes being statistically significant (North Kensington, South Kirkby, Woolwich, Halifax, Norwich and Edinburgh). At suburban and rural background sites concentrations are stable over the period.

The only site to show a statistically significant trend in UV component concentration is Norwich, which shows a reduction in UV component concentrations over the period 2009 to 2011.

From the annual mean and median concentrations over the history of the Network it can be seen that the annual average Black Carbon concentration has fallen over the period 2009 to 2011, while the median concentration rose very slightly from 2009 to 2010 and then fell to below 2009 levels in 2011. Meanwhile both the annual average and median UV component concentrations increased from 2009 to 2010 and then fell to below 2009 levels in 2011.

By converting Black Smoke Index into Black Carbon concentrations it can be shown that there is no discontinuity in results between the two methods and that there is no obvious short-term trend in the Black Carbon concentrations since 2004.

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.

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## 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 Bradford was closed after Defra reviewed its monitoring requirements.

### 1.2 BLACK CARBON

Black Carbon (BC) is a measure of airborne soot-like carbon (in  $\mu\text{g}\cdot\text{m}^{-3}$ ) based on the optical absorption of specific wavelengths by particulates collected on a filter. Ideally it is a similar metric to Elemental Carbon (EC), a measure of soot-like carbon determined by thermo-optical (chemical) techniques, though in practice the EC fraction of total carbon depends strongly on the method chosen. BC should have a close relationship to the Black Smoke measure monitored by the network and its predecessors for many decades before the installation of the Aethalometers<sup>[1]</sup>, 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  $\text{CO}_2$  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.

## 1.2 MEASUREMENT METHOD

### 1.2.1 Aethalometer instrument and data processing

Aethalometers quantify Black Carbon on filter samples based on the transmission of light through a sample. The sample is collected onto a quartz tape, and the change in absorption coefficient of the sample is measured by a single pass transmission of light through the sample, measured relative to a clean piece of filter. The system evaluates changes in two optical sensors (sample and reference), with the light source both on and off, such that independent measurements of the change in attenuation of the sample are produced for averaging periods of typically five minutes. The absorption coefficient for material added during the period,  $\sigma$  [ $\text{m}^{-1}$ ], is calculated from the attenuation change, and the area and volume of the sample, and converted to a Black Carbon concentration for the period, as a first approximation, using a mass extinction coefficient [ $16.6 \text{ m}^2 \text{ g}^{-1}$ ] 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 fictional material ‘UVPM’ is expressed in units of ‘BC Equivalent’.

It is well known that the assumption of constant mass extinction coefficient does not hold as the filter spot darkens, leading to nonlinearity in the Aethalometer response. The effect of this nonlinearity results is that the Aethalometer under-reads at high filter tape loadings. To correct for this nonlinearity, the model developed by A Virkkula<sup>[2]</sup> has been used to correct for increased attenuation due to spot darkening during sampling. This uses the simple equation:

$$BC_{corrected} = 1 + k \cdot ATN \cdot BC_{uncorrected}$$

where ATN is the light attenuation by the filter spot, and k is a parameter determined for each filter spot such that continuity between adjacent filter spots is greatly improved. All of the Black Carbon and UV component results in this report have been corrected by this method.

### 1.2.2 Sampling

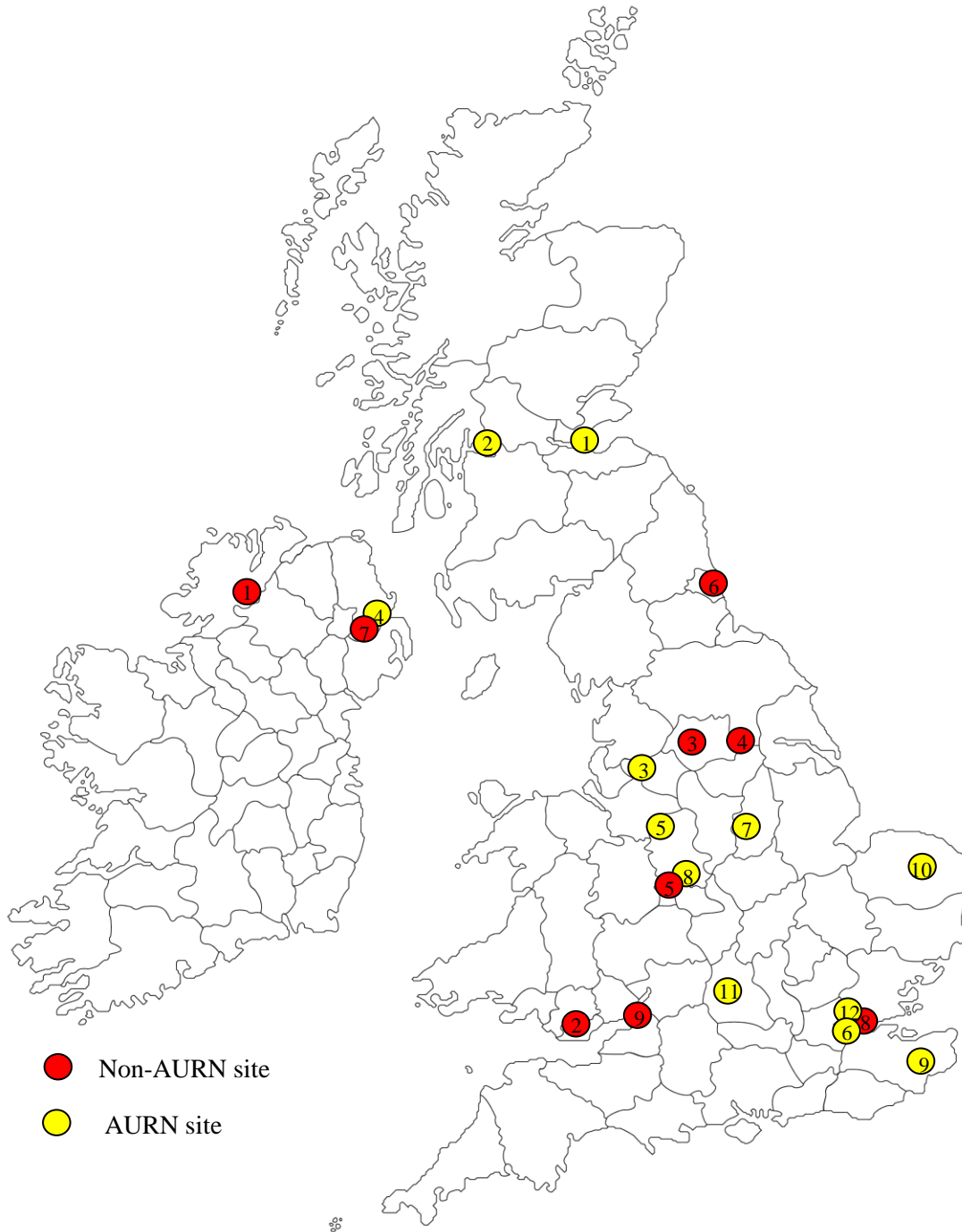
At all sites, ambient air is drawn into the sampling system through a standard stainless steel rain cap mounted on the end of a vertical stainless steel tube. Size selection of the sampled aerosol is made by a PM<sub>2.5</sub> cyclone placed close to the inlet of the Aethalometer. All of the tubing before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

## 2.0 NETWORK INFRASTRUCTURE

The following sections present the design of the Network and describe its operation during 2011.

### 2.1 NETWORK SITES AND DESIGN

Figure 1 shows the locations of the Aethalometers during 2011.



**Figure 1** Location of Aethalometers making up the UK Black Carbon Network in 2011. (key on next page)

Tables 1 and 2 below give the site names and classifications for the UK Black Carbon Network in 2011:

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

**Table 1 Non-AURN sites**

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

**Table 2 AURN sites**

## 2.2 NETWORK OPERATION

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

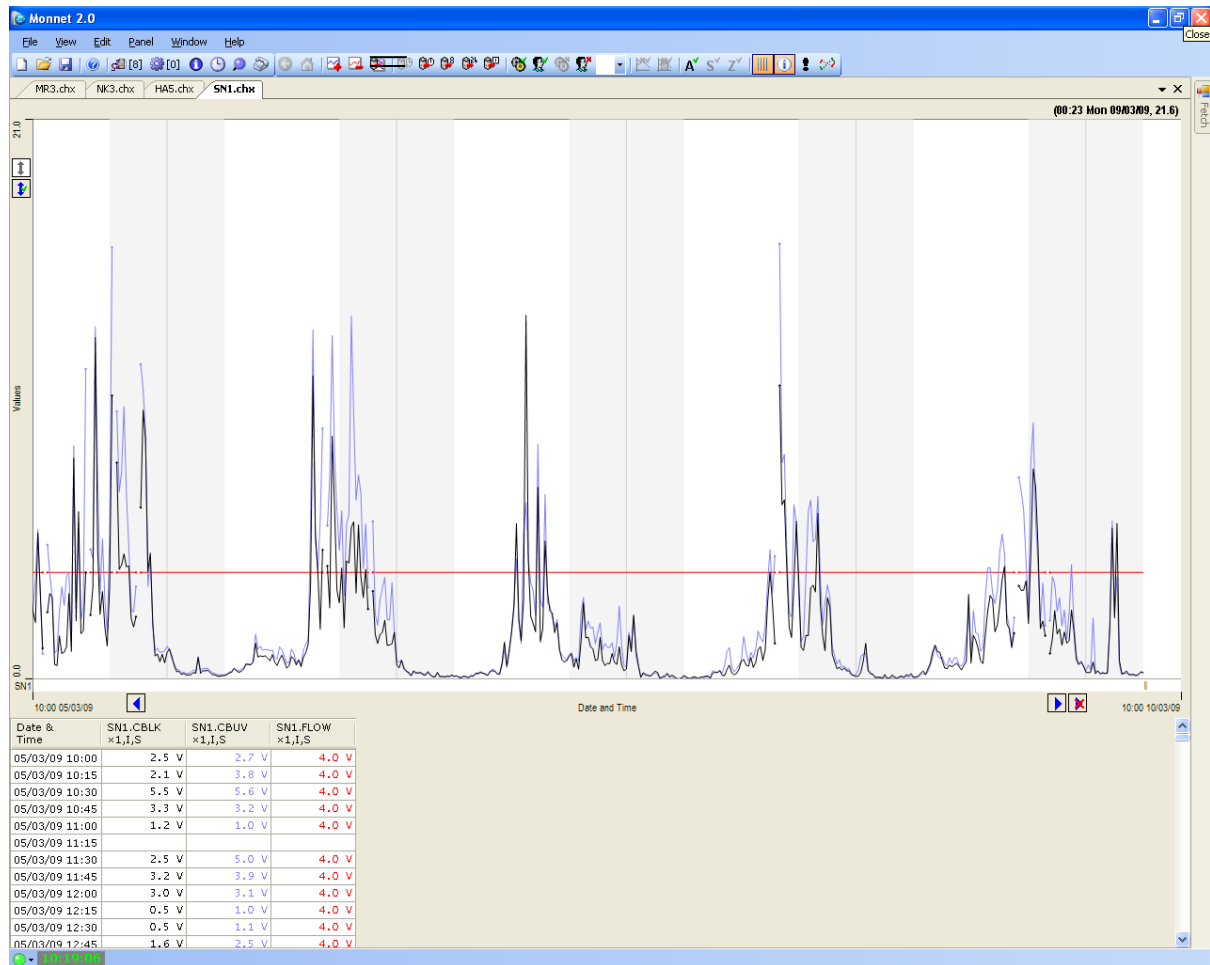
As the Aethalometer produces real-time continuous data it was decided to perform remote data collection and diagnostics at each site via a modem to maximise data capture and minimise LSO costs. A summary of this activity is outlined below:

Measurements are collected from the 20 sites on the Network 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 KCL's database. The 5 minute mean measurements are averaged to 15 minute means so that the averaging period is the same as measurements made using gaseous and particulate monitors on the AURN. A valid 15 minute measurement is only calculated where two valid 5 minute measurements exist in that 15 minute period. A range of sensibility checks are undertaken at this point to ensure measurements are above zero and below a maximum limit ( $100 \mu\text{g m}^{-3}$ ); the flow data is also checked to ensure it is 4 l/min ( $\pm 10\%$ ).

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

- Data warning flags have been attached to the data, either from the instrument or from the sensibility checks during processing.
- Data checking resulted in any notes or actions on the previous day.
- There are any services, local site operator visits or audits being undertaken 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 MONNET every working day; a screen shot of the 5 day data checking graph is shown in Figure 2. This shows the Black Carbon and UV carbon measurements and the flow measured by the instrument. Where  $\text{NO}_x$  measurements are available from the site (such as North Kensington and Marylebone Road) these are included as a method of assessing the impact of local traffic emissions. Further manual checks are made comparing the measurements between sites across the network to identify any outliers.



**Figure 2** MONNET data checking graph

Issues raised during the manual data checking are noted in the database, this information is retained and passed to NPL to inform the ratification process. Occasionally, issues raised during data checking require an intervention from either the local site operator (LSO) or the equipment support unit. If this is the case a visit request is sent to either the LSO or ESU. The reports generated from these visits are processed at KCL and stored according to the site that they pertain to. The directory is mirrored to the web server and accessible via a password protected web portal for access during ratification.

### 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 6 gives the site audit dates and serial numbers of the Aethalometer audited.

Site	Date	Serial No.
Glasgow	15/08/2011	856
Belfast	16/08/2011	863
Dunmurry	16/08/2011	862
Strabane	17/08/2011	848
Halifax	07/09/2011	860
South Kirkby	08/09/2011	852
Edinburgh	13/09/2011	866
Sunderland	14/09/2011	854
Folkestone	21/10/2011	853
Norwich	24/10/2011	864
Marylebone Road	25/10/2011	867
North Kensington	25/10/2011	850
Manchester Piccadilly	26/10/2011	858
Stoke	26/10/2011	861
Nottingham	27/10/2011	857
Woolwich	01/11/2011	865
Cardiff	02/11/2011	868
Harwell	02/11/2011	851
Bath	03/11/2011	869
Birmingham	22/11/2011	859
Dudley	09/12/2011	849

**Table 3 Site Audit Visits**

##### 3.1.1 Sampler Leak Rate and Calibration of Sample Flow

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

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

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

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

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

Site	% Leak Rate	Indicated Flow	Inlet Flow
Glasgow	6.3	4.0	4.167
Belfast	6.4	4.0	4.250
Dunmurry	6.1	3.9	4.090
Strabane	7.9	4.0	4.063
Halifax	5.3	4.0	4.310
South Kirkby	7.4	4.0	4.267
Edinburgh	8.7	4.0	4.410
Sunderland	7.5	4.0	4.097
Folkestone	2.5	4.0	4.187
Norwich	4.4	4.0	4.317
Marylebone Road	7.0	4.0	4.363
North Kensington	3.0	4.0	4.457
Manchester	7.3	4.0	4.170
Stoke	6.7	4.0	4.257
Nottingham	6.7	4.0	4.207
Woolwich	3.6	4.0	4.287
Cardiff	4.7	4.0	4.417
Harwell	6.2	4.0	3.960
Bath	5.1	4.0	4.657
Birmingham Tyburn	4.5	4.0	4.187
Dudley	7.6	3.9	4.103

**Table 4 Aethalometer leak rates and sample flows**

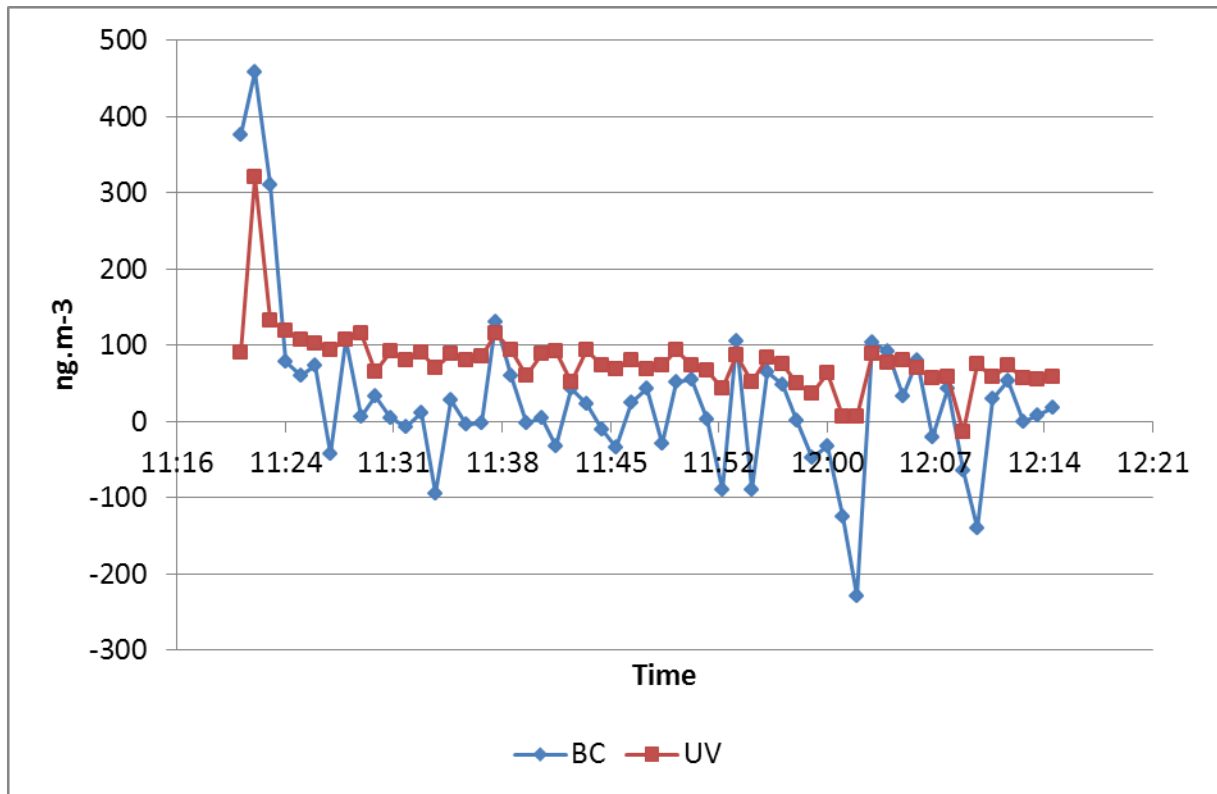
### 3.1.2 Instrument Performance

Two instrument performance tests are carried out at the sites audits: zero noise and comparison with a travelling micro-Aethalometer.

#### 3.1.2.1 ZERO NOISE TEST

The best simple indication of instrument performance can be gained by examining the zero noise of the Aethalometer, as this should give an indication of the optical and electrical stability over the measurement period. This is carried out by generating nominally particle free air using a High Efficiency Particle (HEPA) filter and examining the reported concentrations over an extended period of time. The Aethalometer concentration should fall quickly to a stable value around zero, whose noise is due to noise in the optical system and electronics. To increase the amount of data collected the Aethalometer time base is reduced from the normal Network operation value of 5 minutes to a 1 minute interval. Figure 3 shows a typical Aethalometer response to this test. The data are from the Cardiff site.





**Figure 3 Cardiff Aethalometer sampling HEPA filtered air**

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

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 <sup>-3</sup>	UV Channel, ng.m <sup>-3</sup>
Belfast	327	120
Strabane	366	175
Glasgow	125	58
Dunmurry	35	54
South Kirkby	297	186
Halifax	419	133
Sunderland	524	157
Edinburgh	1357	466
Folkestone	198	298
Norwich	8197	3797
Marylebone Rd	1496	1050
North Kensington	110	52
Manchester	340	98
Stoke	1486	894
Nottingham	334	116
Woolwich	112	48
Harwell	304	142
Cardiff	180	58
Bath	84	56
Birmingham	986	298
Dudley	190	70

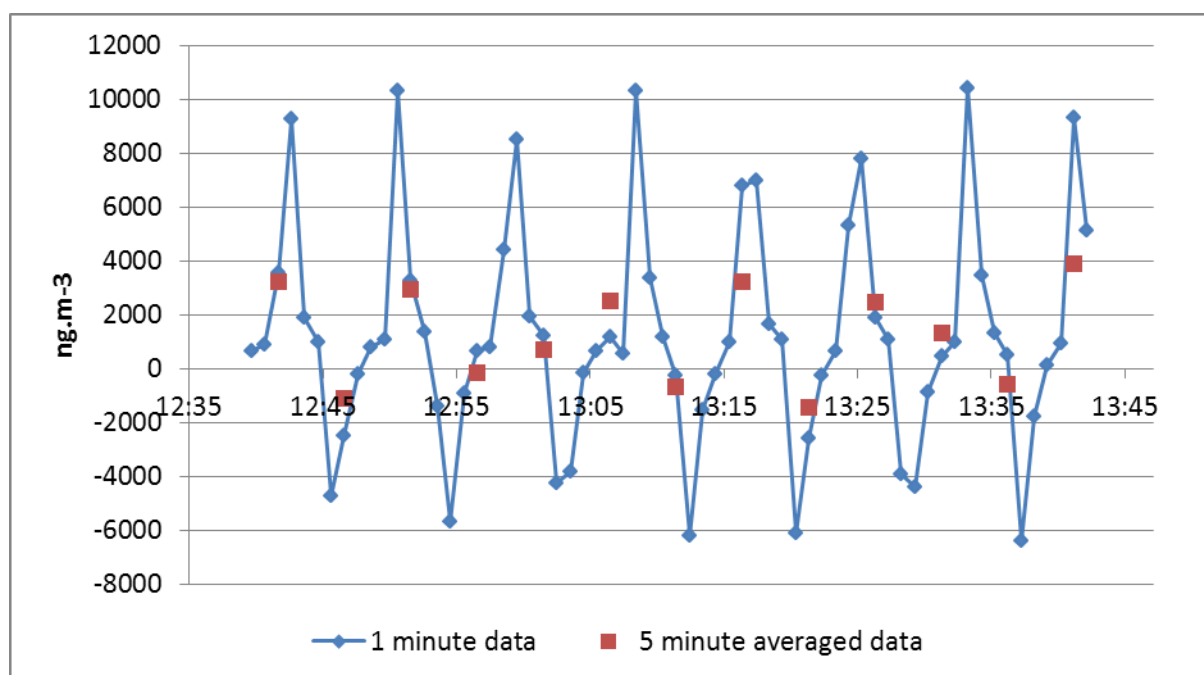
**Table 5 Zero Noise of BC and UV Component channels**

It should be noted that the UV Channel in Table 8 is not the UV component concentration, but the results taken from UV channel. See section 1.2.1 gives a full description of how the UV component is calculated.

The high results at Edinburgh, Norwich, Marylebone Road, Stoke and Birmingham Tyburn Background are probably due to artefacts caused by the site air conditioning systems. In sites where the air conditioning systems are of the on / off variety with no proportional control, there are large drops in room humidity when the air conditioning cooling switches on. This drop in humidity seems to affect the water content of the Aethalometer tape and therefore its transmittance properties. This effect has a direct influence on the measurement. This relative humidity effect is increased as the Aethalometer is sampling air from within the hut for the zero noise test. During normal sampling the Aethalometer only samples outside air, whose humidity level gradually changes over time. Ambient data from these sites show similar noise levels during low concentration periods (<0.5 µg.m<sup>-3</sup>) to the other sites on the Network.

Also the noise tests are done with a shorter time base than the ambient measurements, so during normal sampling this effect is reduced. If the Edinburgh test results are converted to 5 minute averages (equivalent to normal sampling time base) then the calculated zero noise drops from 1357 ng.m<sup>-3</sup> to 336 ng.m<sup>-3</sup>. Using the same methodology, the Norwich result of 8197 ng.m<sup>-3</sup> drops to 4119 ng.m<sup>-3</sup> for a 5 minute time base.

The responses from the Aethalometers at the sites affected by the air conditioning seem to follow a cyclic response which is consistent with the cycling of the air conditioning system. The results from Norwich can be seen in Figure 4.



**Figure 4 Zero Noise data from Norwich Aethalometer.**

The zero noise calculated from the sites not affected by the air conditioning is included in the overall measurement uncertainty. Future procedures will be modified to take account of the air conditioning effect.

### 3.1.2.2 INTERCOMPARISON WITH MICRO-AETHALOMETER

At each site parallel sampling of ambient air is performed using an AE51 micro-Aethalometer. The AE51 is a miniaturised version of the AE22 Network instrument, except that it only has a single BC channel instead of the 2 channels measured by the AE22. The measurement method and calculation algorithms of the AE51 are the same as those in the AE22.

Parallel ambient sampling through the normal site inlet pipe work is performed using the 1 minute time base, with the flow of the Network instrument lowered to give a similar face velocity to that of the AE51 instrument. It is important to ensure similar face velocities to ensure that both instrument filters collect particulate matter at the same rate and therefore darken at the same rate. Both instruments start the parallel running test with clean filter spots to ensure that any non-linearities due to differential spot darkening are removed. The results from the parallel ambient sampling are given in Table 6.

Site	AE22 BC Mean, ng.m <sup>-3</sup>	AE51 BC Mean, ng.m <sup>-3</sup>	Difference, %
Belfast	705	943	-29
Strabane	327	416	-24
Glasgow	816	1060	-26
Dunmurry	111	116	-5
South Kirkby	909	1305	-36
Halifax	577	649	-12
Sunderland	382	399	-4
Edinburgh	398	346	14
Folkestone	1226	1291	-5
Norwich	1656	1721	-4
Marylebone Rd	18952	21331	-12
North Kensington	2020	2388	-17
Manchester	1728	2116	-20
Stoke	3178	4127	-26
Nottingham	3258	3670	-12
Woolwich	864	1037	-18
Harwell	626	478	27
Cardiff	1648	1360	19
Bath	5362	4090	27
Birmingham	2391	2382	0
Dudley	1103	671	49
		<b>Average</b>	-7

**Table 6 Parallel ambient sampling results**

Although the average difference across all the sites is -7% there is quite a scatter in the results. It should be noted that the measurement uncertainty of both instruments is around 17%. The parallel running test gives a good indication of the comparability of the instruments across the Network.

This is a new procedure for 2011 and the implications for measurement uncertainties, and for revisions to the procedure, are under consideration.

## 4.0 MEASUREMENT UNCERTAINTY

### 4.1 SAMPLE VOLUME

From measurements at the site audit the sample volume can be determined with an uncertainty of  $\pm 9.3\%$ , 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 2011 audits was used. As leak rate is considered to be a rectangular distribution, its contribution to the standard uncertainty in sample volume is 3.4%.

## 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  $\pm 0.25 \mu\text{g}\cdot\text{m}^{-3}$ . Using the value obtained from sites not affected by the air conditioning and converting into a standard uncertainty this represents a contribution of 7%, compared to the network mean of  $1.75 \mu\text{g}\cdot\text{m}^{-3}$ .

## 4.3 CORRECTION FOR SPOT DARKENING

The Virkkula model<sup>[2]</sup> was used to correct the measured concentrations due to the fact that the Aethalometer shows nonlinearity with attenuation. This effect and its correction introduce an uncertainty into the measurements. At most sites the correction can be seen to work well on the 15-minute data, in that there is minimal discontinuity when the spot location changes, and the associated uncertainty is considered to be small compared to other components. At sites where the concentration is changing quickly, such as Marylebone Road, this uncertainty in the 15-minute data becomes significant. When hourly averages have been produced from this 15-minute data the effect is less significant.

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

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

## 4.4 PRELIMINARY OVERALL MEASUREMENT UNCERTAINTY

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

When the contributions from sample volume and optical /electrical stability are combined, the overall measurement uncertainty for hourly Black Carbon concentrations is 16.8%, 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	16.8%
Monthly	6.3%
Yearly	6.3%

This is an indicative measurement uncertainty for the Aethalometer method and is calculated from the results of the 2011 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 2011 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<sup>[2]</sup>.

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:

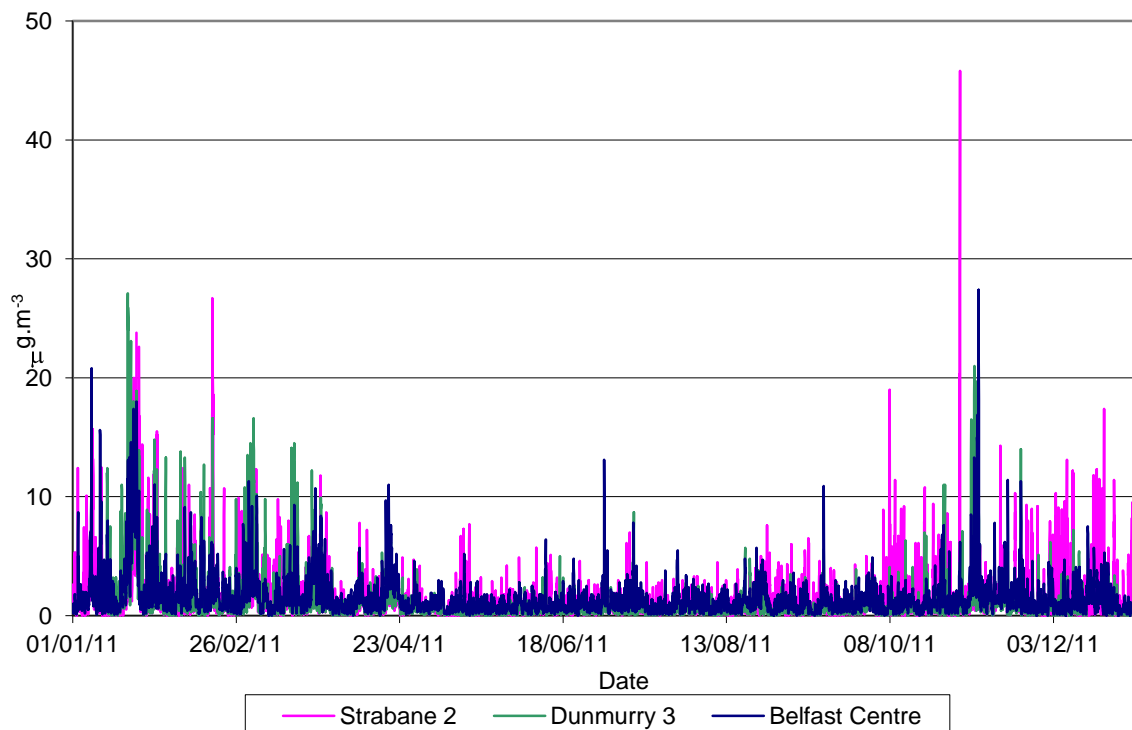
<http://uk-air.defra.gov.uk/>

### 5.1 TIME SERIES

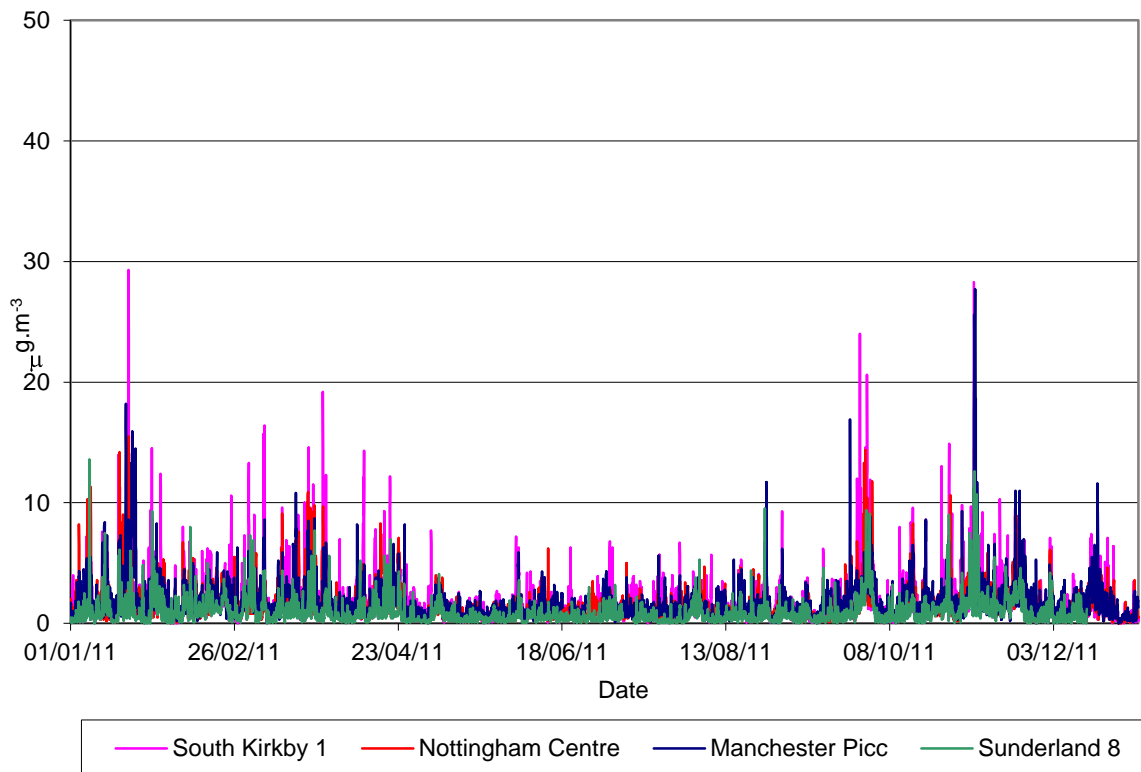
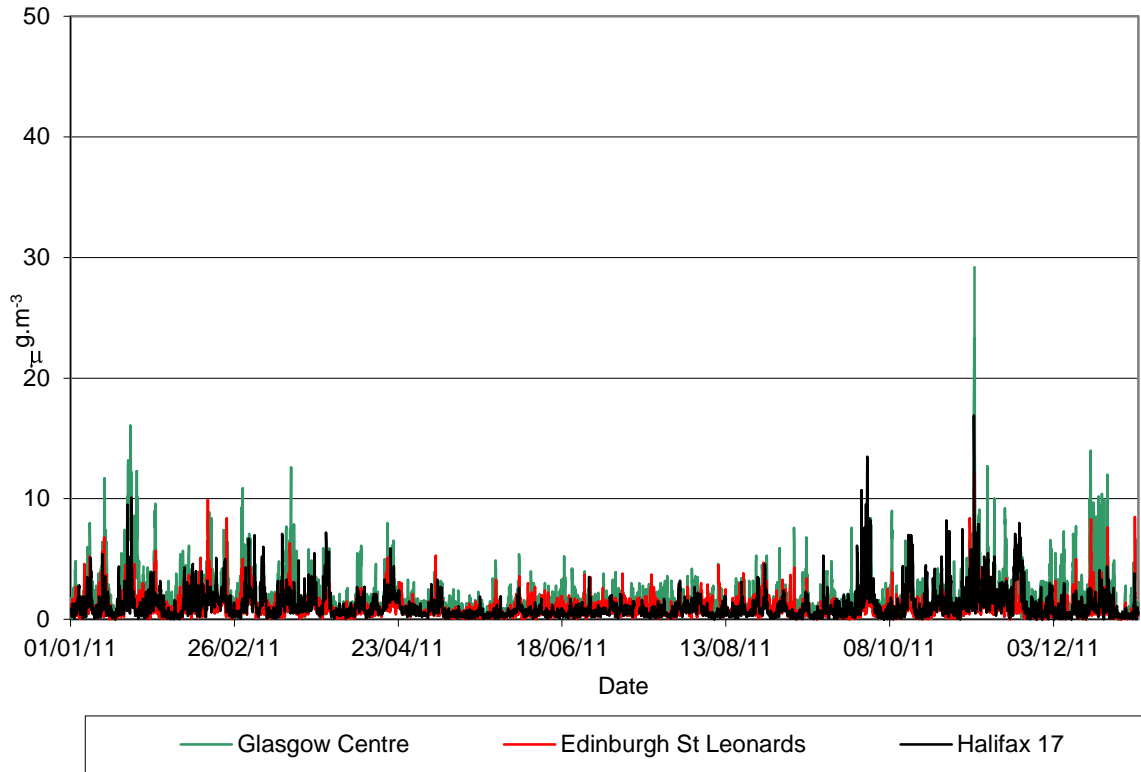
The following sections present time series graphs of the Black Carbon and UV component concentrations.

#### 5.1.1 Black Carbon

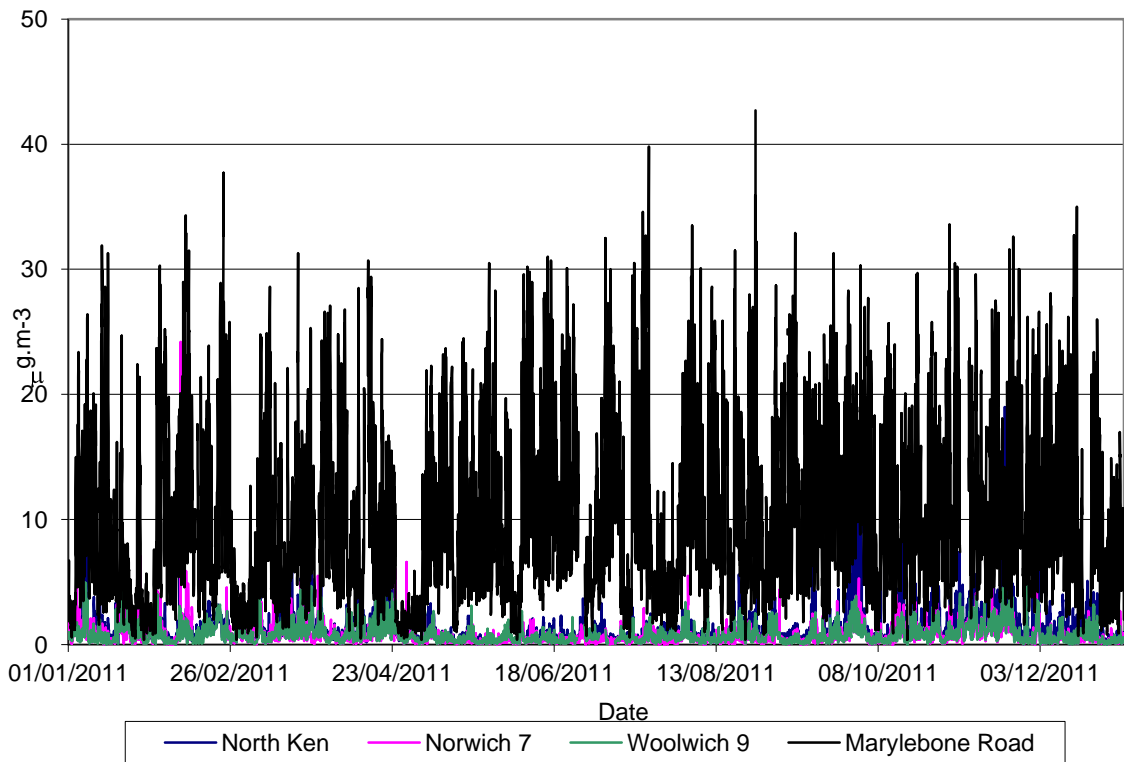
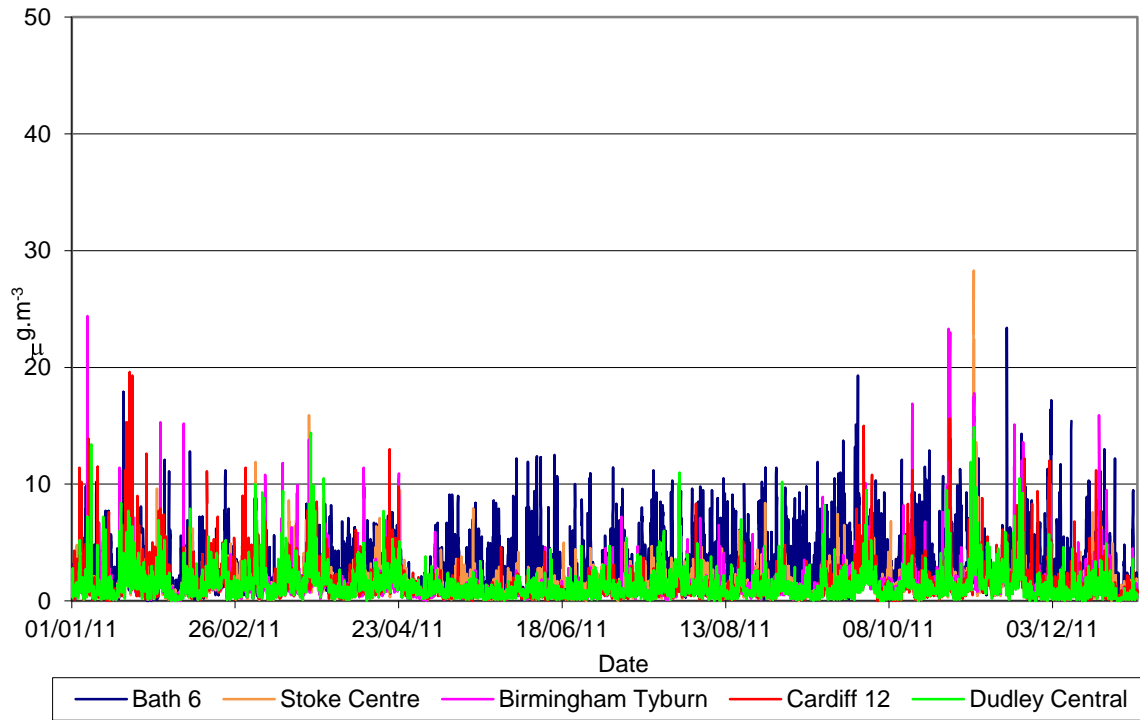
The following charts show the Black Carbon concentrations measured by the UK Black Carbon Network for 2011. The time resolution of the measurements is hourly. Data has been split into regions of the UK for presentation purposes. The y-axis on these charts has been set to 50  $\mu\text{g.m}^{-3}$  to enable easy comparison between charts.



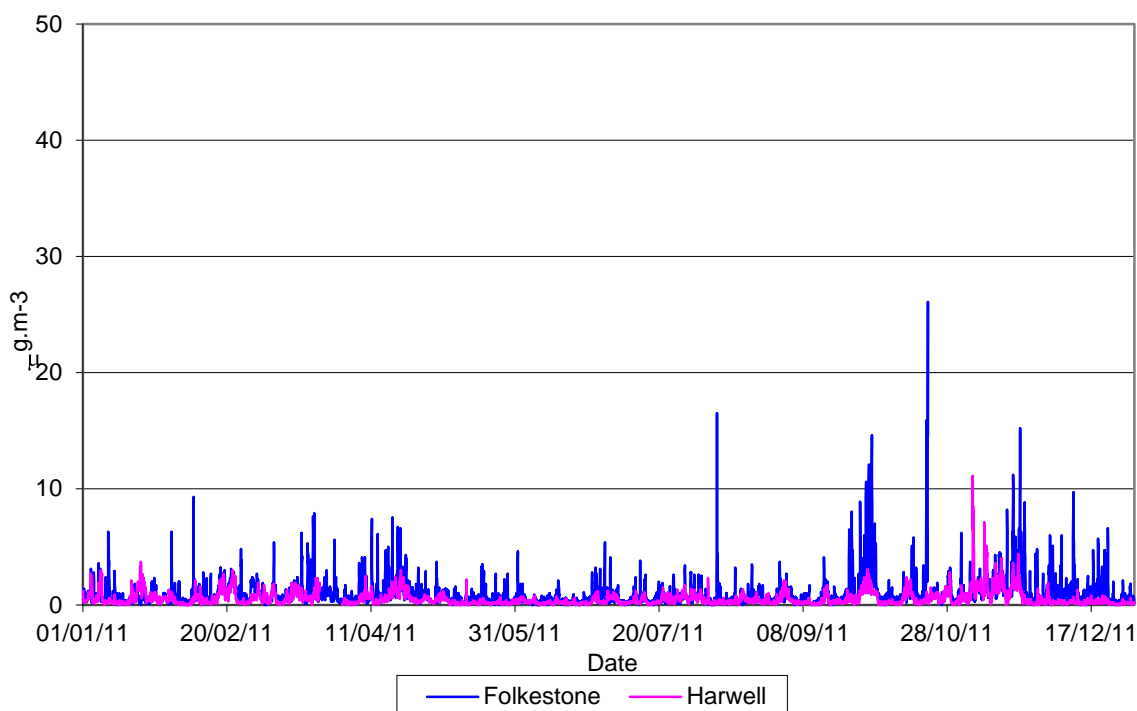
**Figure 5 Black Carbon concentrations during 2011 in Northern Ireland**



**Figure 6 + 7    Black Carbon concentrations during 2011 in Scotland and Northern England**







**Figures 8 to 10 Black Carbon concentrations during 2011 in Southern England and Wales**

All sites measured increased concentrations during the cold periods in January, November and December of 2011, but to a lesser extent when compared to 2010. This is due to the milder conditions in 2011. As before there is a noticeable drop off in BC concentrations from late Christmas Eve until 27<sup>th</sup> January, this is probably due to reduced road traffic across the country. Reduced concentrations were also observed at most sites during the period between Easter and the Royal Wedding (24<sup>th</sup> April – 3<sup>rd</sup> May), probably due to reduced road traffic over the period of the double bank holiday.

The pollution episode seen by many PM sites in Southern England between 18<sup>th</sup> and 20<sup>th</sup> February was not evident in the Black Carbon measurements, however high concentrations were recorded at the Lisburn Dunmurry and Strabane sites on 17<sup>th</sup> and 18<sup>th</sup> February. These elevated concentrations in Northern Ireland are more likely due to solid fuel use than the pollution episode, especially as the UV component concentration is also elevated during this period. These elevated concentrations are probably due to increased fuel usage in cold conditions rather than the influx of particles from continental Europe, which was the driver behind the elevated concentrations in Southern England.

The pollution episode seen by many PM sites in the UK in mid to late March was also evident in the Black Carbon concentrations over the period 11<sup>th</sup> – 31<sup>st</sup> March. This episode was caused by a combination of still conditions plus an influx of particles from Europe on easterly air flows.

The pollution episode between 17<sup>th</sup> – 24<sup>th</sup> April seen by many UK PM and ozone sites was not evident in the Black Carbon concentrations. This episode was caused by a combination of UK pollution sources, an easterly air flow and photo-chemistry.

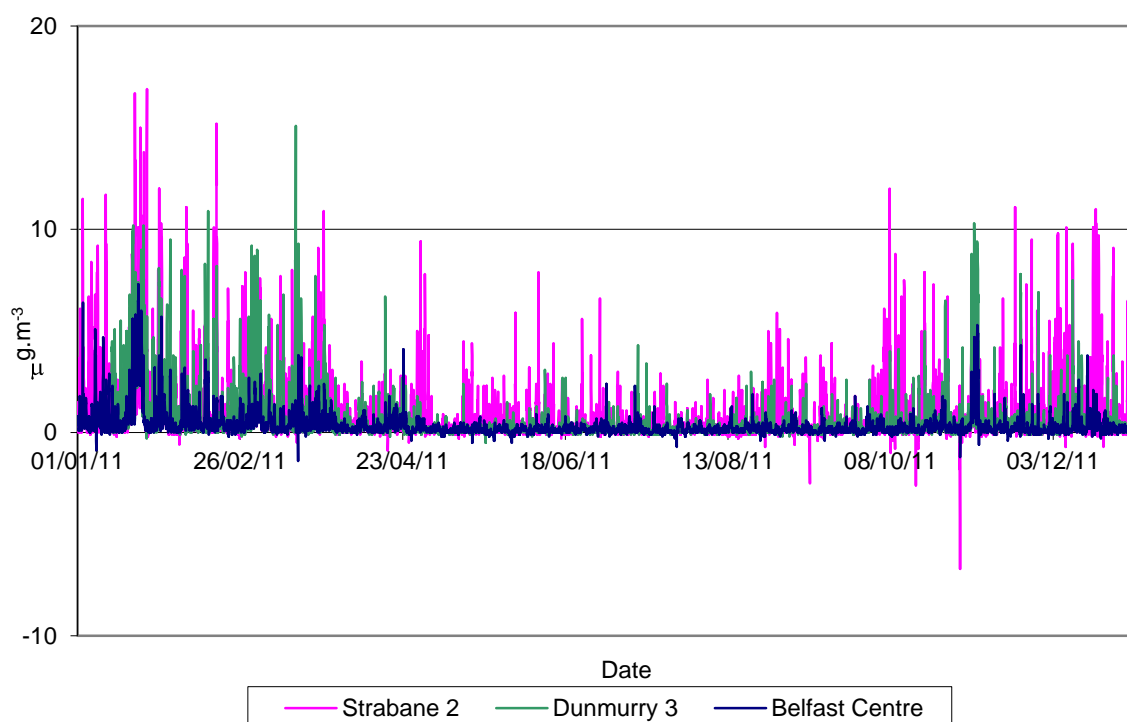
The pollution episode between 26<sup>th</sup> September and 3<sup>rd</sup> October leading to elevated PM, ozone and nitrogen dioxide concentrations measured across the UK was also evident in the Black Carbon concentrations. This episode was caused by unseasonably high temperatures and the recirculation of the air mass over Northern Europe due to the sustained high pressure covering the region.

Guy Fawkes Night celebrations lead to high Black Carbon concentrations between the 5<sup>th</sup> and 7<sup>th</sup> November at most sites.

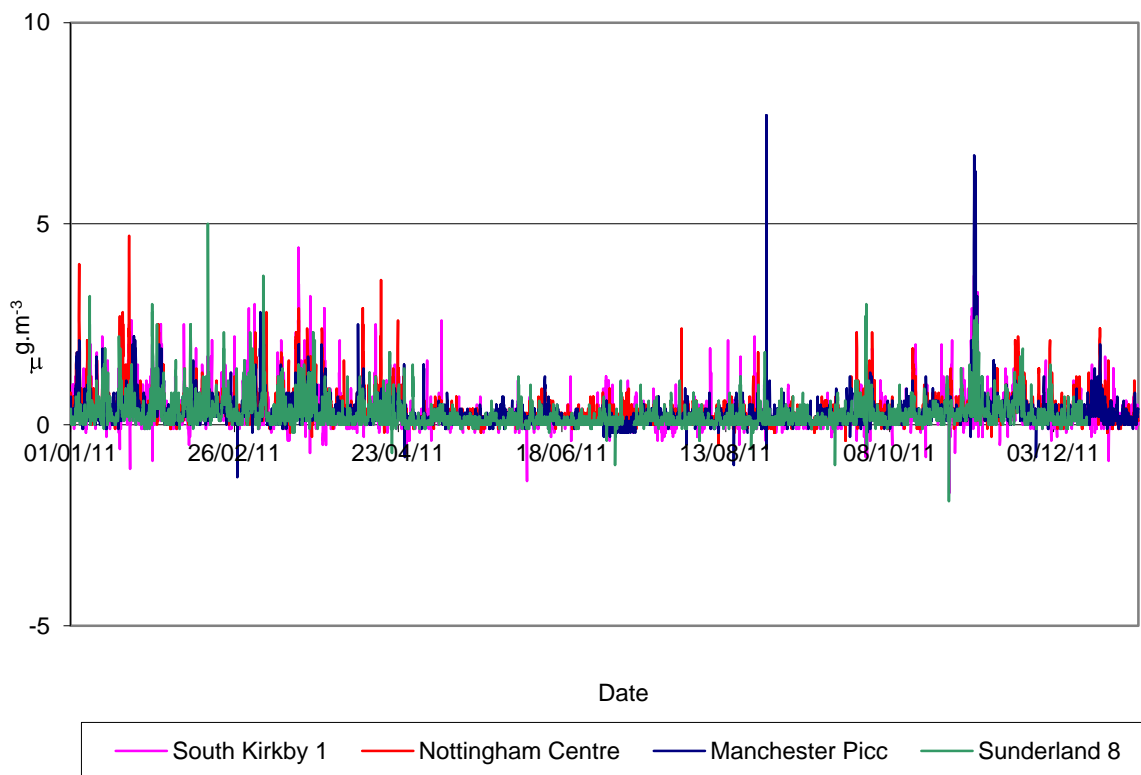
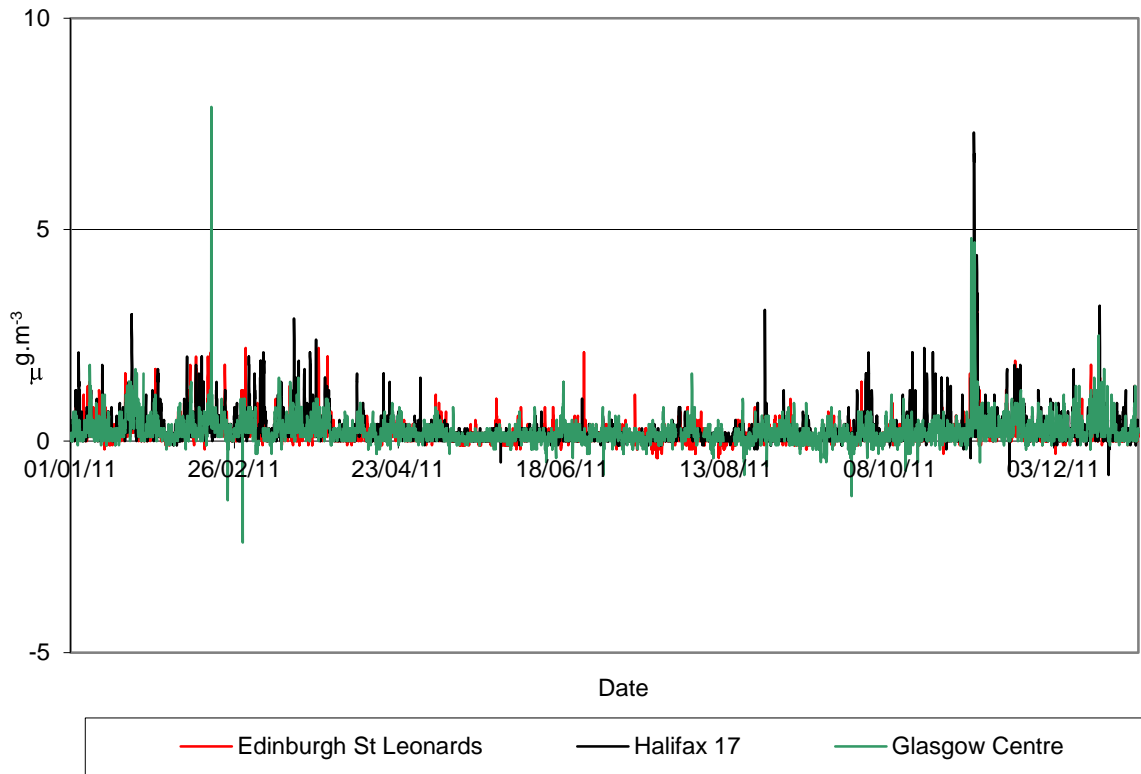
Calm and foggy conditions over the period 19<sup>th</sup> – 23<sup>rd</sup> November lead to elevated Black Carbon concentrations at many sites across the UK.

### 5.1.2 UV Component

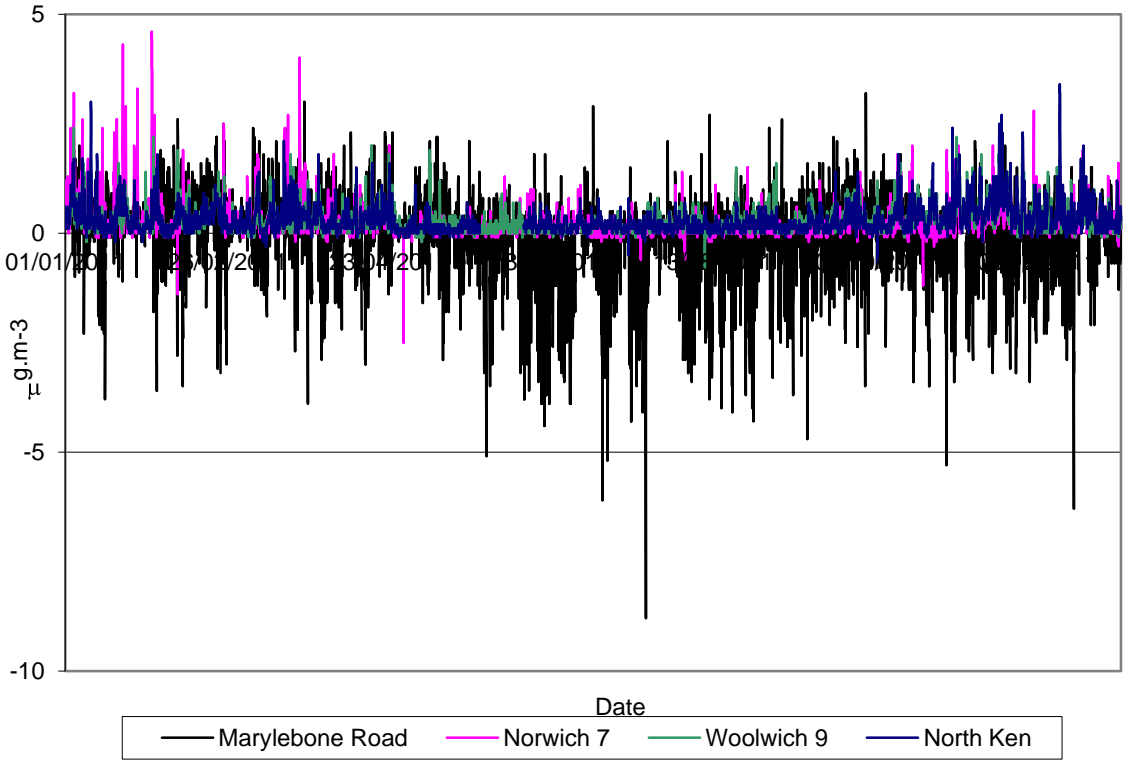
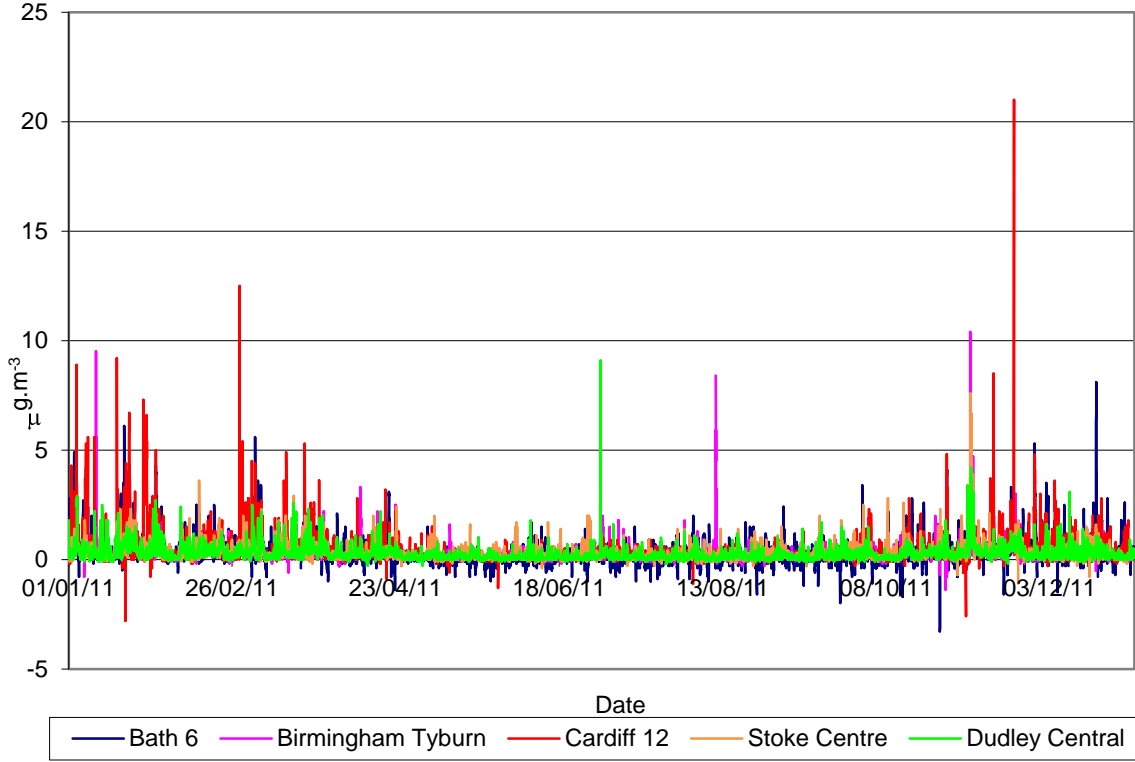
The following charts show the UV component concentrations measured by the UK Black Carbon Network for 2011. The time resolution of the measurements is hourly. Data has been split into regions of the UK for presentation purposes. The y-axis on the UV component time series graph has not been fixed to the same value for every chart, because the UV component is much more dependent on local site-specific conditions.

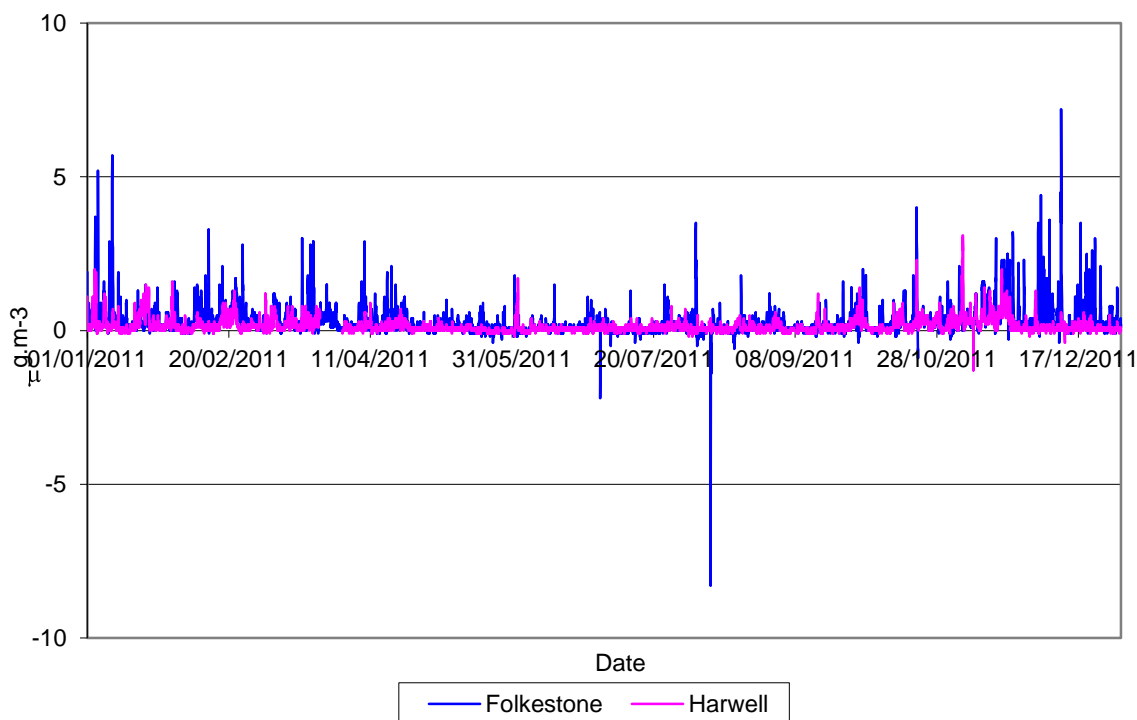


**Figure 11** UV component concentrations during 2011 in Northern Ireland



**Figure 12+13 UV component concentrations during 2011 in Scotland and Northern England**





**Figure 14 to 16 UV component concentrations during 2011 in Southern England and Wales**

The cause of the occurrence of negative concentration spikes in the “UV component”, especially at roadside sites, is not clear. It may be due to the semi-volatile nature of the aromatic organic species that adsorb at the 370nm wavelength. In well-aged ambient air samples these volatile organics will be found almost exclusively in the gas phase, and the UV response of the Aethalometer will show little enhancement over the BC response. However, combustion exhaust streams may contain filterable particles at high concentrations together with semi-volatile UV-active material that will be temporarily retained on the filter tape leading to a distinct increase in UV absorption. Over time these organic species boil off the tape and reduce the enhanced UV adsorption. If equilibrium between organic species deposit and boil off is not reached due to cleaner air being sampled, the amount of organic enhancement will drop and will lead to negative UV component concentrations.

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

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

All sites measured increased concentrations during the cold periods in January, November and December of 2011, but to a lesser extent when compared to 2010. This is due to the milder conditions in 2011.

Raised UV component concentrations were also observed between 11<sup>th</sup> – 31<sup>st</sup> March at many sites across the Network, this ties in with the raised Black Carbon concentrations and the possible use of

wood for secondary heating.

There were no raised UV component concentrations corresponding to the raised Black Carbon concentrations during the pollution episode over the period 26<sup>th</sup> September to 3<sup>rd</sup> October. The lack of a UV component signature during this period may be due to warmer conditions leading to little use of domestic heating.

Guy Fawkes Night celebrations lead to high UV component concentrations between the 5<sup>th</sup> and 7<sup>th</sup> November. Raised concentrations in Northern Ireland on 7<sup>th</sup> November may be more to do with cold weather than Guy Fawkes Night celebrations.

Calm and foggy conditions over the period 19<sup>th</sup> – 23<sup>rd</sup> November lead to elevated UV component concentrations at many sites across the UK.

## 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

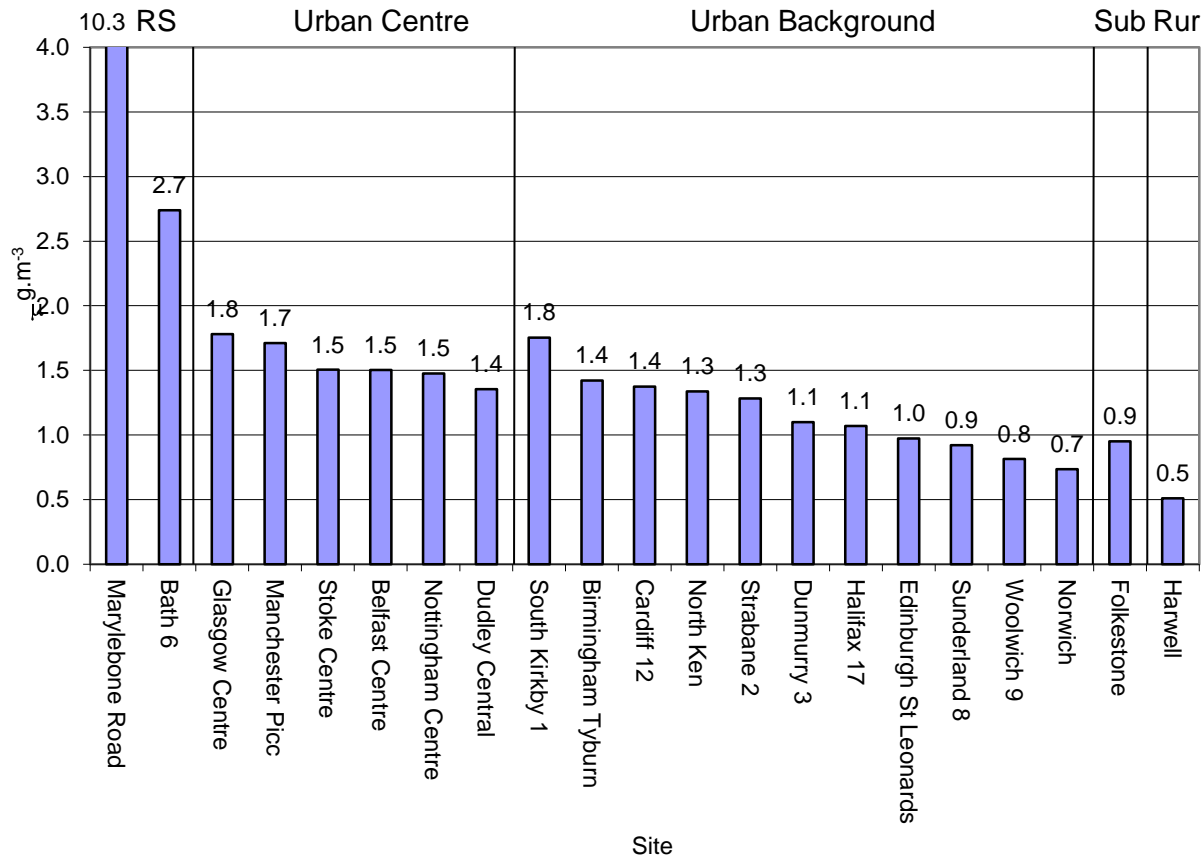
Table 7 gives the annual average for each site for 2011.

Site	Mean concentration $\mu\text{g.m}^{-3}$
Bath	2.7
Belfast Centre	1.5
Birmingham Tyburn	1.4
Cardiff	1.4
Dudley Central	1.4
Dunmurry	1.1
Edinburgh St Leonards	1.0
Folkestone	0.9
Glasgow Centre	1.8
Halifax	1.1
Harwell	0.5
Manchester Piccadilly	1.7
Marylebone Road	10.3
North Kensington	1.3
Norwich Lakenfields	0.7
Nottingham Centre	1.5
South Kirkby	1.8
Stoke Centre	1.5
Strabane	1.3
Sunderland	0.9
Woolwich	0.8

**Table 7 Annual Mean Black Carbon Concentration for 2011**

The increments in concentration from the rural background site at Harwell to the suburban site in Folkestone to the urban background sites in London (North Kensington and Woolwich) and from these to the Marylebone Roadside site in Central London are  $0.4 \mu\text{g.m}^{-3}$ ,  $0.2 \mu\text{g.m}^{-3}$  and  $9.2 \mu\text{g.m}^{-3}$  respectively.

The annual mean concentrations are presented as a bar graph (Figure 17) to aid the comparison of sites:



**Figure 17 Annual Mean Black Carbon Concentrations for 2011**

## 5.2.2 UV Component

Table 8 gives the annual average for each site for 2011.

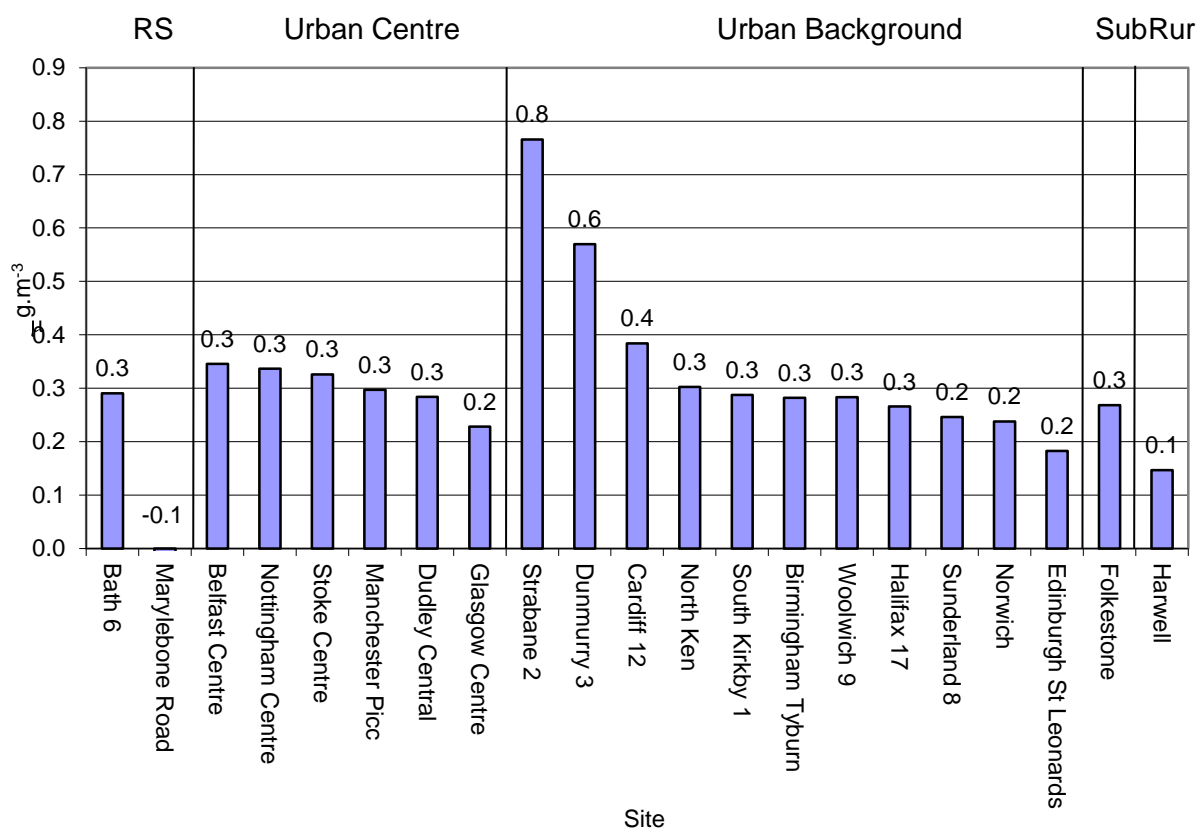
Site	Mean concentration, $\mu\text{g}\cdot\text{m}^{-3}$
Bath	0.3
Belfast Centre	0.3
Birmingham Tyburn	0.3
Cardiff	0.4
Dudley Central	0.3
Dunmurry	0.6
Edinburgh St Leonards	0.2
Folkestone	0.3
Glasgow Centre	0.2
Halifax	0.3
Harwell	0.1
Manchester Piccadilly	0.3
Marylebone Road	-0.1
North Kensington	0.3
Norwich Lakenfields	0.2
Nottingham Centre	0.3
South Kirkby	0.3
Stoke Centre	0.3
Strabane	0.8
Sunderland	0.2
Woolwich	0.3

**Table 8**

**Annual Mean UV Component Concentrations for 2011**



The annual mean concentrations are presented as a bar graph (Figure 18) to aid the comparison of sites:



**Figure 18 Annual mean UV Component concentrations for 2011**

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

## 5.2.3 Data Capture

Table 9 gives the data capture for each site for 2011.

<b>Site</b>	<b>Data Capture %</b>
Bath 6	94
Belfast Centre	100
Birmingham Tyburn	100
Cardiff 12	98
Dudley Central	100
Dunmurry 3	95
Edinburgh St Leonards	99
Folkestone	99
Glasgow Centre	98
Halifax 17	99
Harwell	98
Manchester Piccadilly	98
Marylebone Road	96
North Ken	95
Norwich 7	96
Nottingham Centre	100
South Kirkby 1	98
Stoke Centre	99
Strabane 2	99
Sunderland 8	94
Woolwich 9	98

**Table 9 Data capture rates of the Aethalometers for 2011**

The average data capture for the Network is 98% and there are no sites with a data capture of below 90%.

### 5.3 TEMPORAL VARIATIONS

The following section presents analysis of the Black Carbon and UV component concentrations with regards to the hour of the day, the day of the week and the month in which the measurements are made during 2011.

These results have been grouped by site and are batched together by site classification. The site order for the Roadside and Urban Centre sites is in decreasing Black Carbon Concentration, while the site order for the Urban Background, Suburban and Rural Background sites is in decreasing UV component concentration. The units on the y-axis are:  $\mu\text{g.m}^{-3}$  for Black Carbon and equivalent  $\mu\text{g.m}^{-3}$  for the UV component. The results are presented in Figures 19 to 22.

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

#### Chart Key

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

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

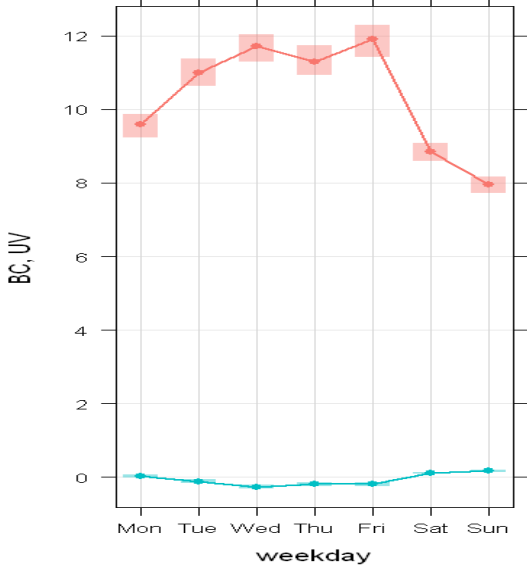
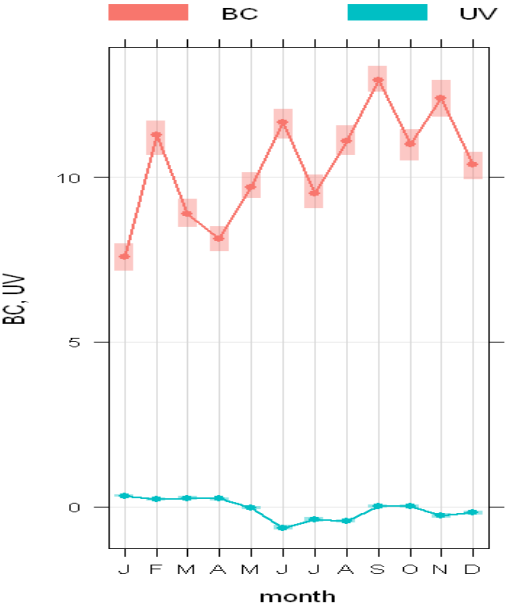
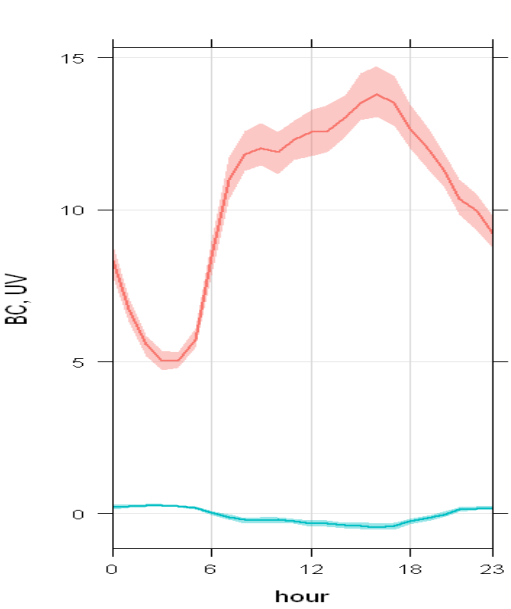
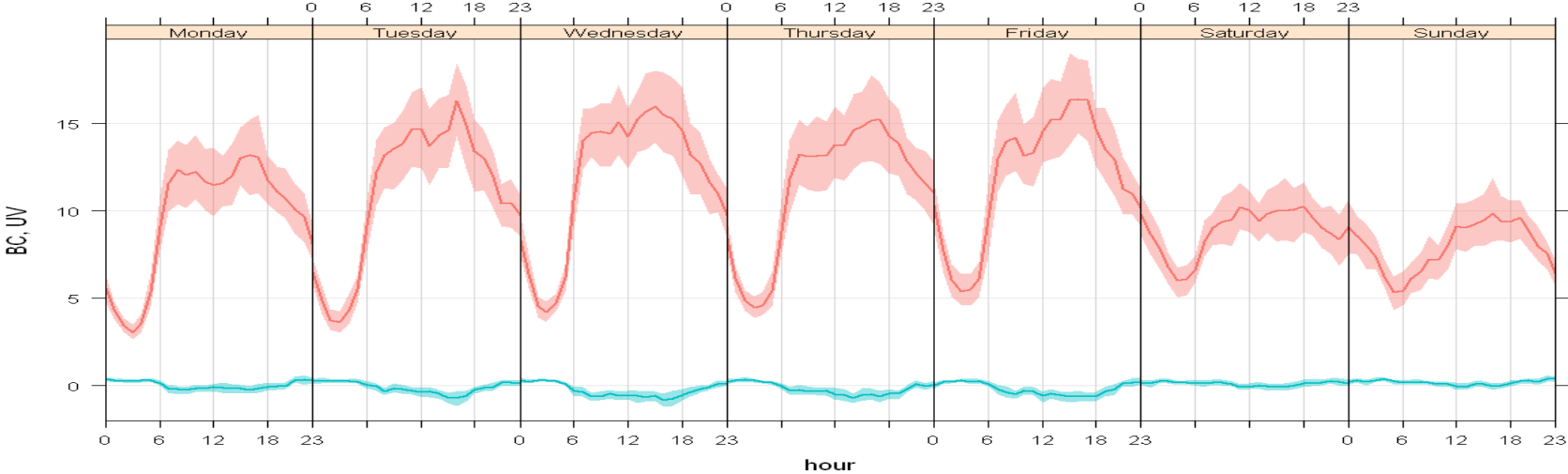
The bottom centre chart shows the same data grouped by month of the year.

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

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

#### Acknowledgement

Figures 19 to 23 are generated using the Open-Air Tools run on the R software platform<sup>[5,6]</sup>.



Marylebone Road

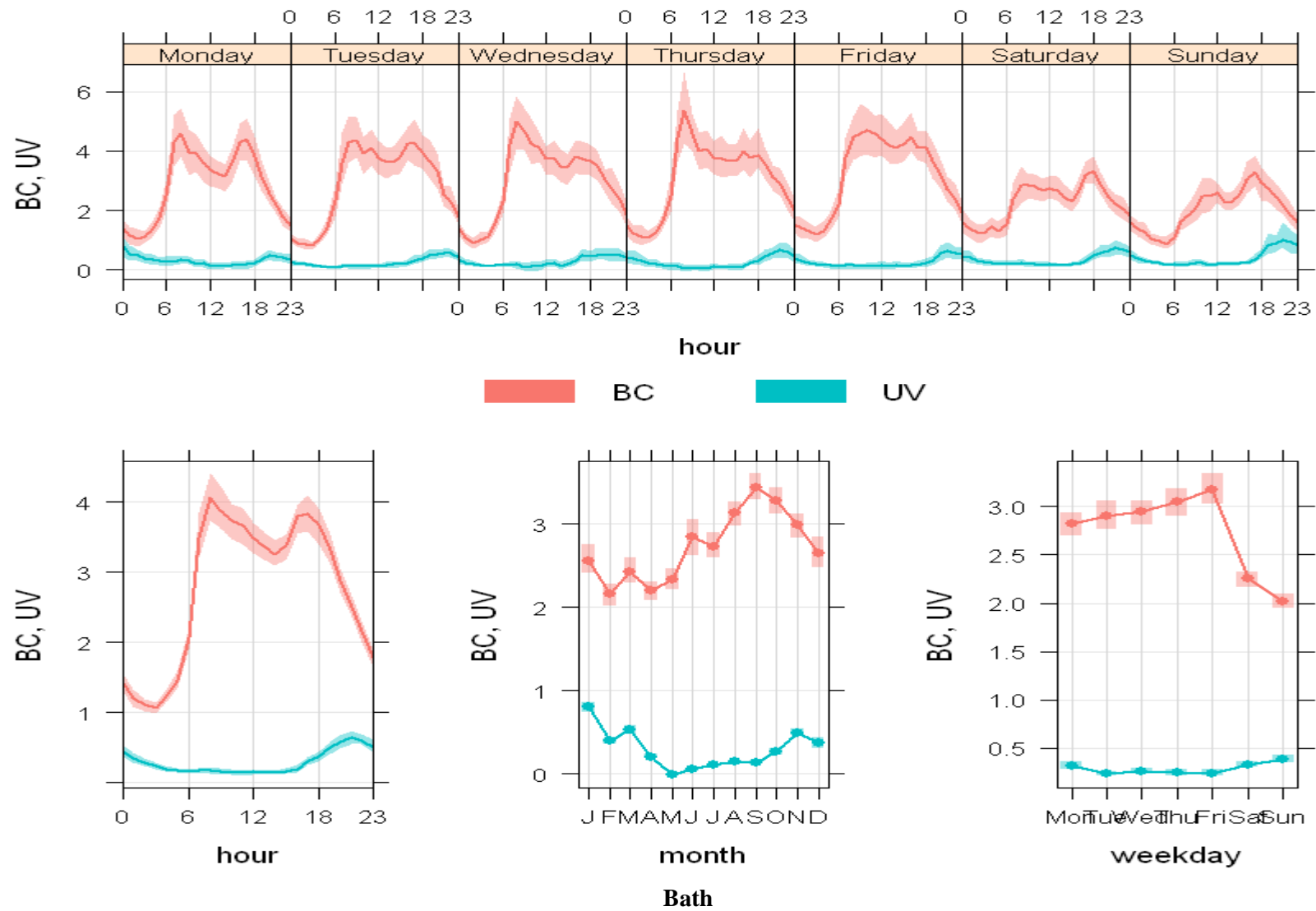
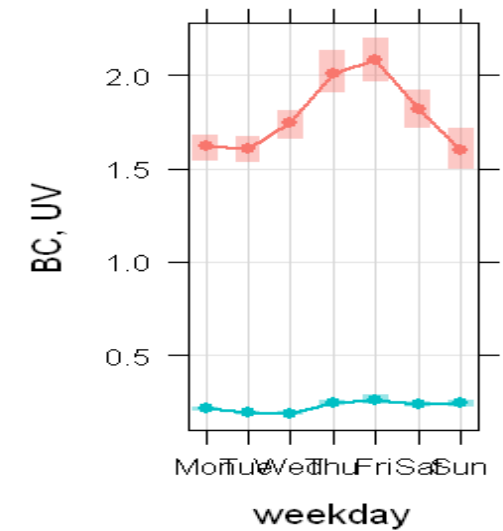
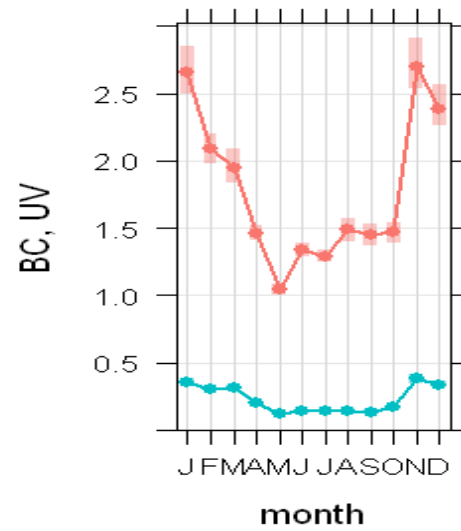
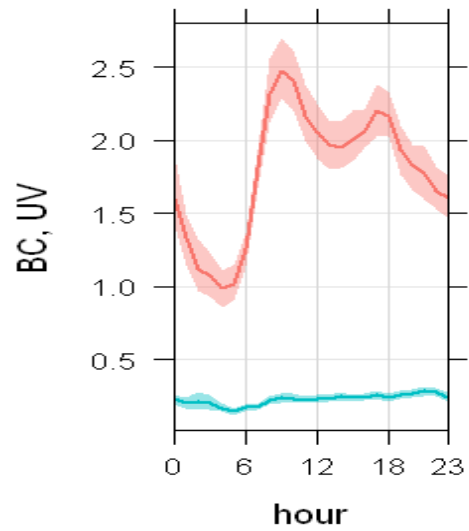
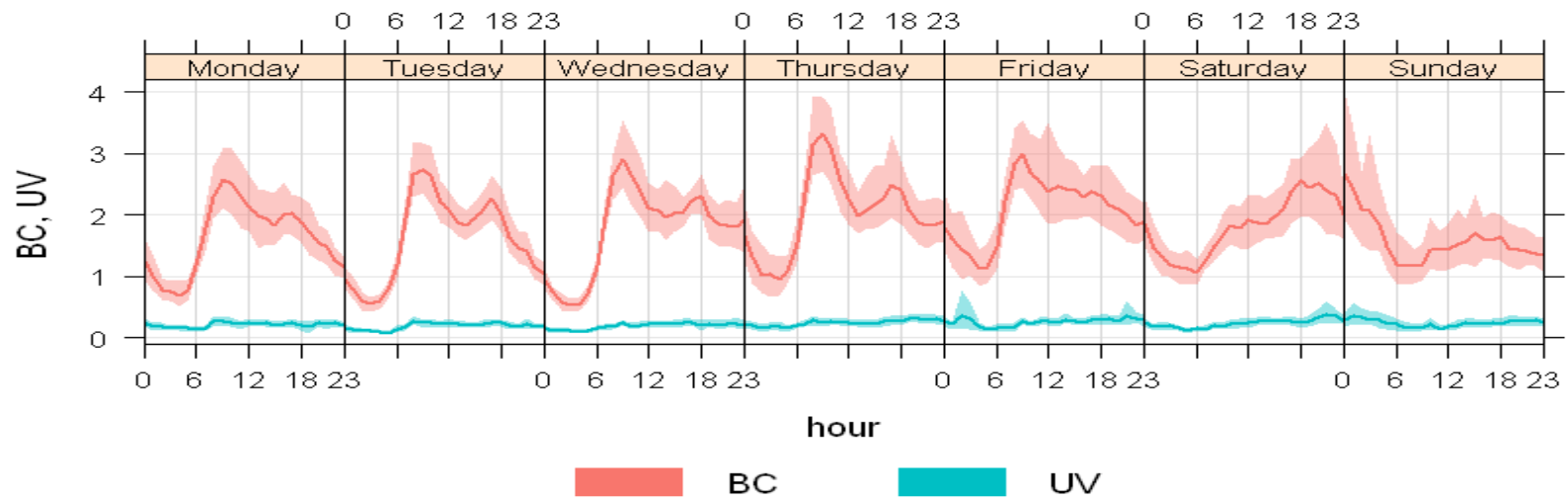
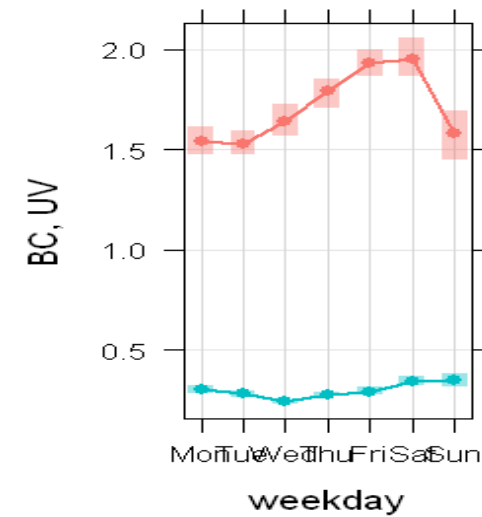
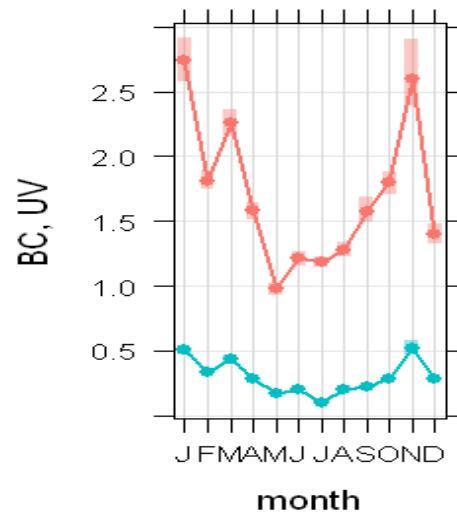
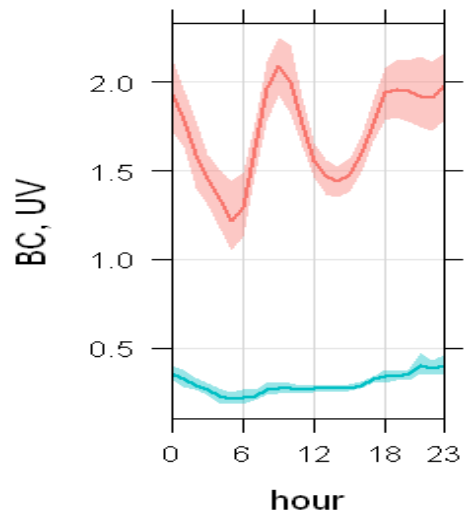
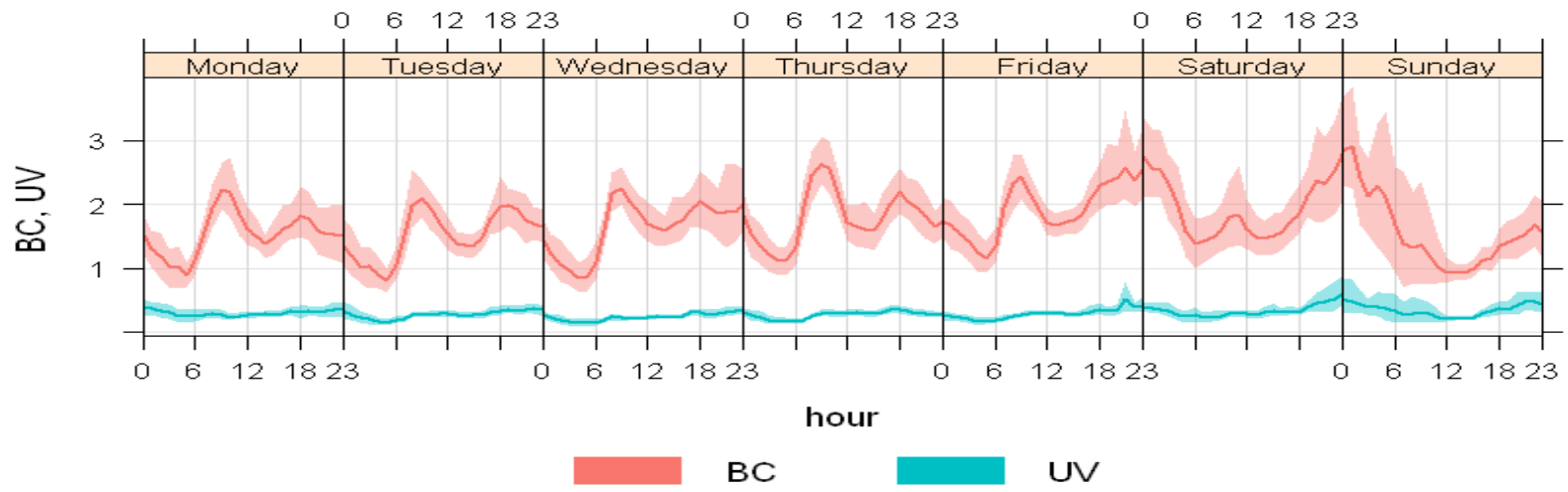


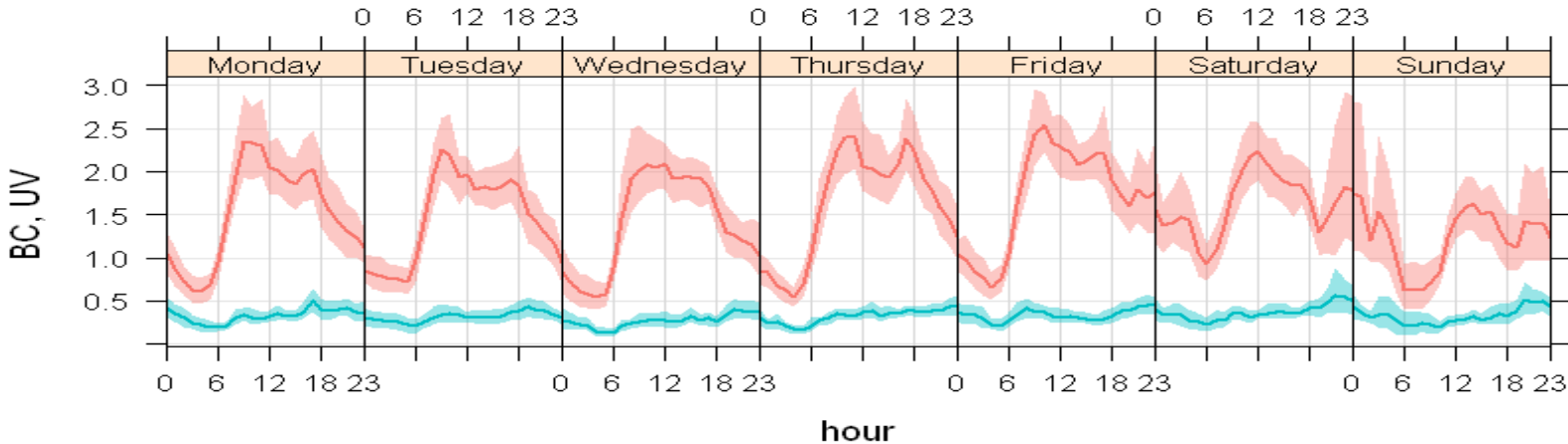
Figure 19 Roadside Sites



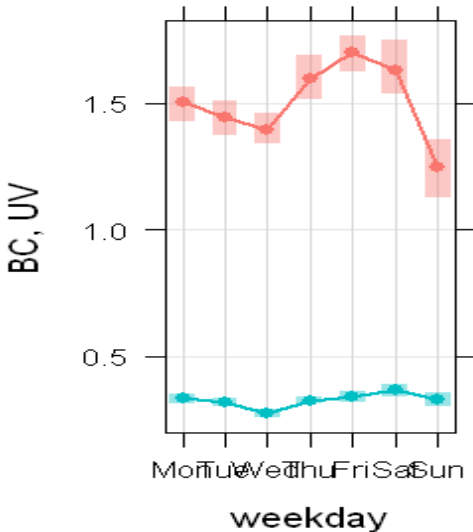
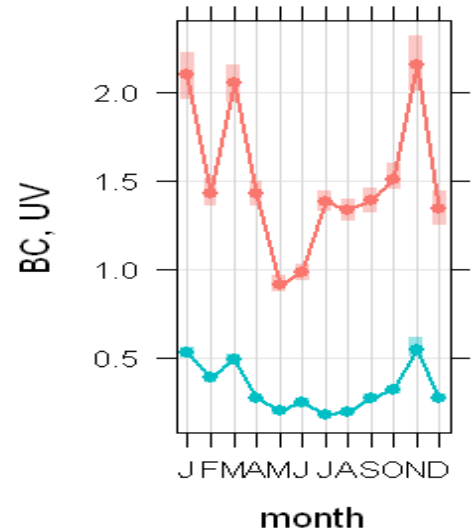
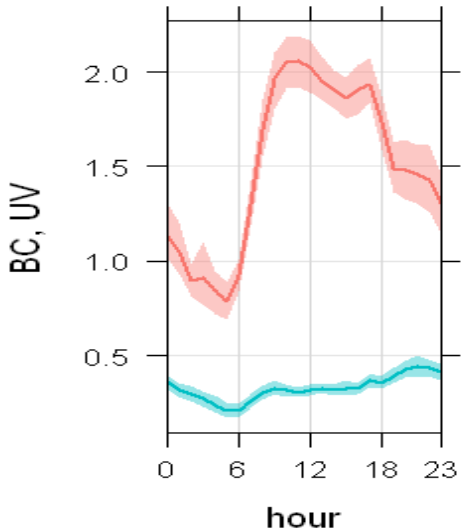
Glasgow Centre



Manchester Piccadilly

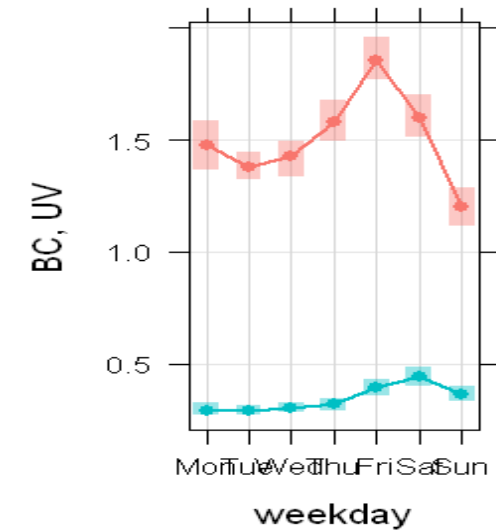
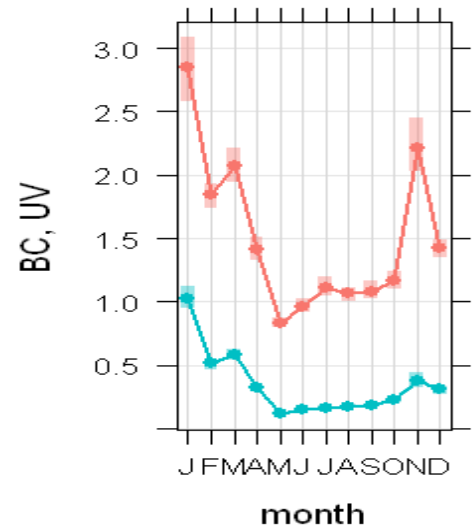
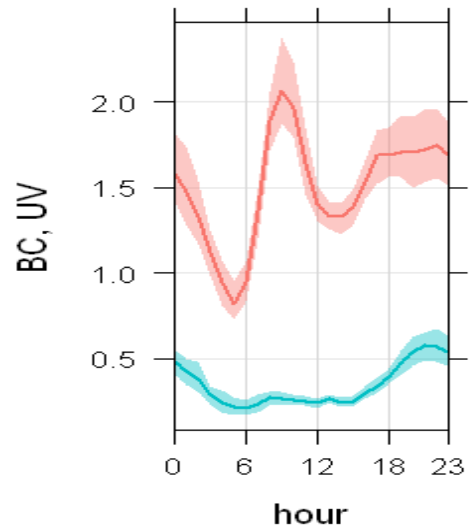
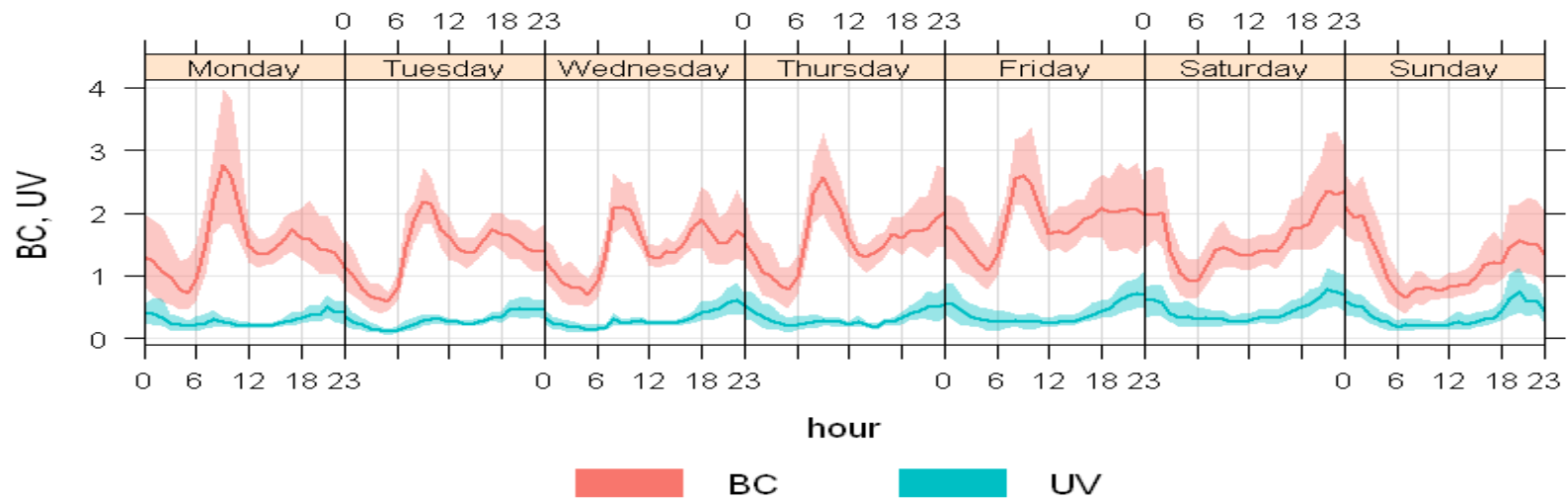


BC UV

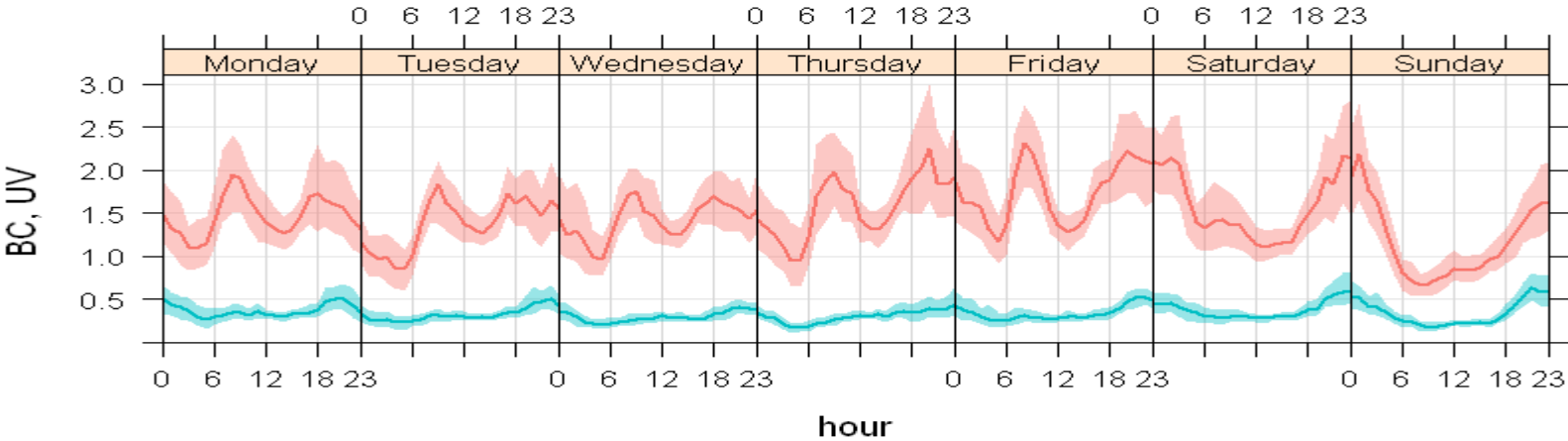


Stoke Centre

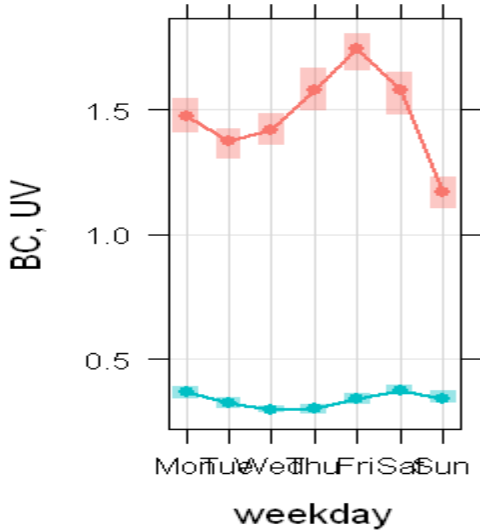
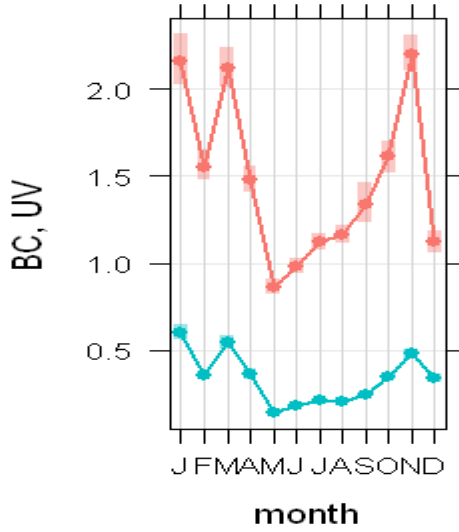
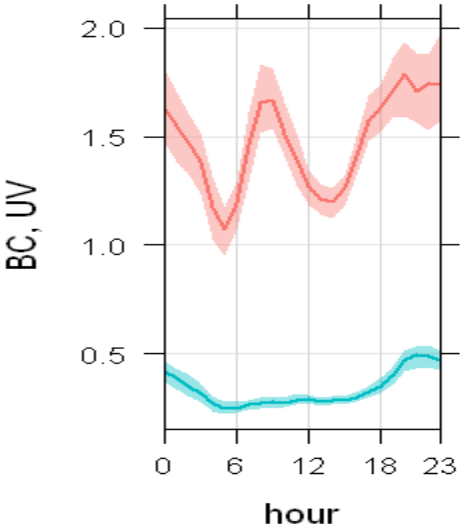




**Belfast Centre**



BC UV



Nottingham Centre

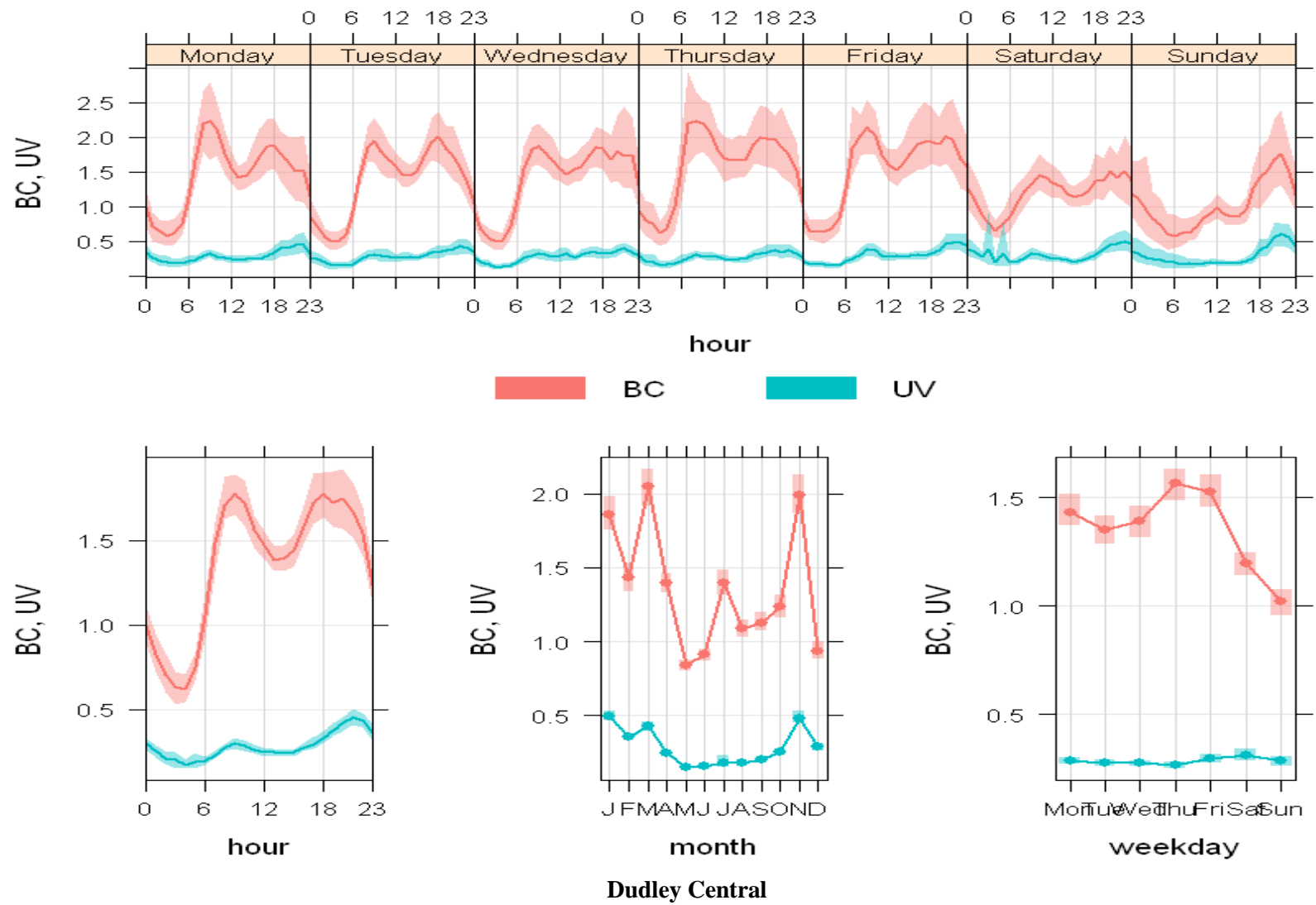
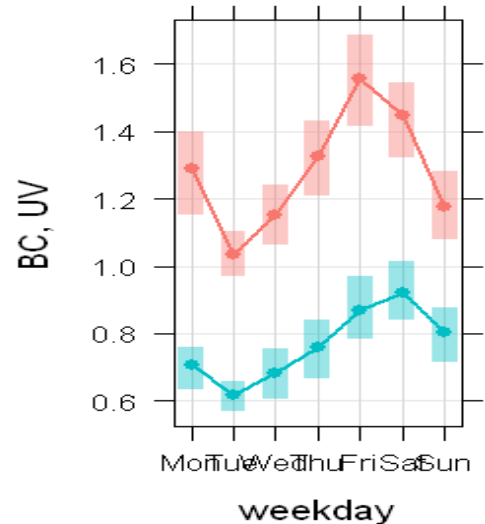
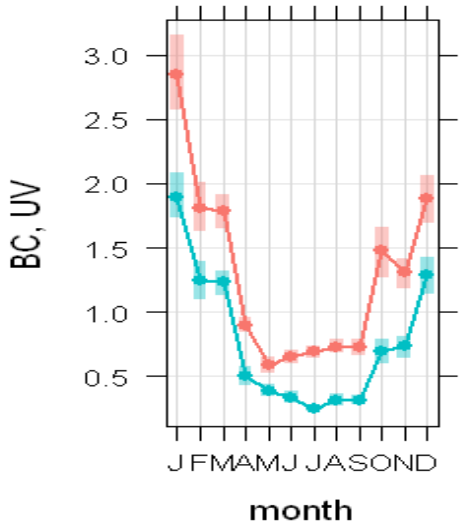
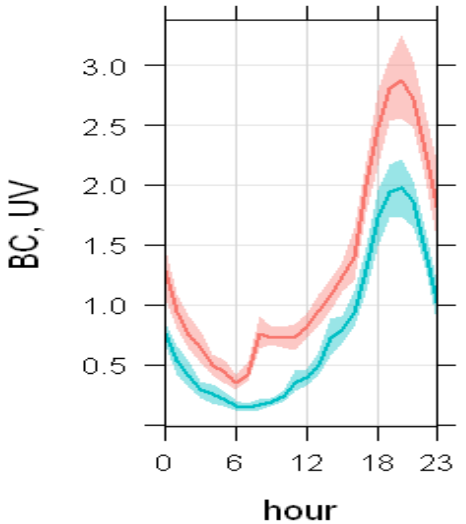
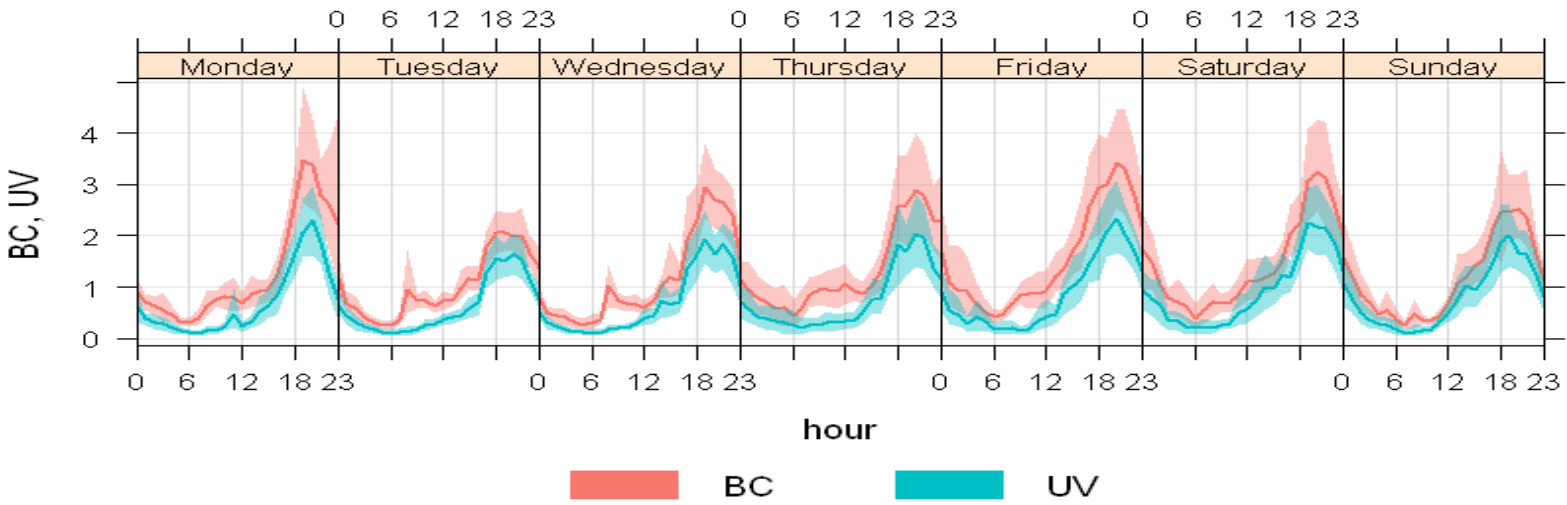
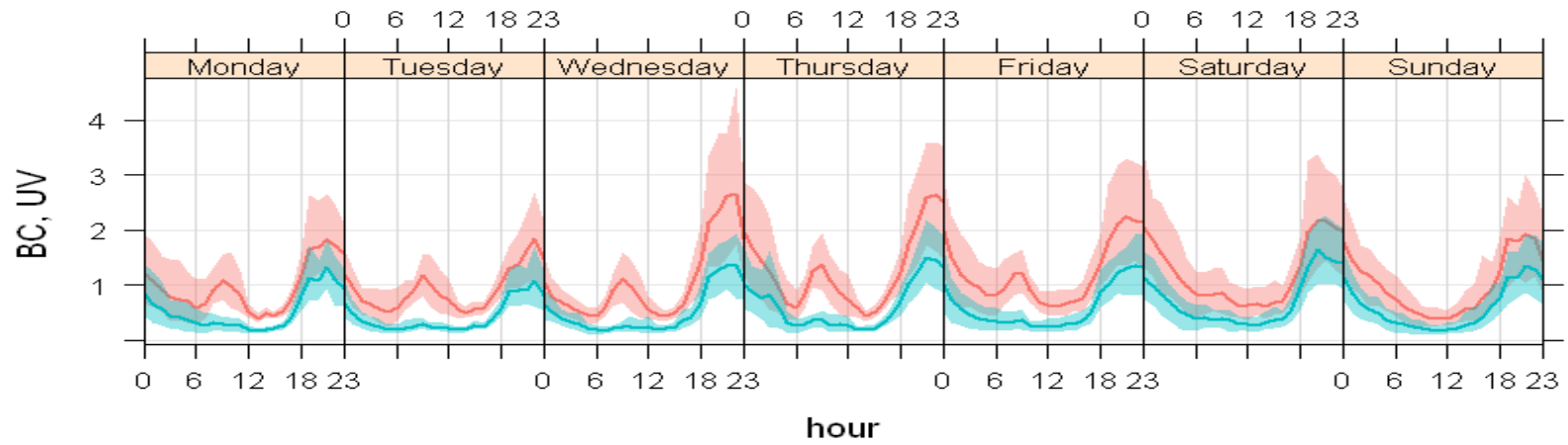


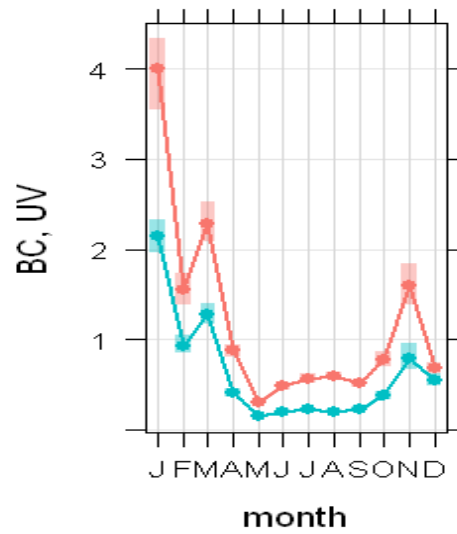
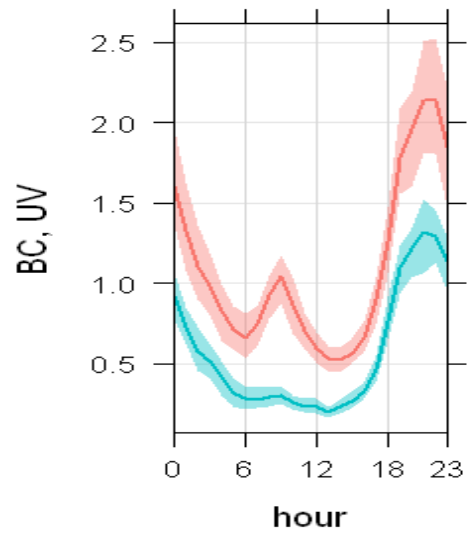
Figure 20 Urban Centre Sites



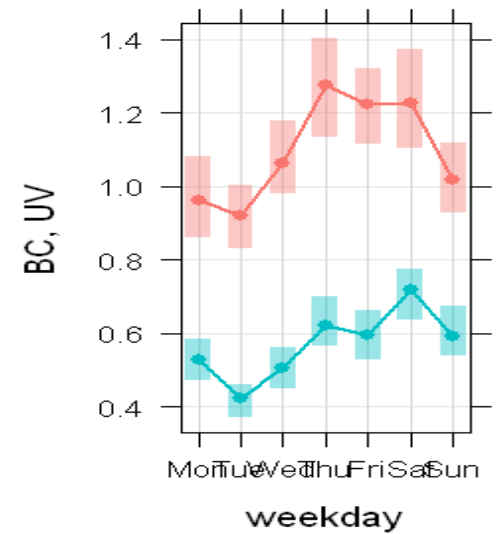
Strabane

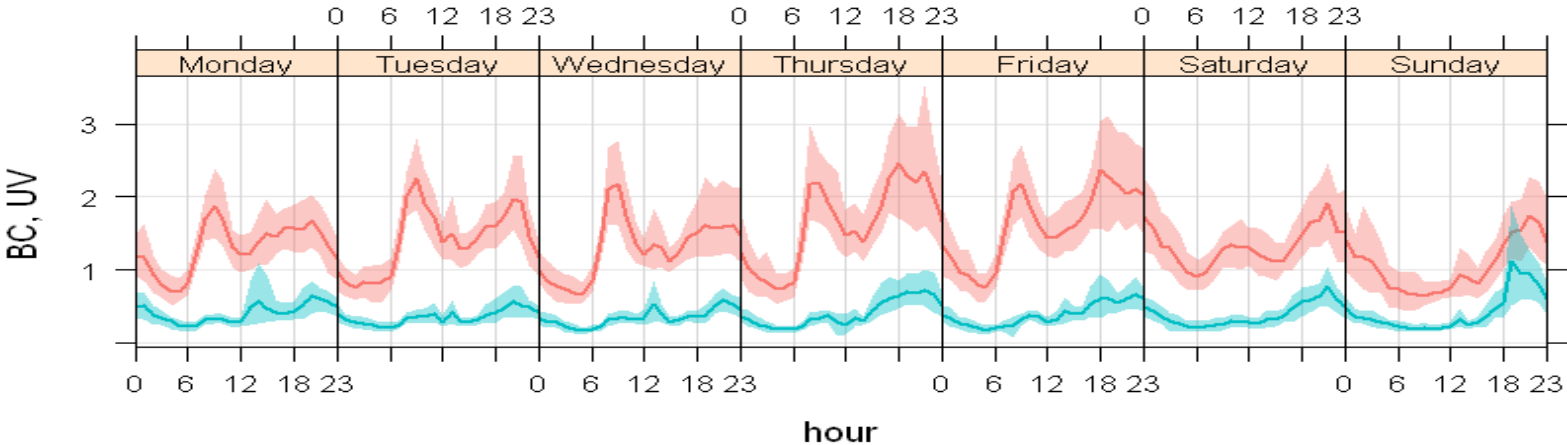


BC UV

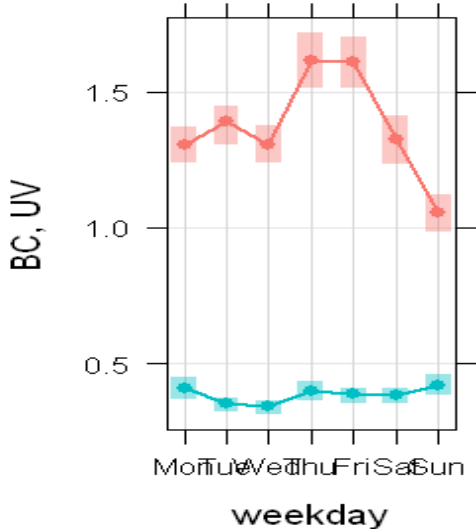
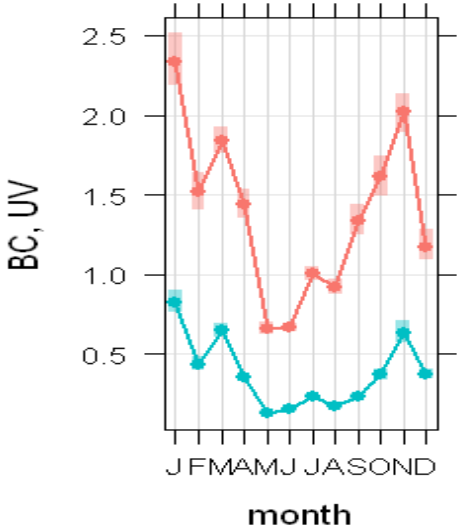
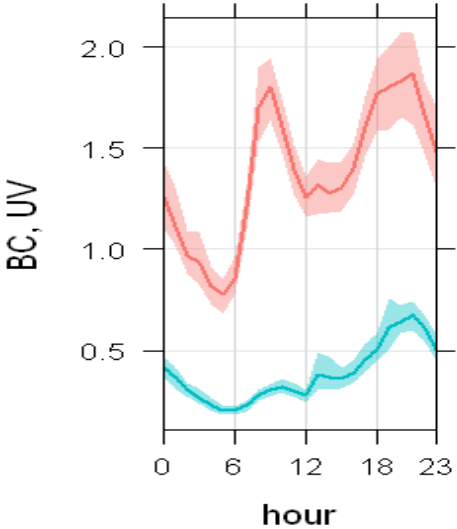


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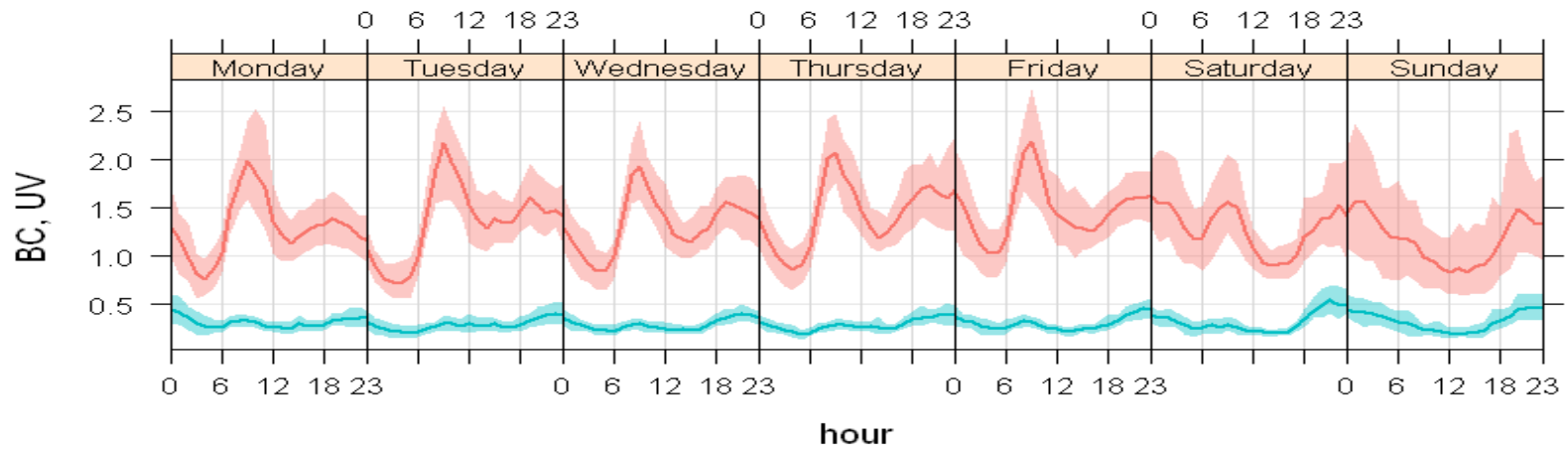




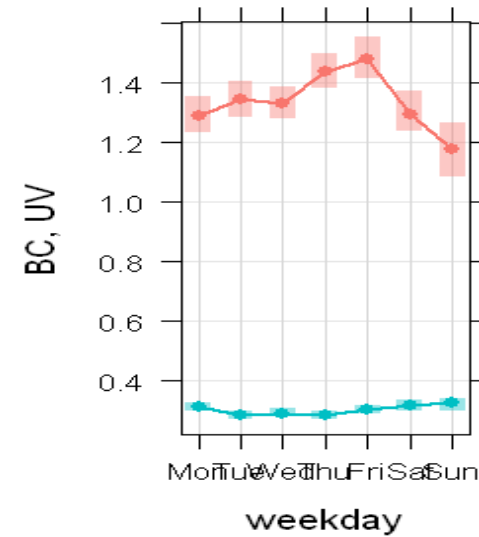
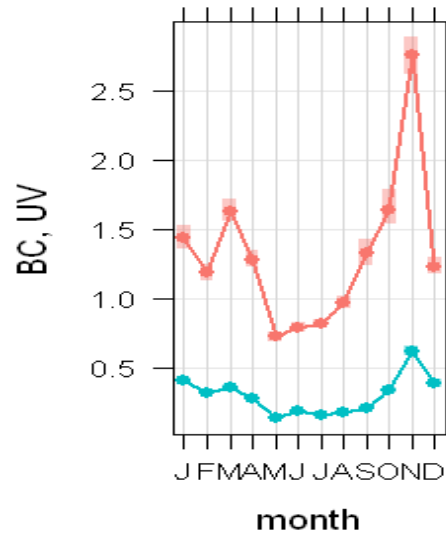
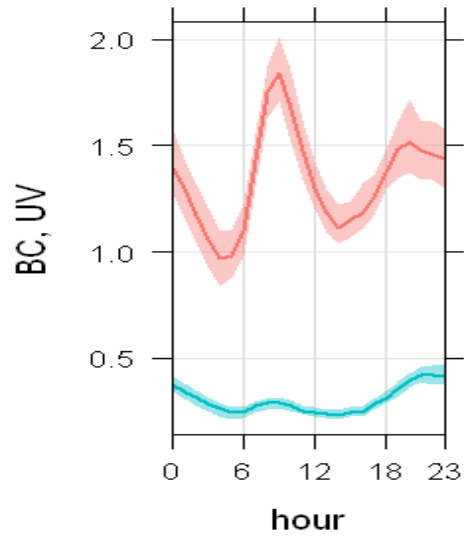
BC UV



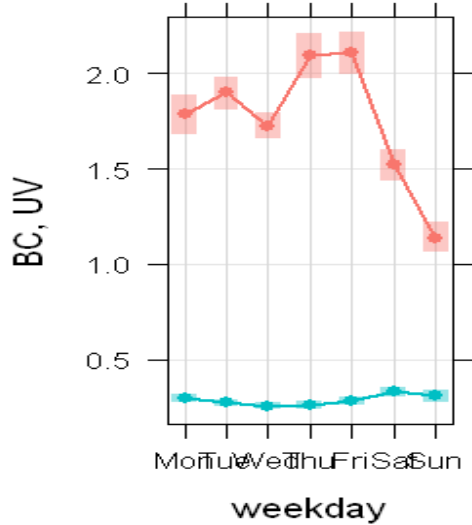
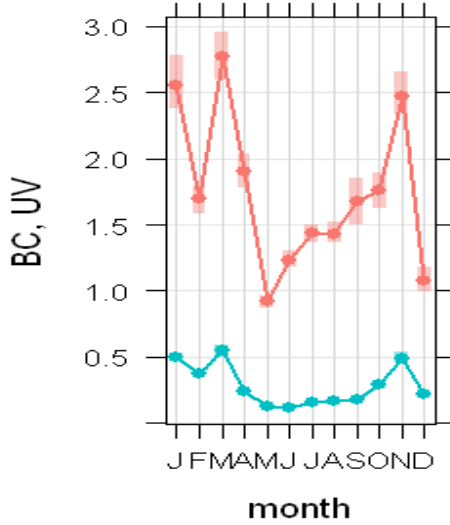
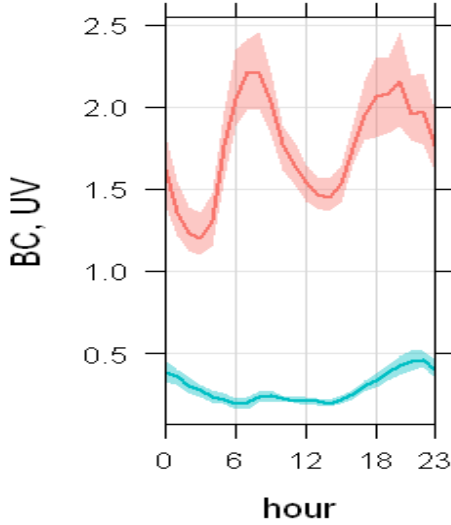
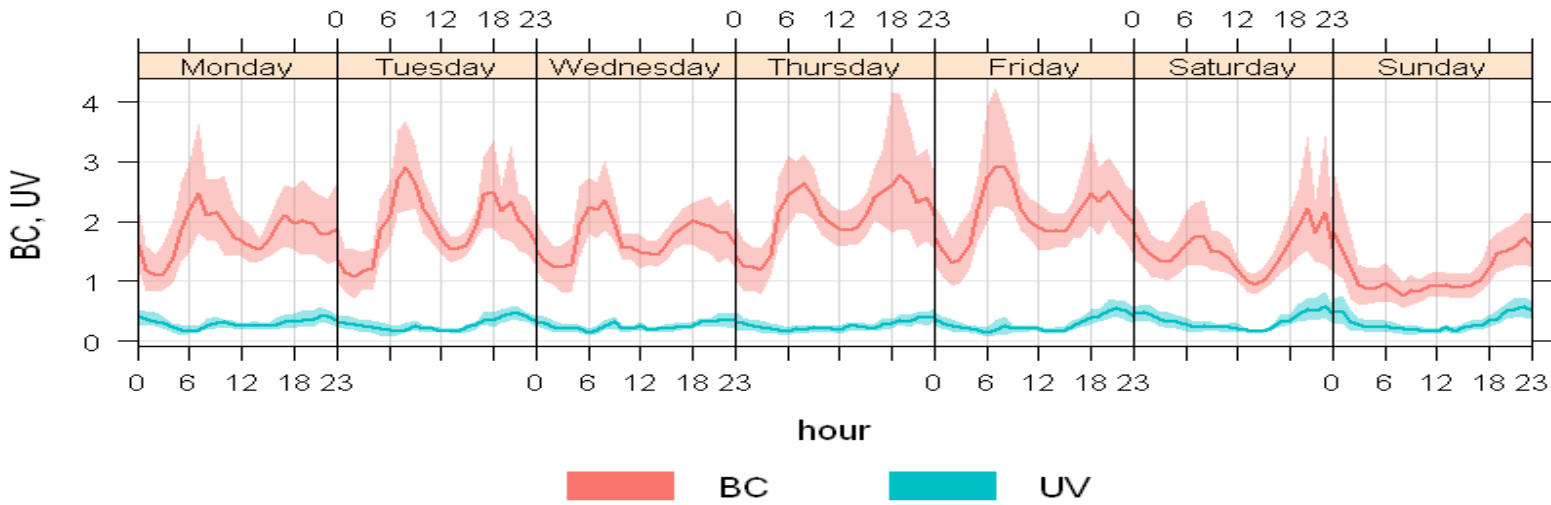
Cardiff



BC UV

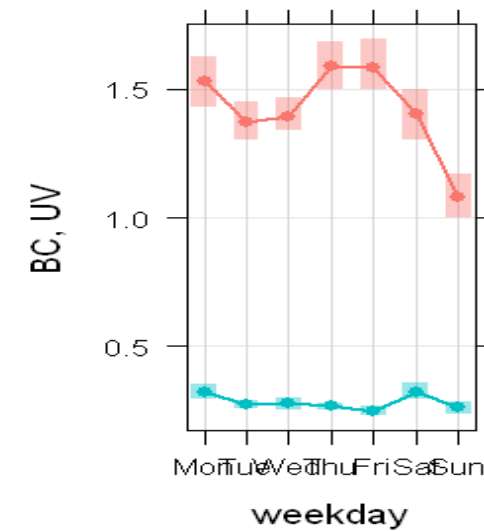
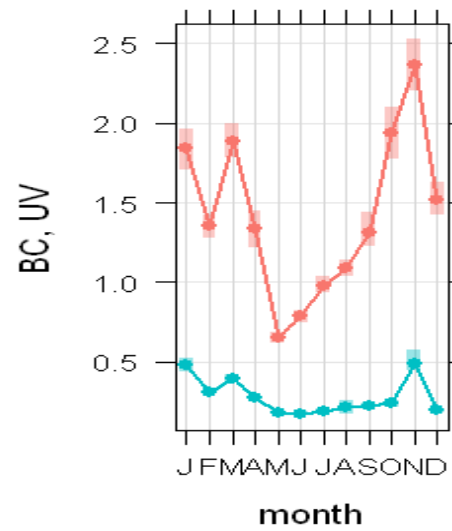
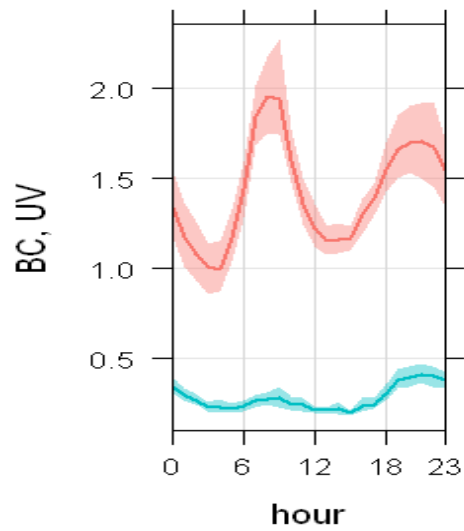
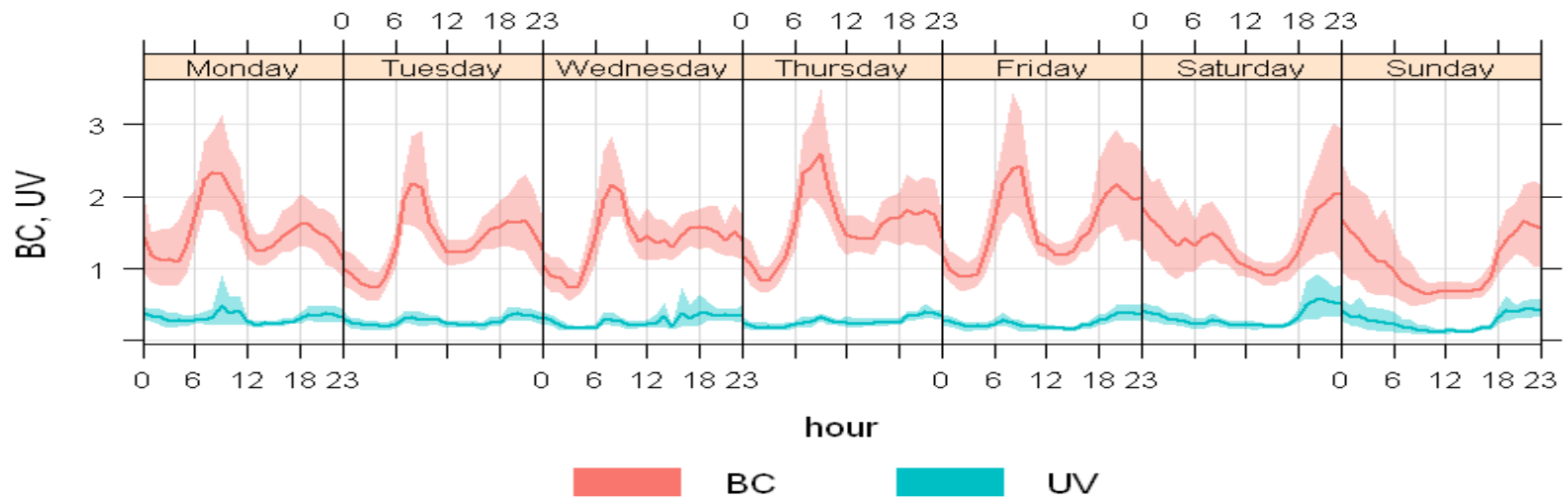


North Kensington

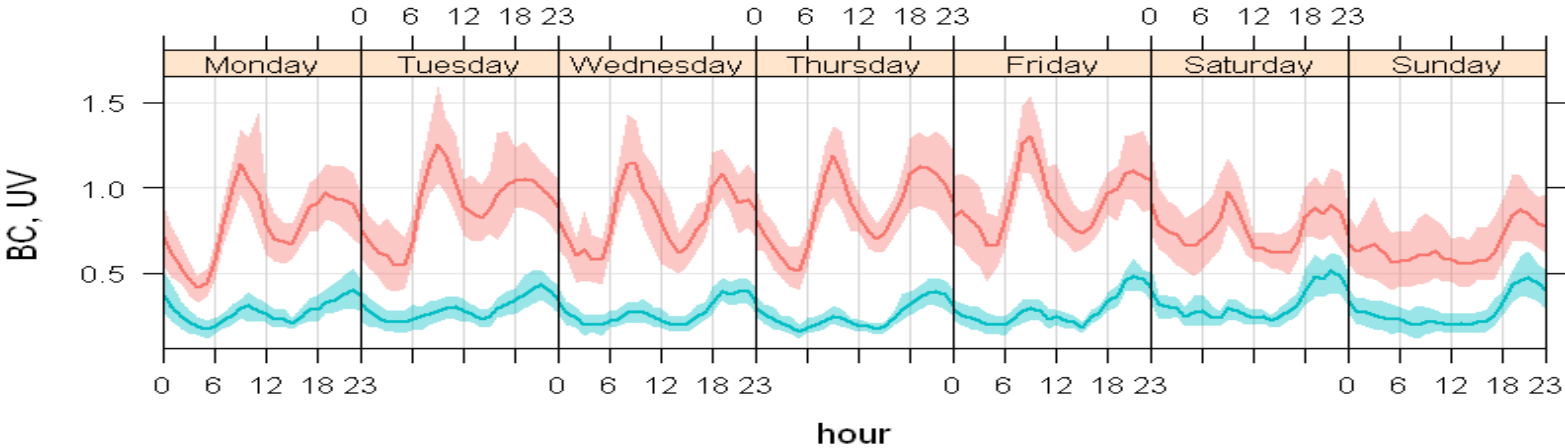


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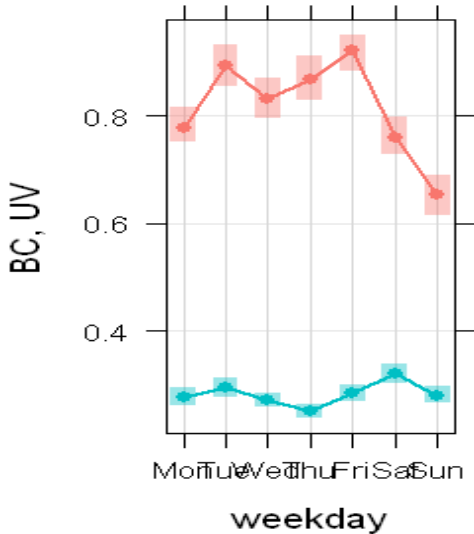
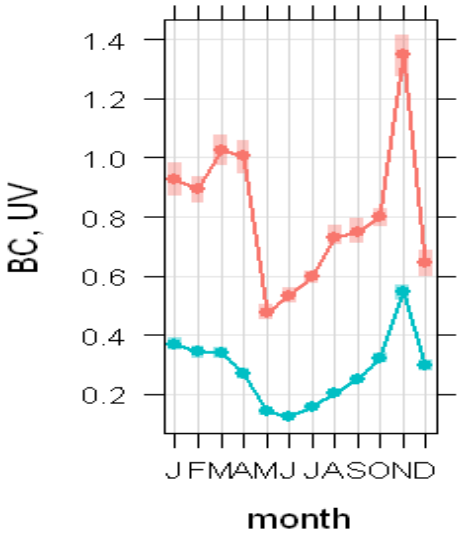
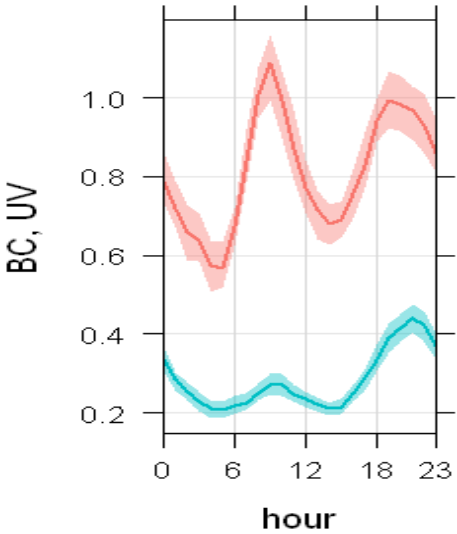




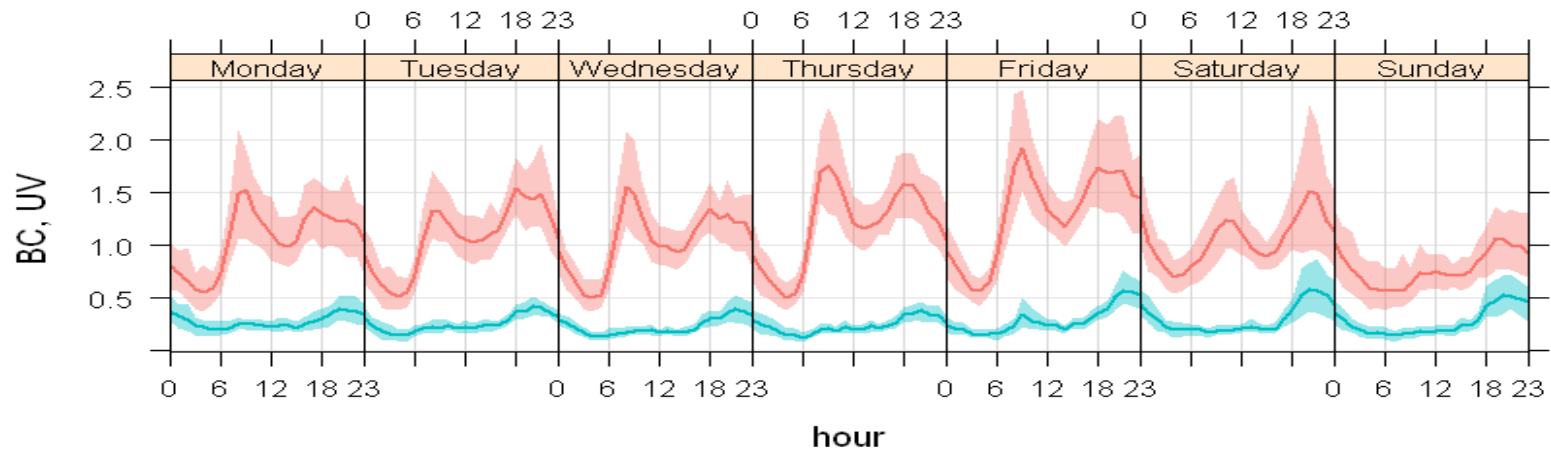
**Birmingham Tyburn**



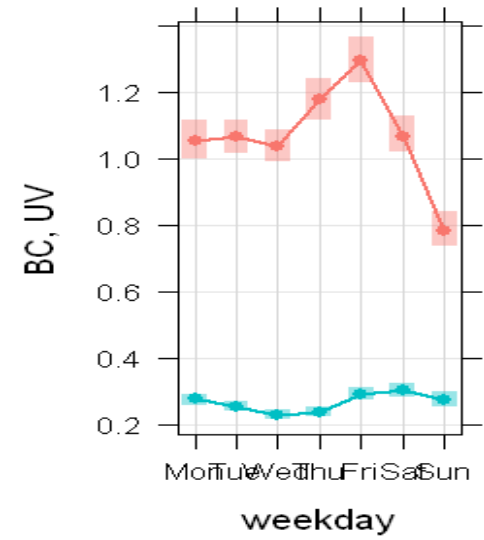
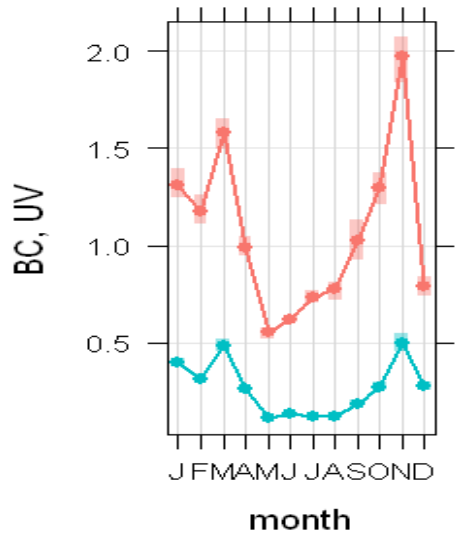
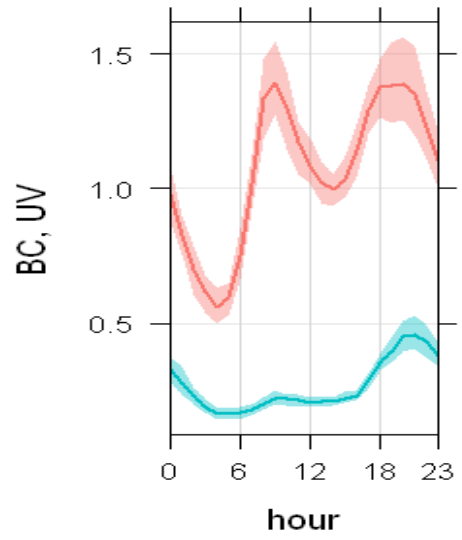
BC UV



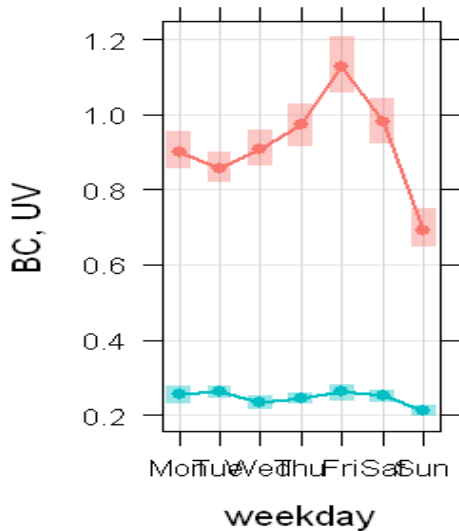
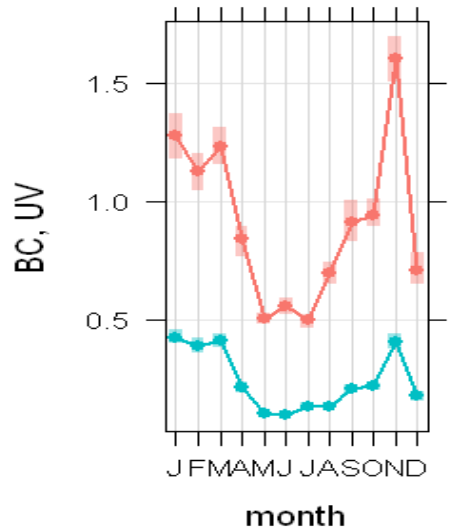
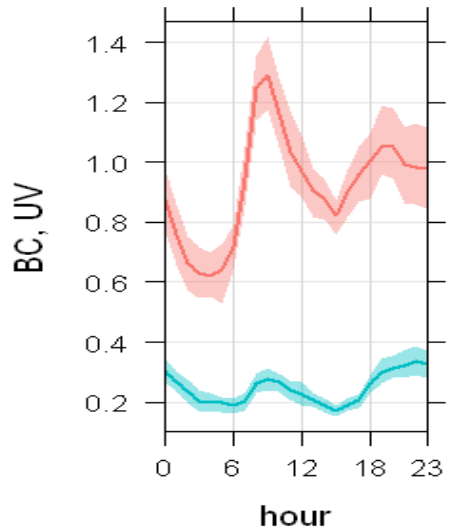
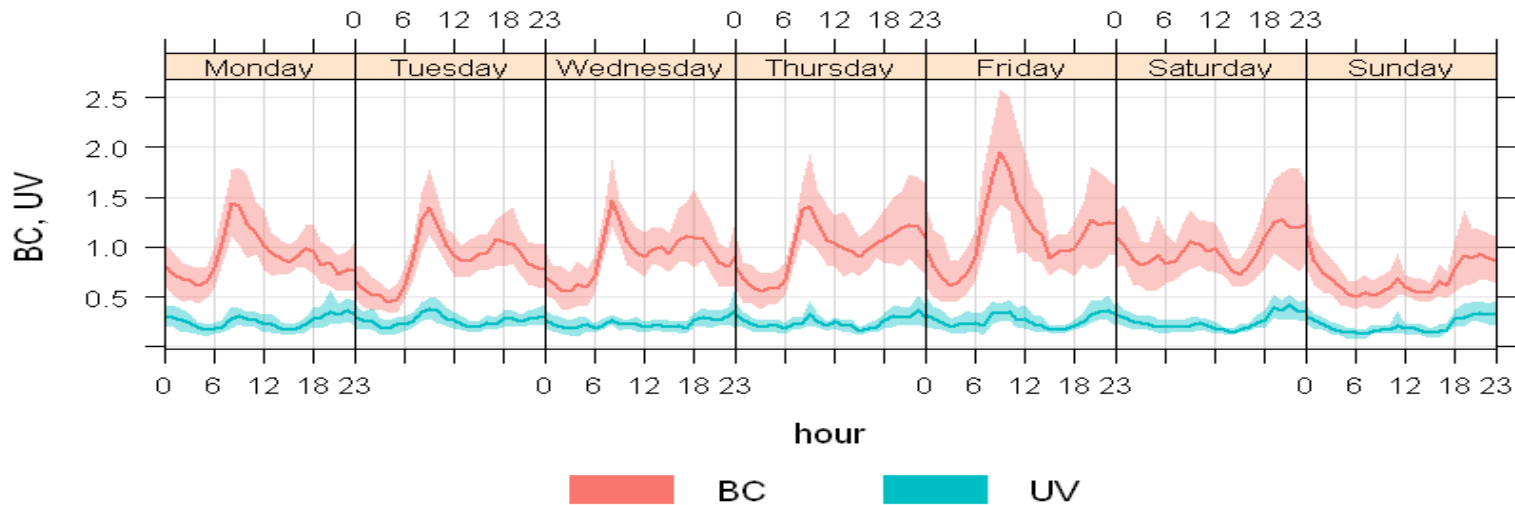
Woolwich



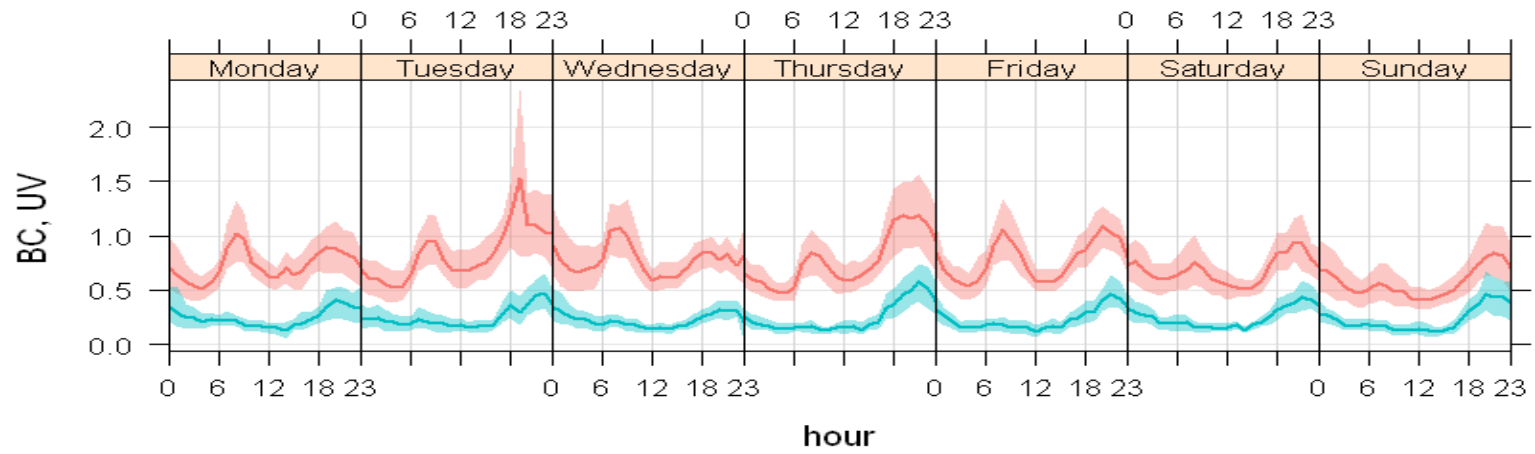
BC UV



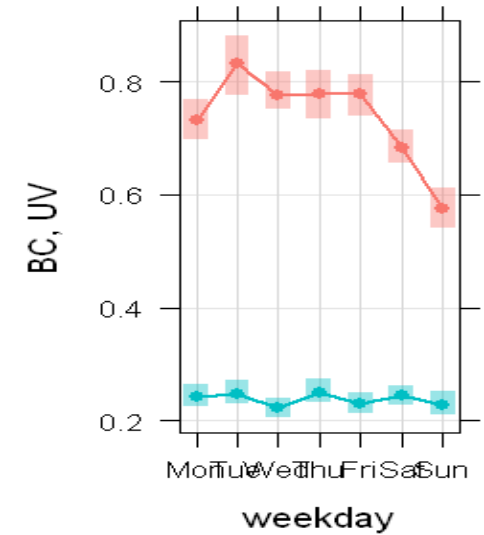
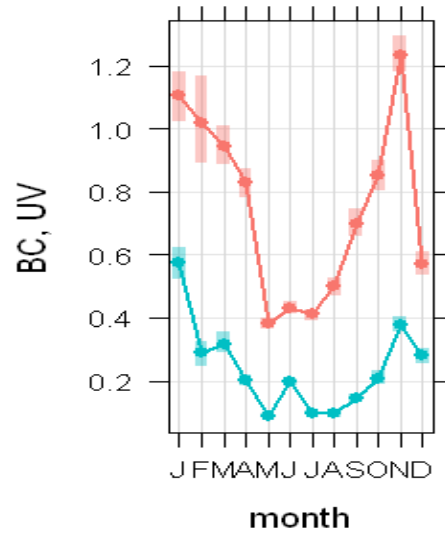
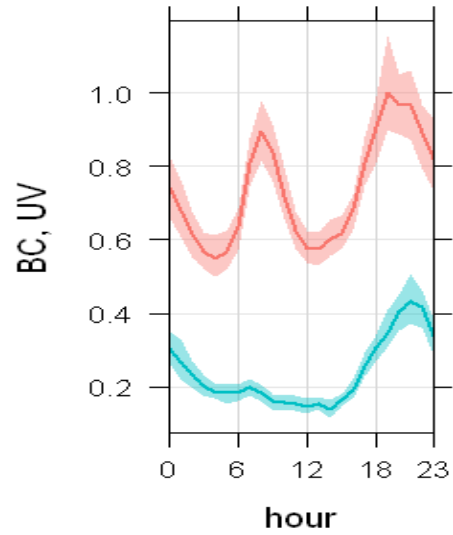
Halifax



Sunderland



BC UV



Norwich

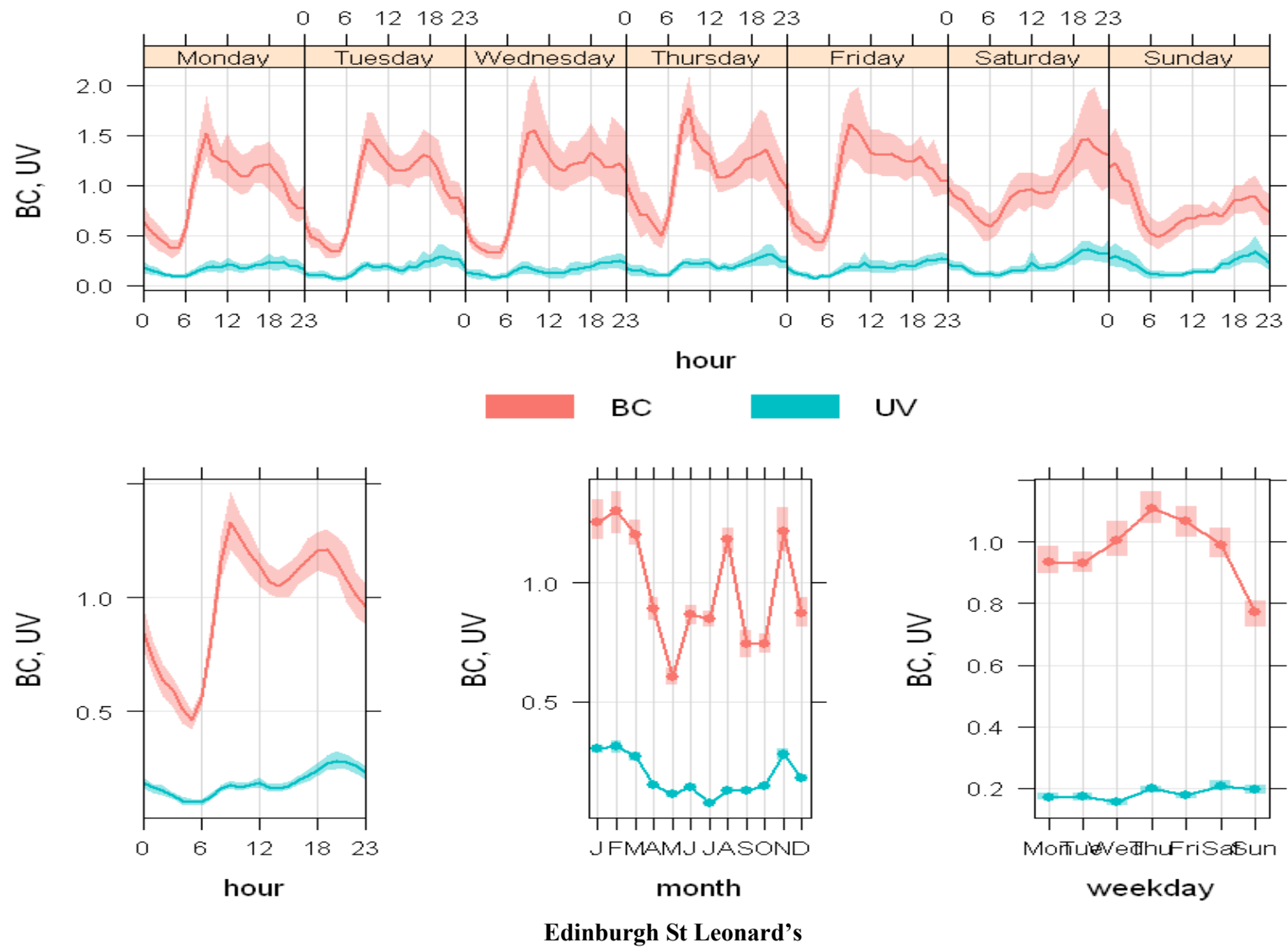
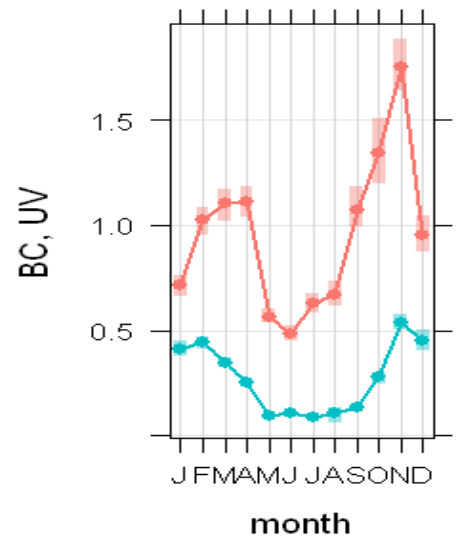
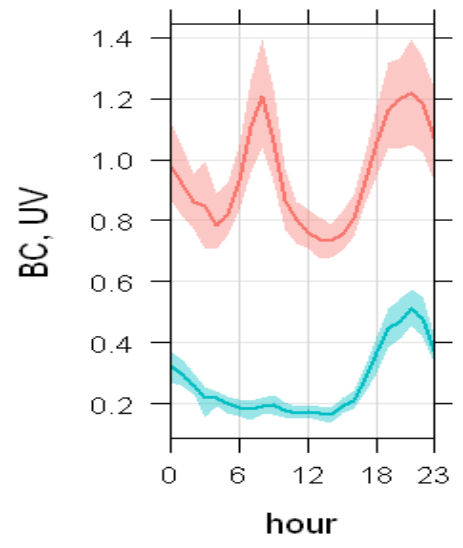
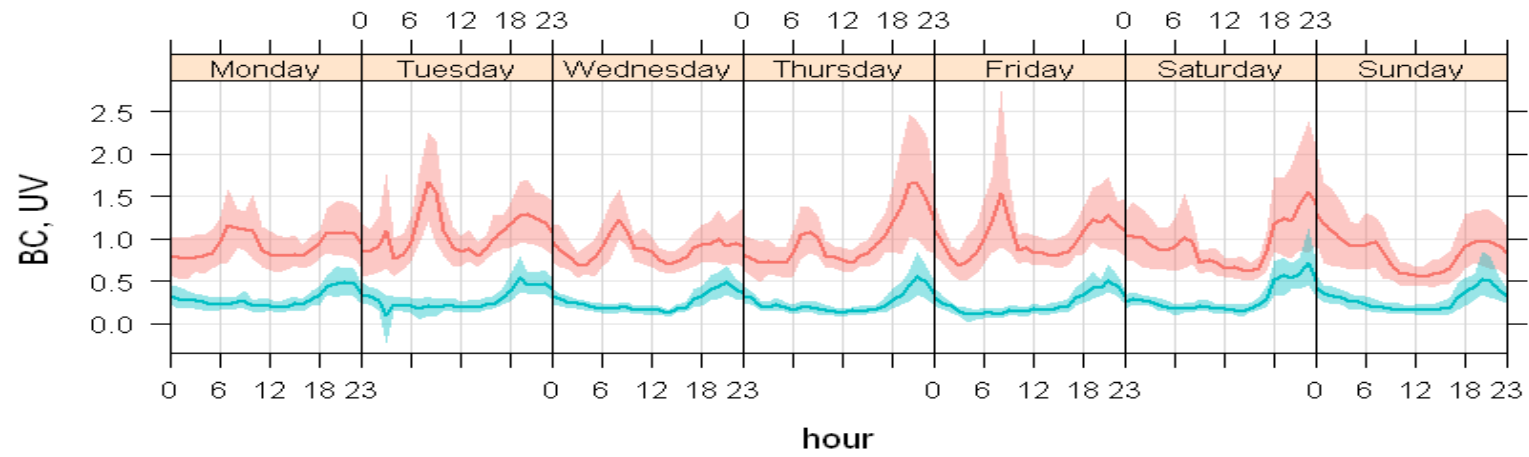
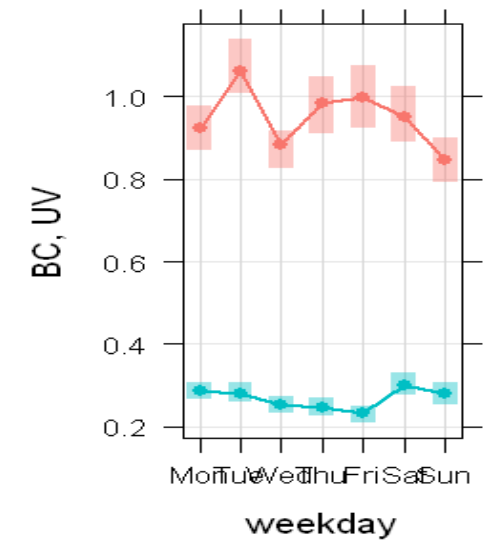


Figure 21 Urban Background Sites



Folkestone



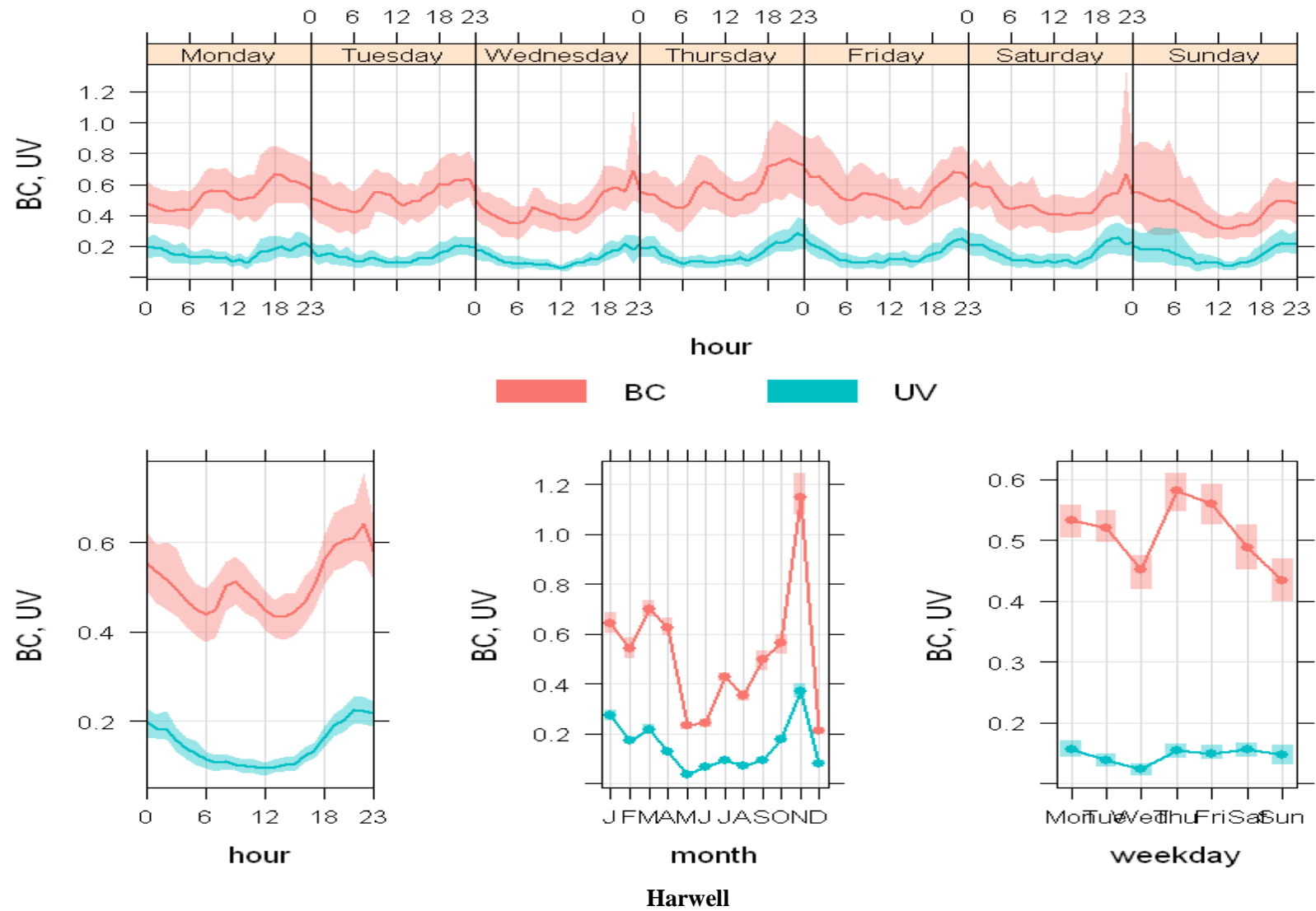


Figure 22 Suburban and Rural Background Sites



### Roadside sites

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

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

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

### Urban Centre sites

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

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

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

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

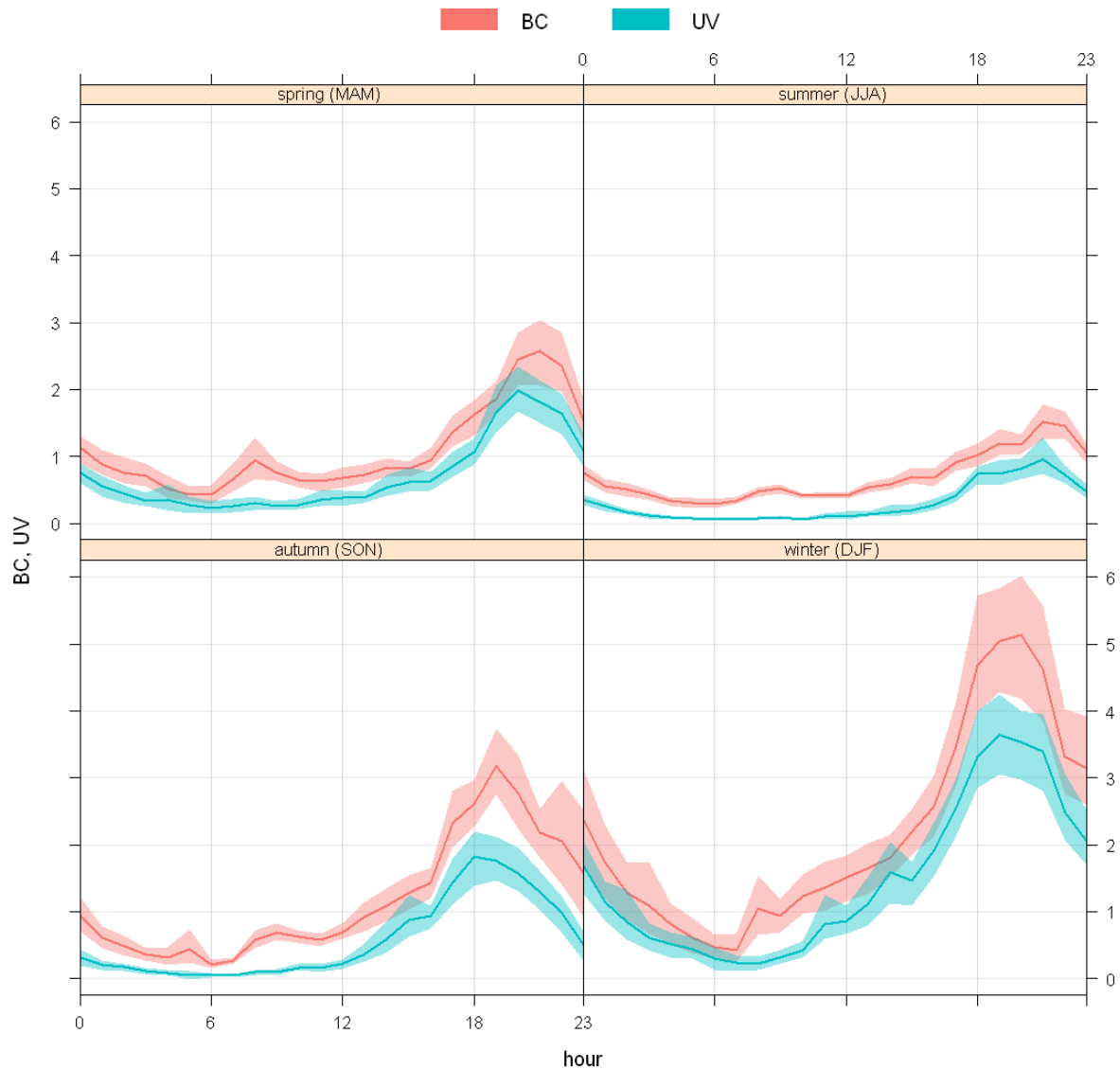
The 09:00 hrs increment in Black Carbon concentration at Belfast Centre may be due to lorries parking next to the site while they unload goods to the local shops; there are a significant number of lorry movements past the site at this time.

### Urban Background sites

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

The Strabane, Dunmurry, Norwich and Cardiff concentrations are dominated by evening fuel use, probably due to the use of oil and solid fuel burning as a domestic fuel. At these sites the UV component concentration is significant, reaching up to 75% of the Black Carbon concentration.

Both Black Carbon and UV component concentrations show strong seasonality dependence, with a marked decrease in concentration over the summer months and a significant increase in concentration in the winter months. This is most apparent in the Strabane and Dunmurry sites due to the meteorological conditions during winter months and the reliance on solid fuel for domestic heating. This is illustrated in Figure 23 showing the Strabane diurnal concentrations for Black Carbon and UV component split into seasons.



**Figure 23 Seasonal Black Carbon and UV component concentrations measured at Strabane in 2011**

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

Suburban and Rural Background sites

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

Diurnal discrepancies

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

- |         |                       |  |
|---------|-----------------------|--|
| Glasgow | Early Friday mornings | high UV component on 18 <sup>th</sup> February |
| Norwich | Tuesday 19:00hrs      | high BC on 8 <sup>th</sup> February            |

Both PM<sub>10</sub> and PM<sub>2.5</sub> concentrations measured by the AURN at the Glasgow Centre site reach very high levels on 18<sup>th</sup> February. The concentrations reach maximums of 189 µg.m<sup>-3</sup> and 168 µg.m<sup>-3</sup>, respectively.

Both PM<sub>10</sub> and PM<sub>2.5</sub> concentrations measured by the AURN at the Norwich Lakenfields site reach very high levels on 18<sup>th</sup> February. The concentrations reach maximums of 101 µg.m<sup>-3</sup> and 73 µg.m<sup>-3</sup>, respectively.

### 5.3.1 Weekly Periodicity

Tables 10a and 10b shows the difference between the Monday to Friday average concentration and the Sunday average concentration for Black Carbon and UV component. The sites have been sorted into site classification and are in descending order of annual average in each site classification.

Site	Monday - Friday	Sunday	Ratio
<b>Roadside</b>			
Marylebone Road	11.1	7.9	1.40
Bath 6	3.0	2.0	1.48
<b>Urban Centre</b>			
Glasgow Centre	1.8	1.6	1.13
Manchester Piccadilly	1.7	1.6	1.07
Stoke Centre	1.5	1.2	1.22
Dudley Central	1.5	1.0	1.42
Belfast Centre	1.5	1.2	1.28
Nottingham Centre	1.5	1.2	1.30
<b>Urban Background</b>			
South Kirkby 1	1.9	1.1	1.70
Birmingham Tyburn	1.5	1.1	1.39
Cardiff 12	1.4	1.1	1.37
North Ken	1.4	1.2	1.17
Strabane 2	1.3	1.2	1.08
Dunmurry 3	1.1	1.0	1.07
Halifax 17	1.1	0.8	1.44
Edinburgh St Leonard's	1.0	0.8	1.31
Sunderland 8	1.0	0.7	1.38
Woolwich 9	0.9	0.7	1.31
Norwich Lakenfields	0.8	0.6	1.36
<b>Suburban</b>			
Folkestone	1.0	0.8	1.14
<b>Rural</b>			
Harwell	0.5	0.4	1.22

**Table 10a Average Monday to Friday and Sunday Concentrations of Black Carbon**

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

Site	Monday - Friday	Sunday	Ratio
<b>Roadside</b>			
Bath 6	0.26	0.39	0.67
Marylebone Road	-0.15	0.17	-0.86
<b>Urban Centre</b>			
Nottingham Centre	0.33	0.34	0.95
Belfast Centre	0.32	0.37	0.88
Stoke Centre	0.32	0.33	0.97
Manchester Piccadilly	0.28	0.35	0.79
Dudley Central	0.28	0.28	0.98
Glasgow Centre	0.22	0.24	0.91
<b>Urban Background</b>			
Strabane 2	0.73	0.81	0.90
Dunmurry 3	0.54	0.59	0.91
Cardiff 12	0.38	0.42	0.90
North Ken	0.30	0.32	0.91
Birmingham Tyburn	0.28	0.26	1.06
Woolwich 9	0.28	0.28	0.98
South Kirkby 1	0.27	0.31	0.89
Halifax 17	0.26	0.27	0.94
Sunderland 8	0.25	0.21	1.18
Norwich Lakenfields	0.24	0.23	1.04
Edinburgh St Leonard's	0.17	0.20	0.88
<b>Suburban</b>			
Folkestone	0.26	0.28	0.92
<b>Rural</b>			
Harwell	0.14	0.15	0.99

**Table 10b Average Monday to Friday and Sunday Concentrations of the UV Component, all data included**

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

#### 5.4 COMPARISONS WITH OTHER POLLUTANTS

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

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

5.4.1 Elemental Carbon

Daily Elemental Carbon (EC) measurements are made at the North Kensington, Marylebone Road and Harwell sites by the Particle Number and Speciation Network<sup>[3]</sup>. 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 24 to 26.

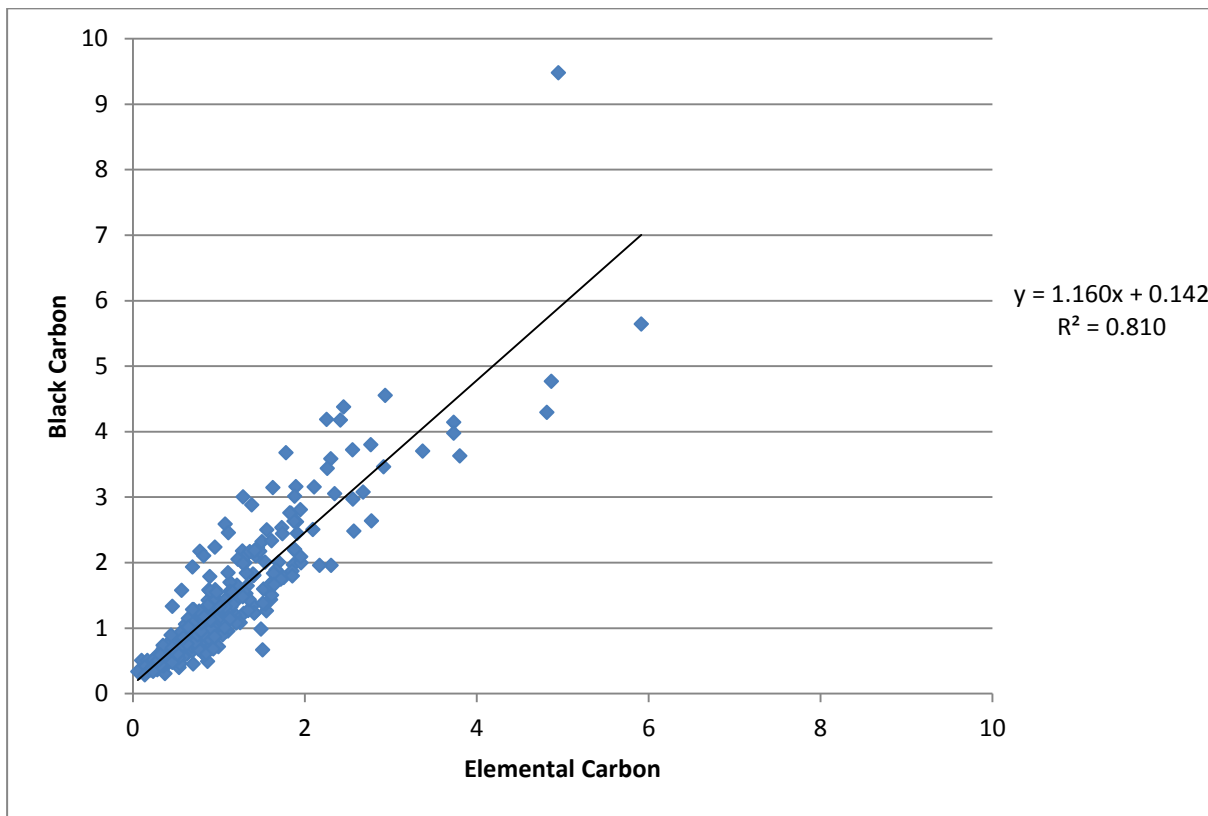


Figure 24 2011 EC and BC Measurements at North Kensington

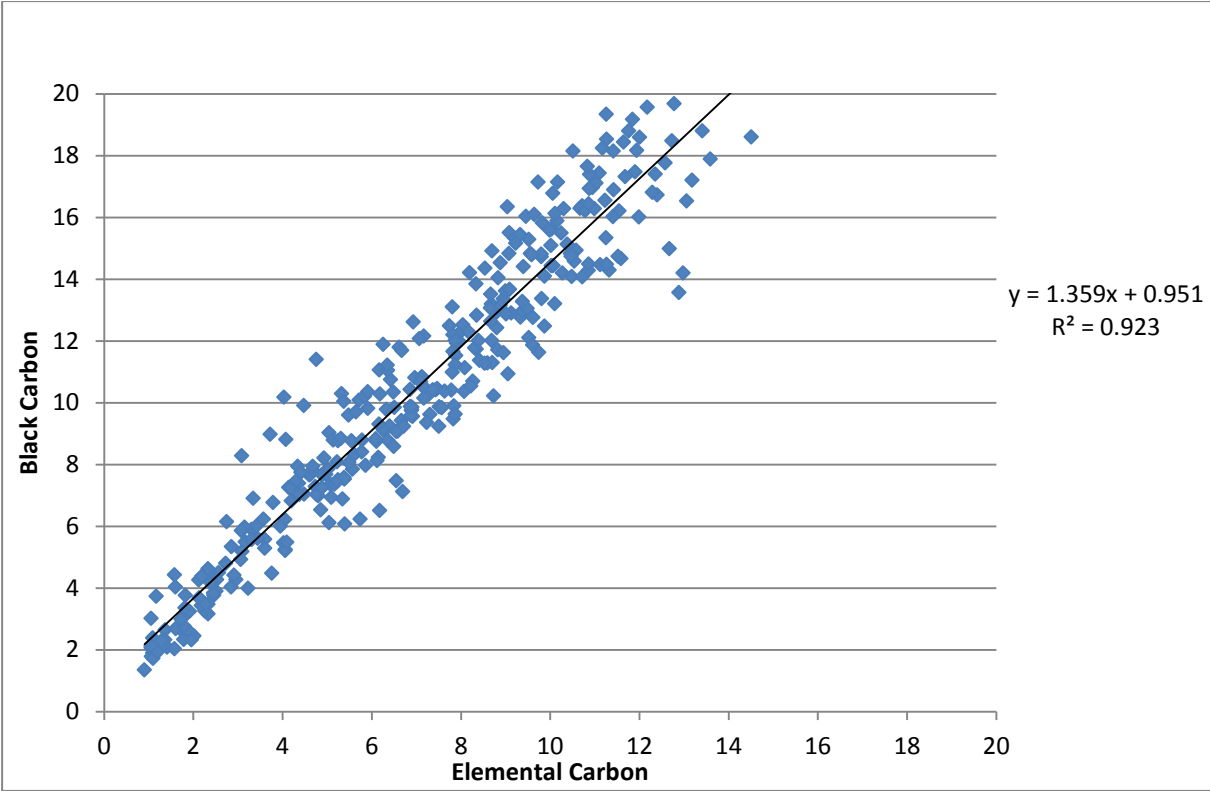


Figure 25 2011 EC and BC Measurements at Marylebone Road

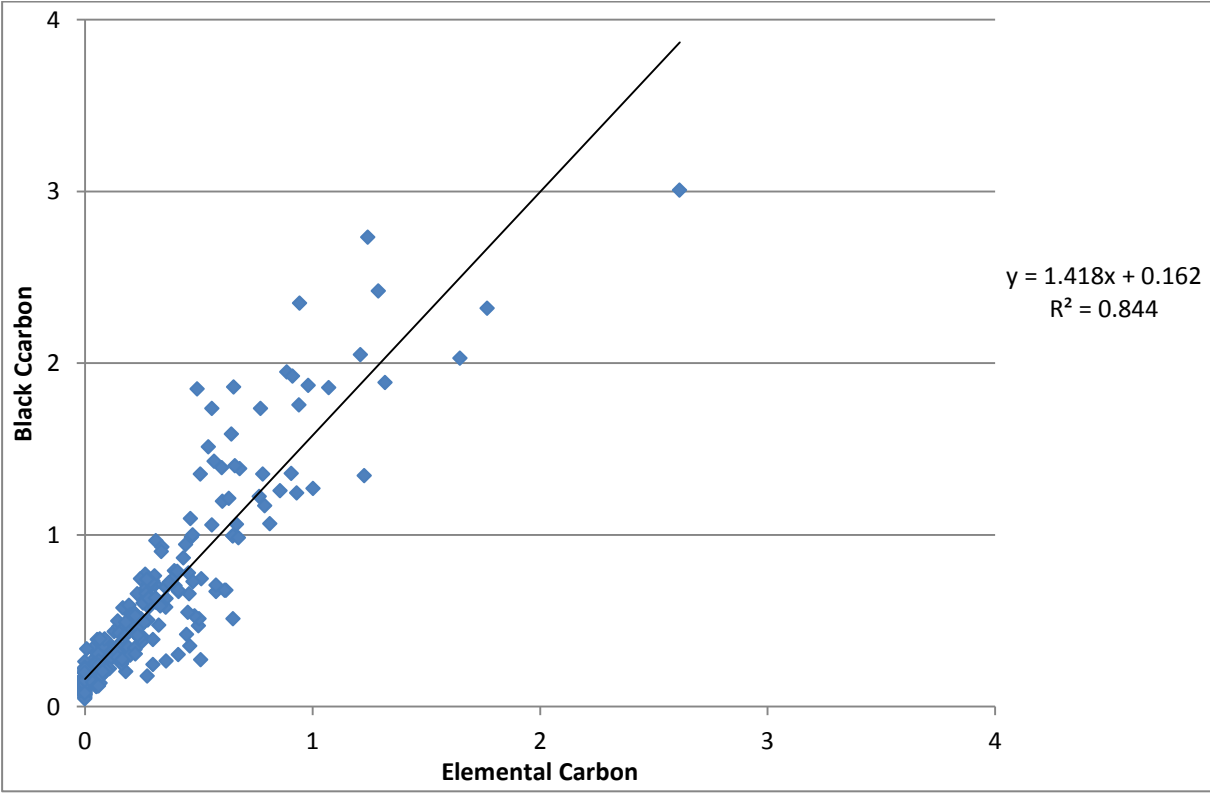
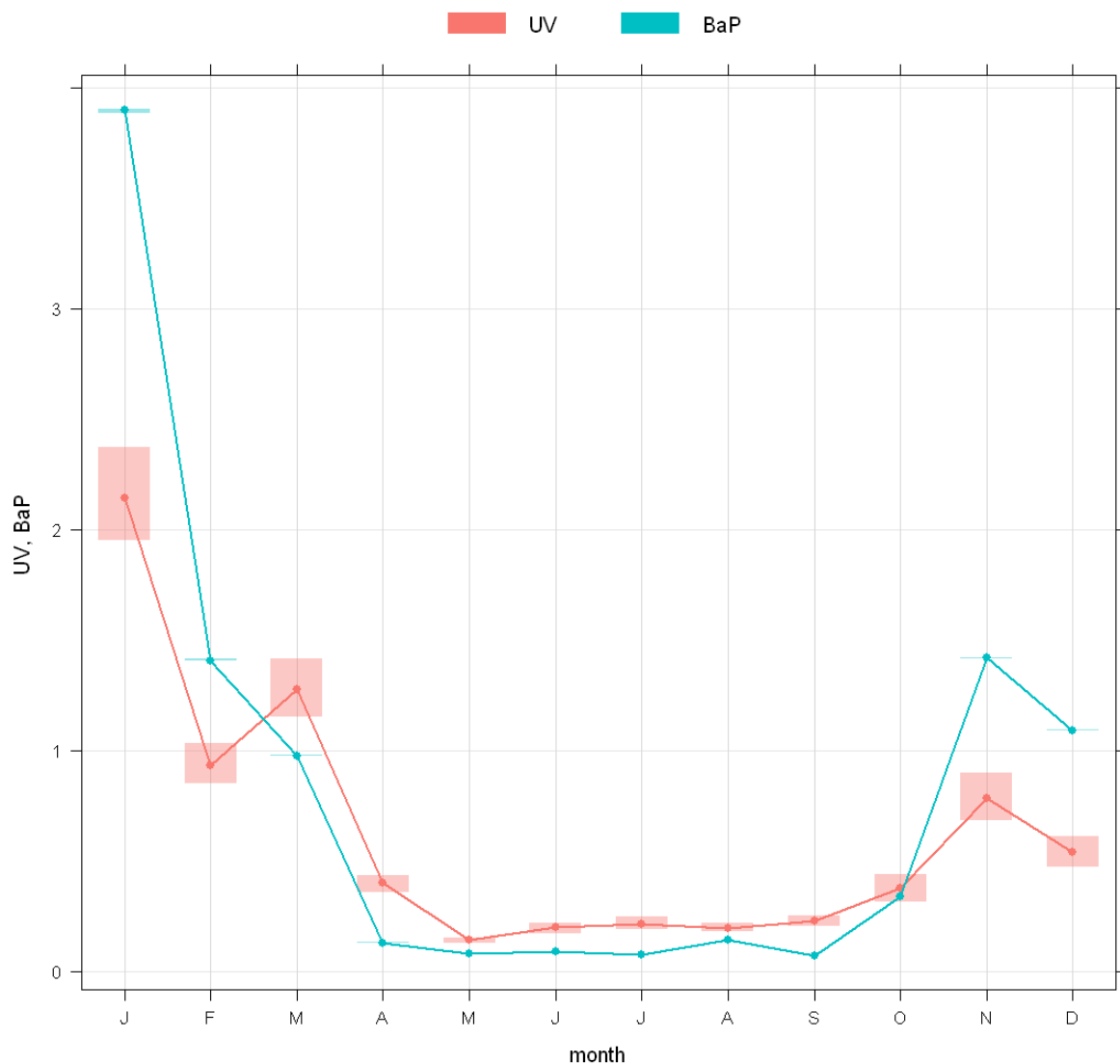


Figure 26 2011 EC and BC Measurements at Harwell

It can be seen that there is a good relationship between the EC and BC concentrations measured at all sites. The improved agreement at Harwell over 2009 and 2010 is probably due to the slightly increased Elemental Carbon concentrations in 2011. This lack of agreement is likely to be due to measurement method issues at low concentrations, as described in a joint 2009 paper<sup>[4]</sup>.

#### 5.4.2 Poly Cyclic Aromatic Hydrocarbons (PAH)

Monthly concentrations of Benzo[a]pyrene are measured at the Dunmurry site under the UK PAH Network. Aethalometer concentrations (UV component) have been averaged into monthly measurements and plotted as a time series with the Benzo[a]pyrene concentration in Figure 27



**Figure 27** UV component and Benzo[a]pyrene concentrations measured at Dunmurry in 2011

The shaded area on the y-axis represents the uncertainty in the mean y-value due to the spread of the results over that averaging period, expressed with a level of confidence of 95%. It is not the overall measurement uncertainty. As the PAH measurements are a monthly average there is no spread in the

result over the month and therefore no uncertainty displayed in the y-value. The shaded area on the x-axis is for display purposes only, to allow the uncertainty in the mean value to be seen more clearly.

The units are different for the two quantities, the PAH measurements are represented in  $\text{ng.m}^{-3}$  while the UV component is represented as  $\mu\text{g.m}^{-3}$ , however it can be seen that there is good temporal agreement between the two species due to similar emission sources such as solid fuel burning. A detailed analysis of PAH concentrations in Northern Ireland is contained in an NPL Report for the Department for the Environment Northern Ireland<sup>[8]</sup>.

### 5.4.3 Particulate Mass

The annual average particulate mass concentration was compared with the Black Carbon concentration at collocated sites where automatic particulate mass instrumentation was installed. Three different types of instruments provide particulate mass concentrations across the Black Carbon Network: TEOM FDMS Model CB drier, TEOM Model AB and MetOne BAM – reference equivalent. As different automatic methods provide different results the concentrations reported by these automatic instruments have been separated into instrument type and the results shown in Table 11.

Site	BC $\mu\text{g.m}^{-3}$	TEOM FDMS PM10 $\mu\text{g.m}^{-3}$	TEOM FDMS PM2.5 $\mu\text{g.m}^{-3}$	MetOne BAM PM10 $\mu\text{g.m}^{-3}$	TEOM Model AB PM10 $\mu\text{g.m}^{-3}$	Percent BC PM10 %	Percent BC PM2.5 %
Belfast Centre	1.5	20.6	14.0			7.3	10.7
Birmingham Tyburn	1.4	22.3	15.9			6.3	8.8
Edinburgh St Leonard's	1.0	15.4	11.6			6.5	8.6
Harwell	0.5	18.1	11.9			2.8	4.2
Marylebone Road	10.3	38.4	24.4			26.8	42.2
North Kensington	1.3	23.7	16.3			5.5	8.0
Norwich Lakenfields	0.7	19.8	14.2			3.5	4.9
Nottingham Centre	1.5	24.8	13.2			6.1	11.3
Stoke Centre	1.5	22.3	16.3			6.7	9.2
Glasgow Centre	1.8	16.5	10.2			10.9	17.7
Dudley Central	1.4				15.4	9.1	
Strabane	1.3			17.4		7.5	
Dunmurry	1.1	16.2	13.1			6.8	8.4
Folkestone	0.9				13.1	6.9	

Grey shaded cells indicate no measurements were made.

PM<sub>10</sub> measurements at Belfast Centre, PM<sub>2.5</sub> measurements at Dunmurry have a data capture less than 75%, but greater than 50%.

**Table 11 Comparison of Black Carbon and Particulate Mass Concentrations**



The particulate mass measurements made by the bottom four sites are made by Local Authorities and may not have the same QA/QC procedures applied to the data as that applied to the AURN sites shown in Table 14.

It can be seen that the  $PM_{10}$  and  $PM_{2.5}$  mass concentration measured at Marylebone Road have a much higher percentage of Black Carbon than the other sites.

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

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

If the same comparison can not 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. This fictional material 'UVPM' is expressed in units of 'BC Equivalent'.

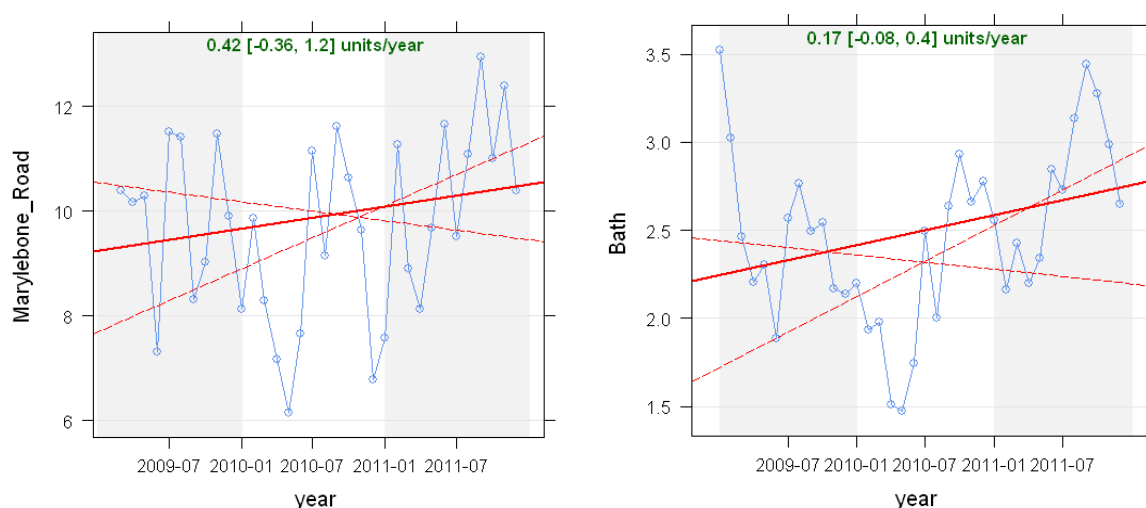
## 5.5 TRENDS

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

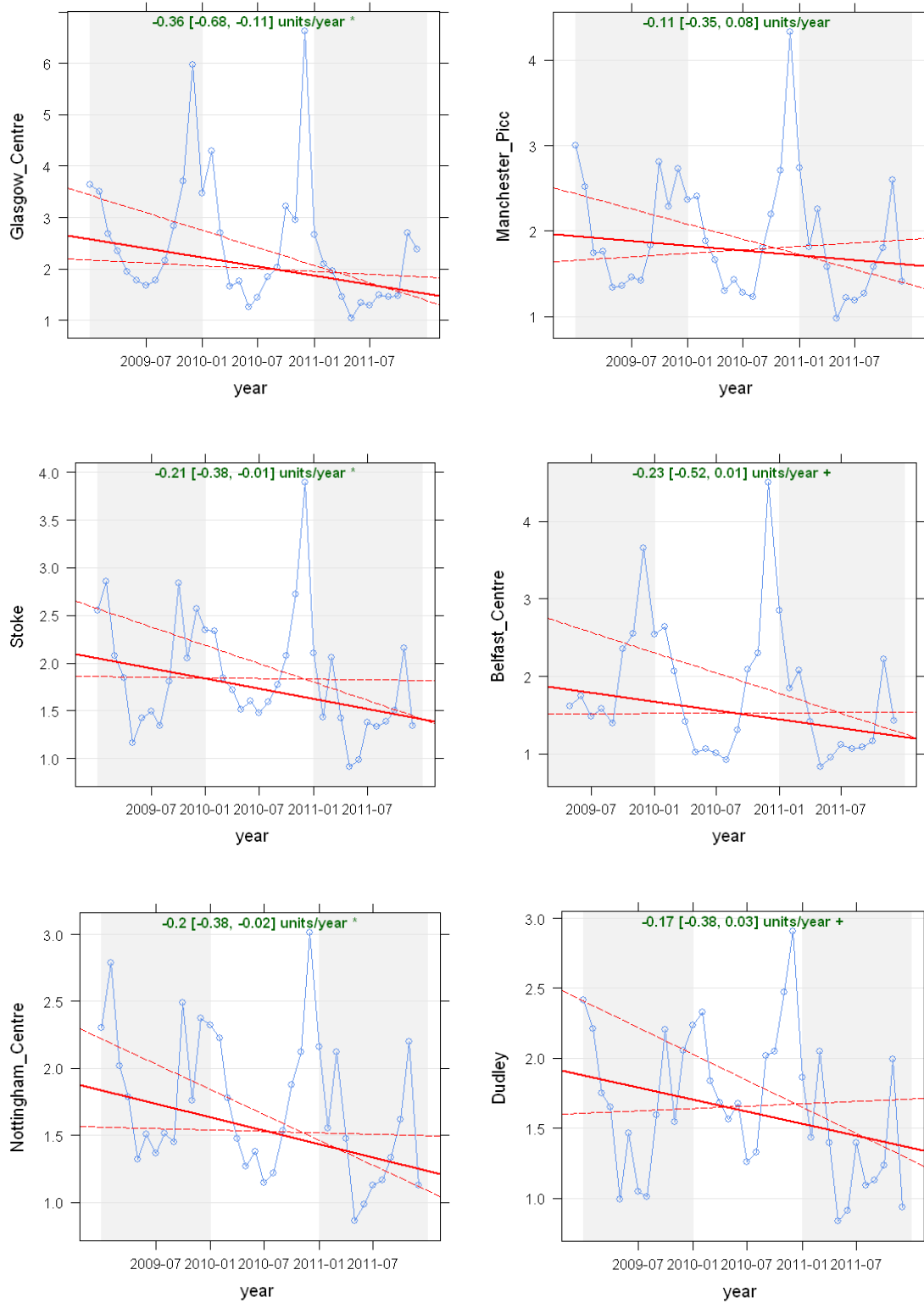
### 5.5.1 Short-Term Trends

Figures 28 to 35 show the trend in Black Carbon and UV component concentrations as monthly averages over the full calendar years 2009 to 2011. The Theil-Sen method in OpenAir<sup>[5,6]</sup> was used to calculate the regression parameters including slope and uncertainty in the slope.

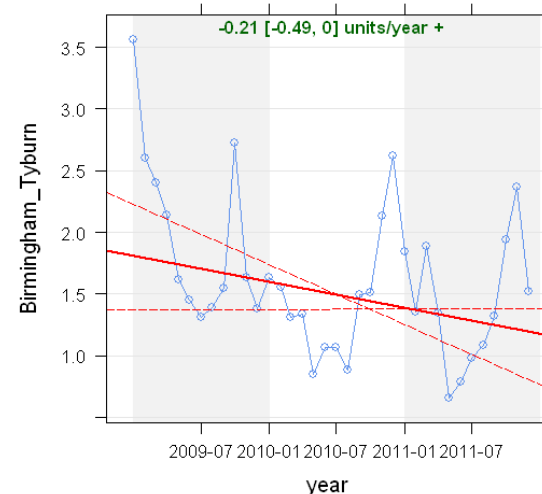
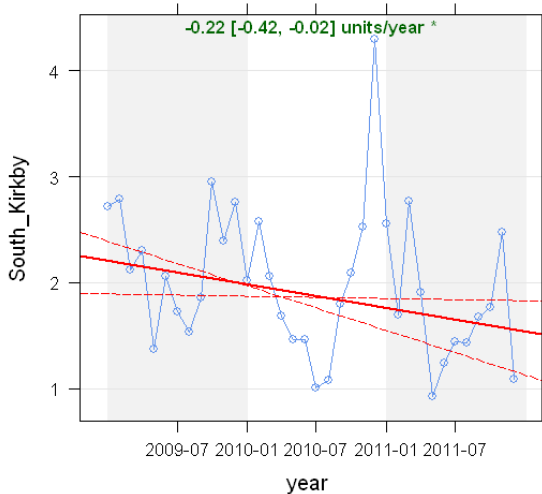
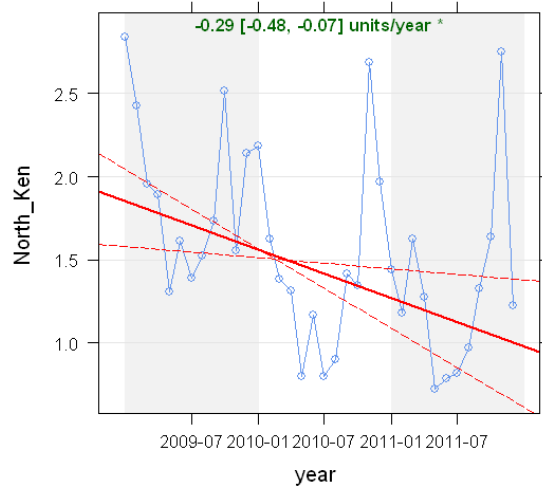
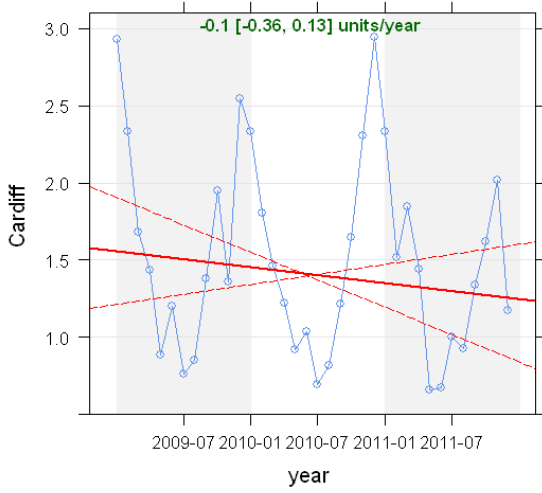
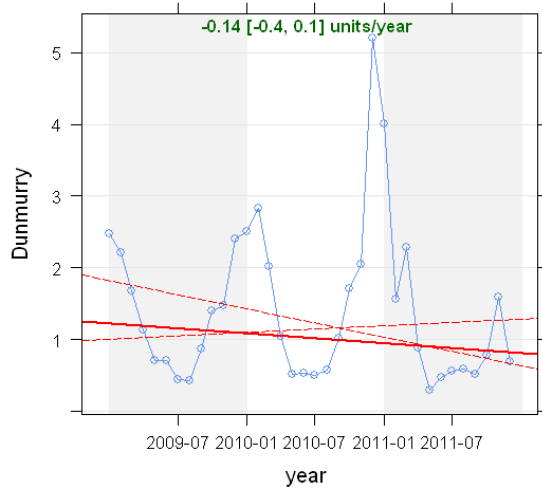
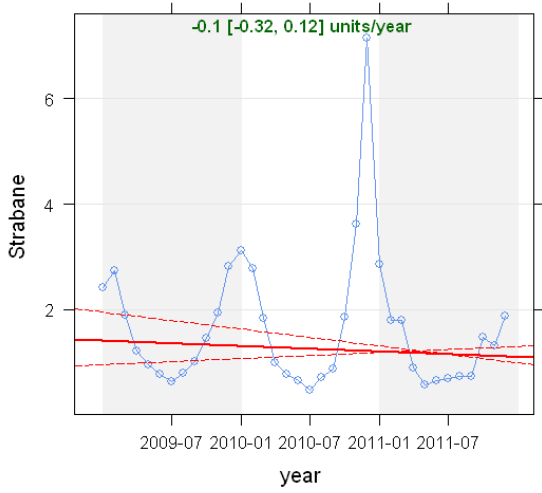
#### 5.5.1.1 BLACK CARBON

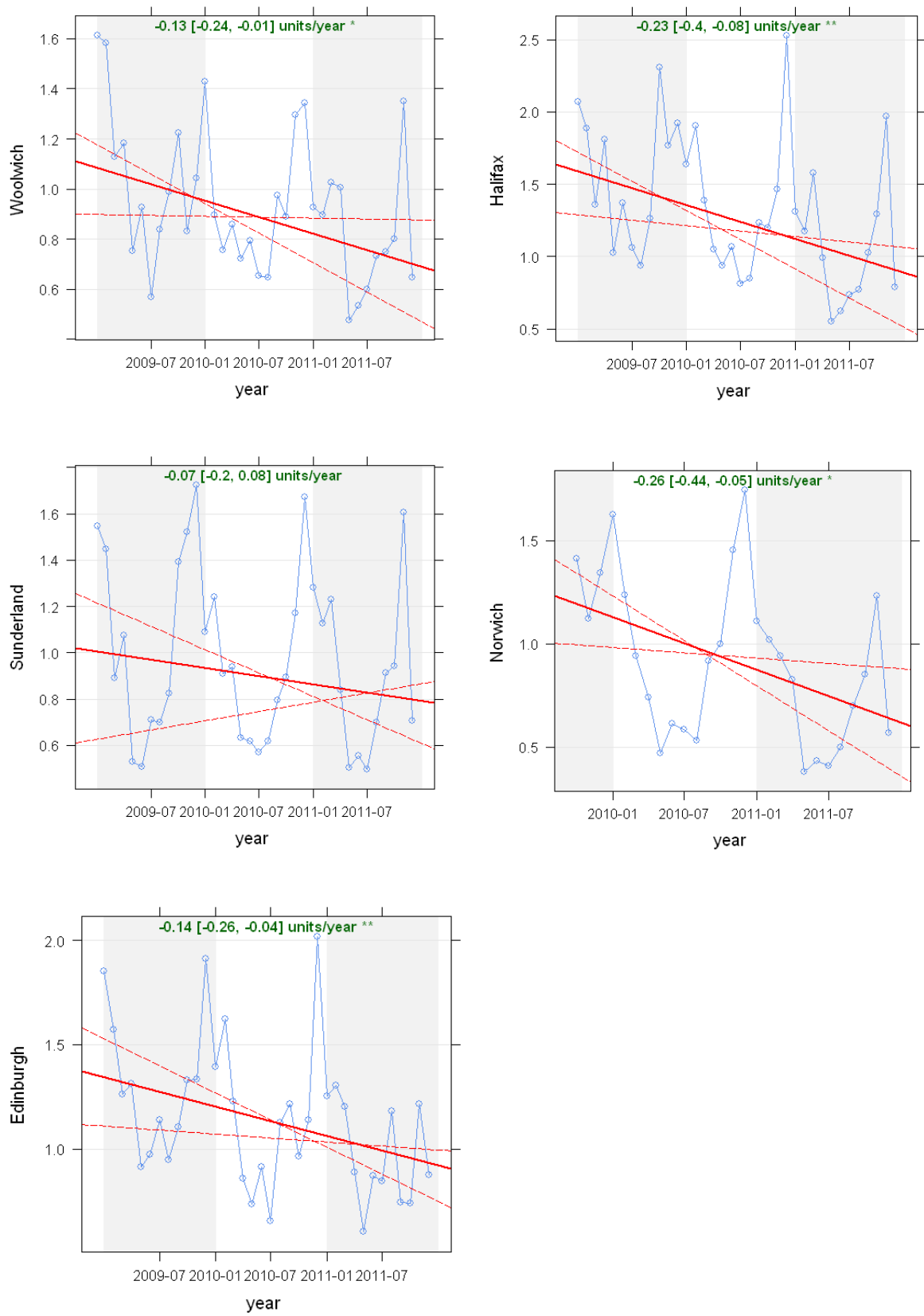


**Figure 28 Black Carbon concentrations measured at roadside sites, 2009 – 2011**

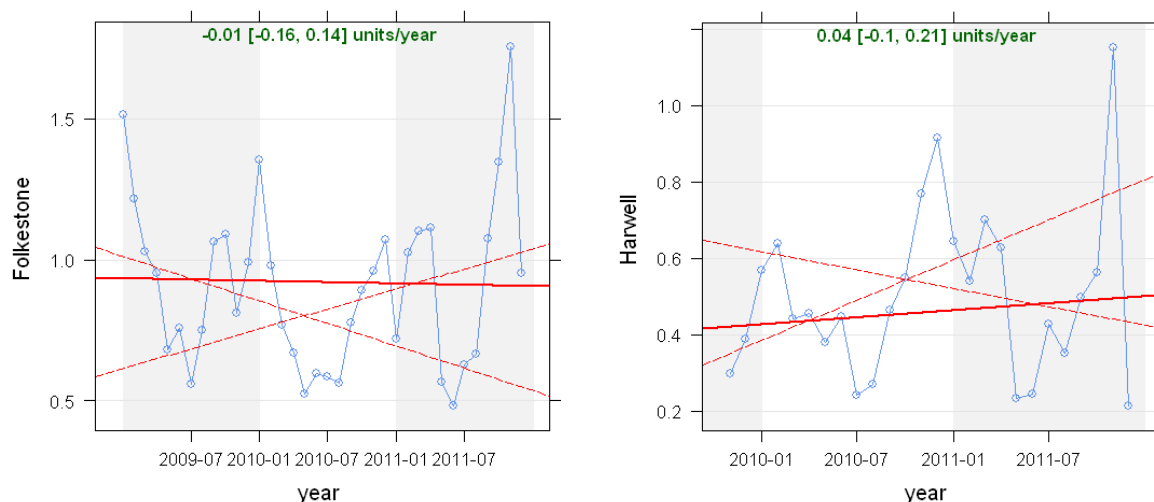


**Figure 29** Black Carbon concentrations measured at urban centre sites, 2009 - 2011





**Figure 30** Black Carbon concentrations measured at urban background sites, 2009 - 2011



**Figure 31** Black Carbon concentrations measured at suburban and rural background sites, 2009 - 2011

Site	Slope	Lower limit	Upper limit	Slope significant
<b>Roadside</b>				
Marylebone Road	0.42	-0.36	1.20	N
Bath 6	0.17	-0.08	0.40	N
<b>Urban Centre</b>				
Glasgow Centre	-0.36	-0.68	-0.11	Y
Stoke Centre	-0.21	-0.38	-0.01	Y
Nottingham Centre	-0.20	-0.38	-0.02	Y
Belfast Centre	-0.23	-0.52	0.01	N
Dudley Central	-0.17	-0.38	0.03	N
Manchester Piccadilly	-0.11	-0.35	0.08	N
<b>Urban Background</b>				
North Ken	-0.29	-0.48	-0.07	Y
Norwich Lakenfields	-0.26	-0.44	-0.05	Y
Halifax 17	-0.23	-0.40	-0.08	Y
South Kirkby 1	-0.22	-0.42	-0.02	Y
Birmingham Tyburn	-0.21	-0.49	0.00	Y
Edinburgh St Leonard's	-0.14	-0.26	-0.04	Y
Woolwich 9	-0.13	-0.24	-0.01	Y
Dunmurry 3	-0.14	-0.40	0.10	N
Strabane 2	-0.10	-0.32	0.12	N
Cardiff 12	-0.10	-0.36	0.13	N
Sunderland 8	-0.07	-0.20	0.08	N
<b>Suburban</b>				
Folkestone	-0.01	-0.16	0.14	N
<b>Rural</b>				
Harwell	0.04	-0.10	0.21	N

**Table 12** Summary of Black Carbon trends

It can be seen that the Black Carbon concentrations at roadside sites may have increased over the period 2009 to 2011. The uncertainties in the slope encompass stable or slightly negative slopes.

At urban centre sites concentrations are generally decreasing over the same period with some slopes being statistically significant (Glasgow, Stoke and Nottingham).

At urban background sites concentrations are generally decreasing over the same period with some slopes being statistically significant (North Kensington, Norwich, Halifax, South Kirkby, Birmingham Tyburn, Edinburgh and Woolwich).

At suburban and rural background sites concentrations are stable over the period.

5.5.1.2 UV COMPONENT

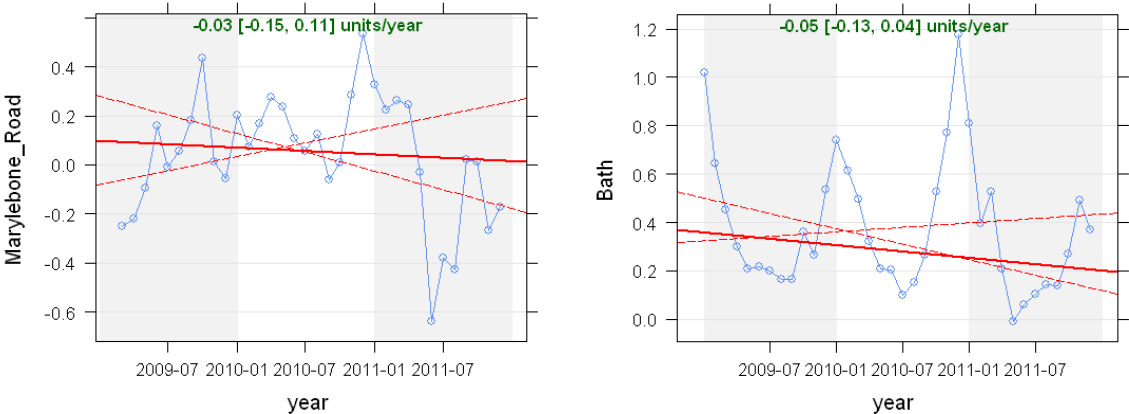
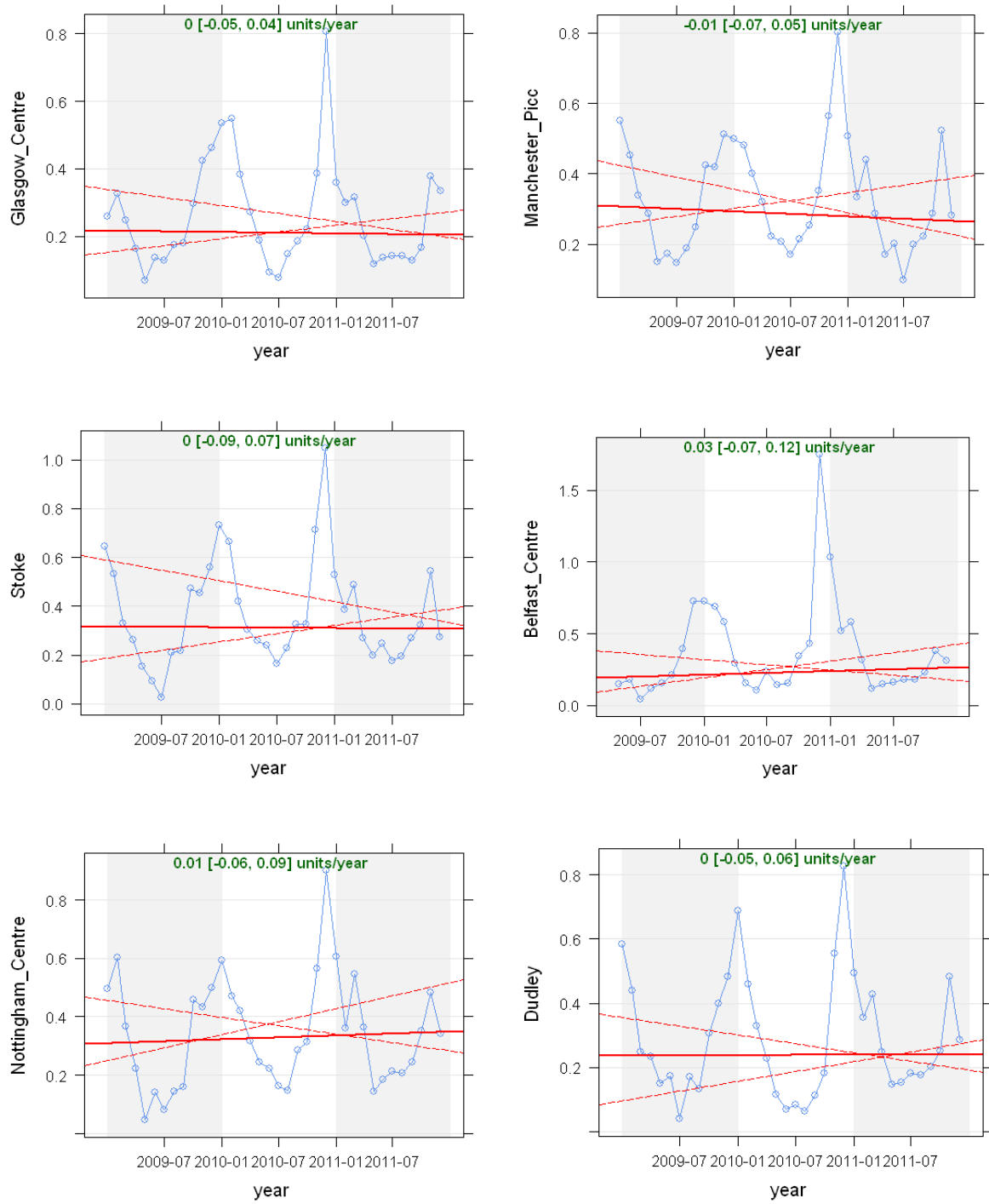
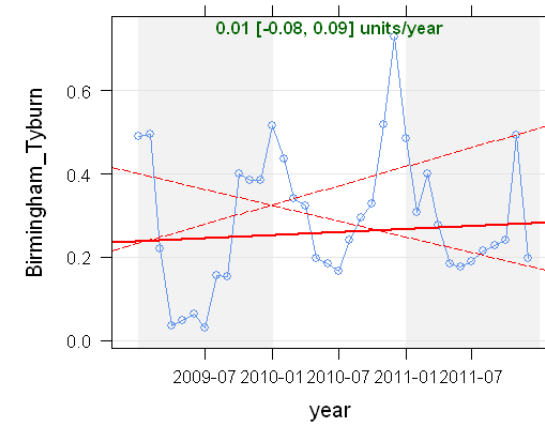
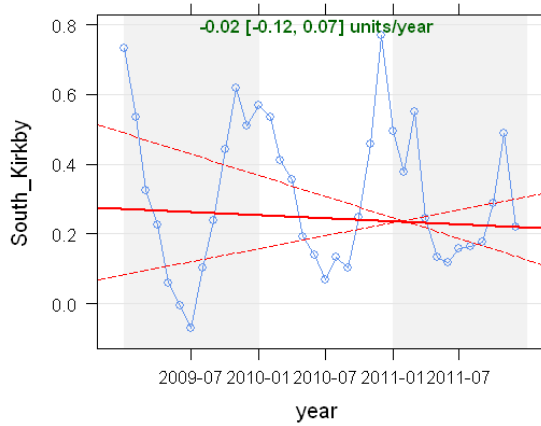
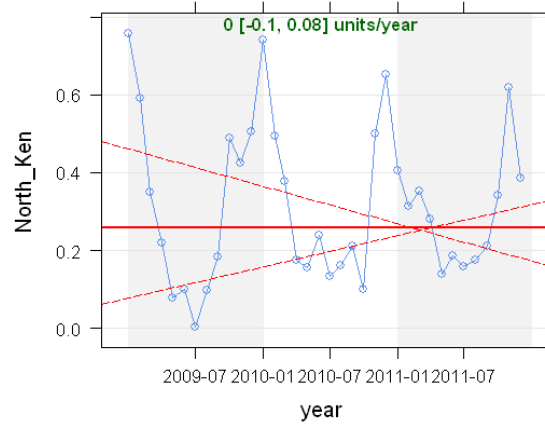
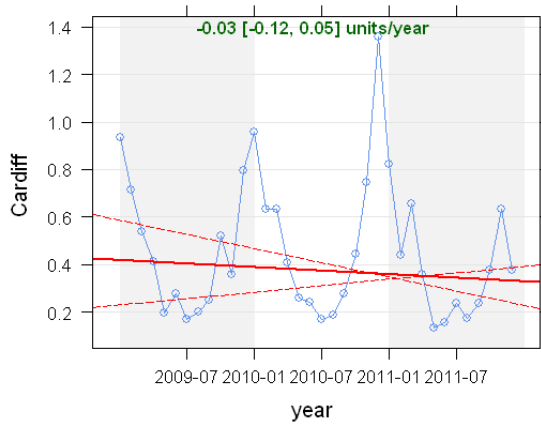
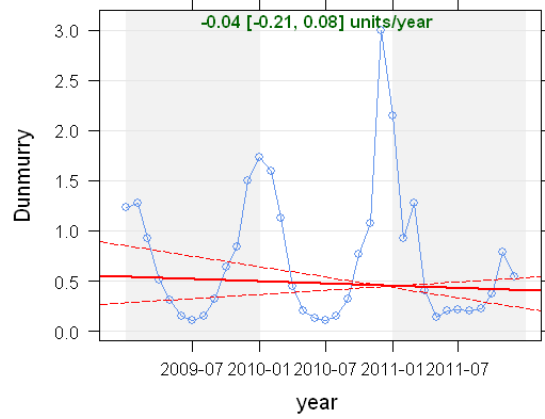
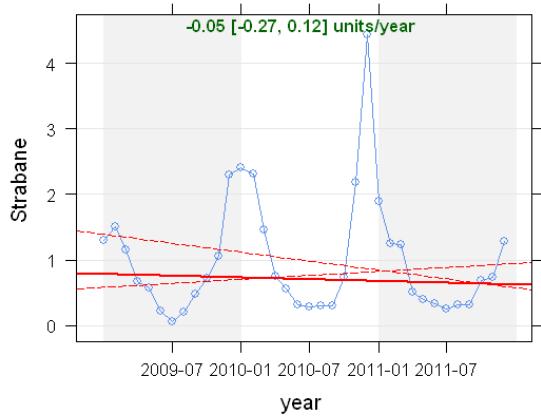


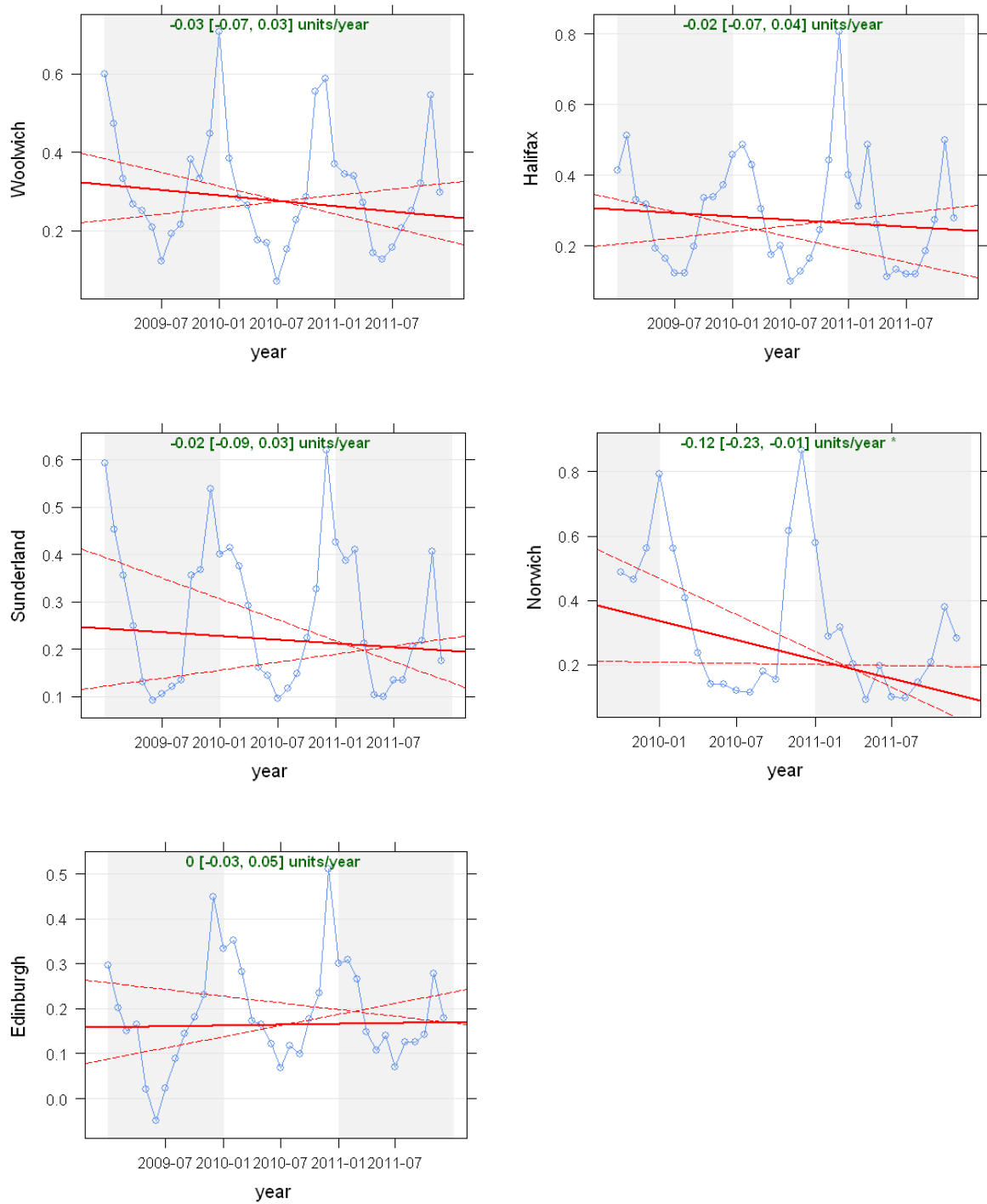
Figure 32 UV Component concentrations measured at roadside sites, 2009 – 2011



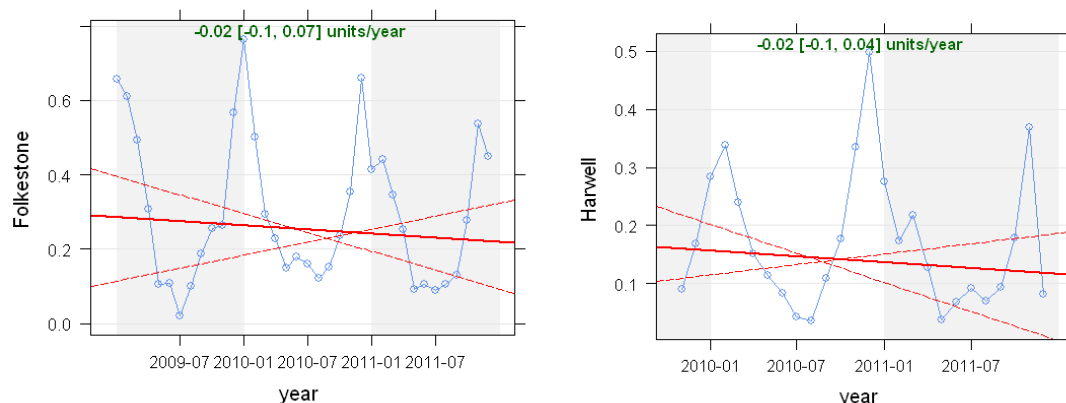
**Figure 33** UV Component concentrations measured at urban centre sites, 2009 – 2011







**Figure 34** UV Component concentrations measured at urban background sites, 2009 – 2011



**Figure 35** UV Component concentrations measured at suburban and rural background sites, 2009 – 2011

Site	Slope	Lower limit	Upper limit	Slope significant
<b>Roadside</b>				
Marylebone Road	-0.03	-0.15	0.11	N
Bath 6	-0.05	-0.13	0.04	N
<b>Urban Centre</b>				
Belfast Centre	0.03	-0.07	0.12	N
Nottingham Centre	0.01	-0.06	0.09	N
Glasgow Centre	0.00	-0.05	0.04	N
Stoke Centre	0.00	-0.09	0.07	N
Dudley Central	0.00	-0.05	0.06	N
Manchester Piccadilly	-0.01	-0.07	0.05	N
<b>Urban Background</b>				
Birmingham Tyburn	0.01	-0.08	0.09	N
North Ken	0.00	-0.10	0.08	N
Edinburgh St Leonard's	0.00	-0.03	0.05	N
Halifax 17	-0.02	-0.07	0.04	N
South Kirkby 1	-0.02	-0.12	0.07	N
Sunderland 8	-0.02	-0.09	0.03	N
Woolwich 9	-0.03	-0.07	0.03	N
Cardiff 12	-0.03	-0.12	0.05	N
Dunmurry 3	-0.04	-0.21	0.08	N
Strabane 2	-0.05	-0.27	0.12	N
Norwich Lakenfields	-0.12	-0.23	-0.01	Y
<b>Suburban</b>				
Folkestone	-0.02	-0.10	0.07	N
<b>Rural</b>				
Harwell	-0.02	-0.10	0.04	N

**Table 13** Summary of UV component trends

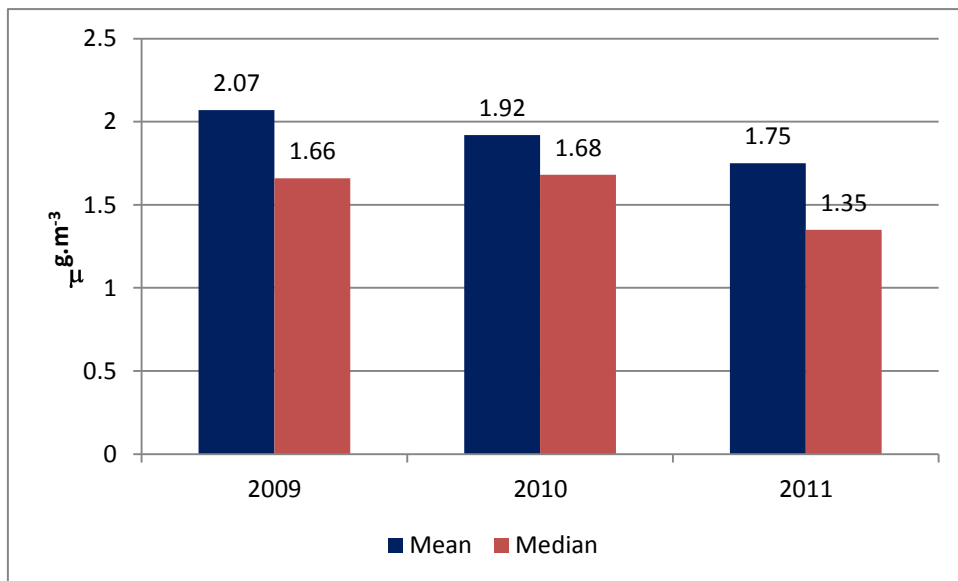
The only site to show a statistically significant trend is Norwich, which shows a reduction in UV component concentrations over the period 2009 to 2011. The slopes in all of the other sites are not statistically significant.

### 5.5.2 Long-Term Trends

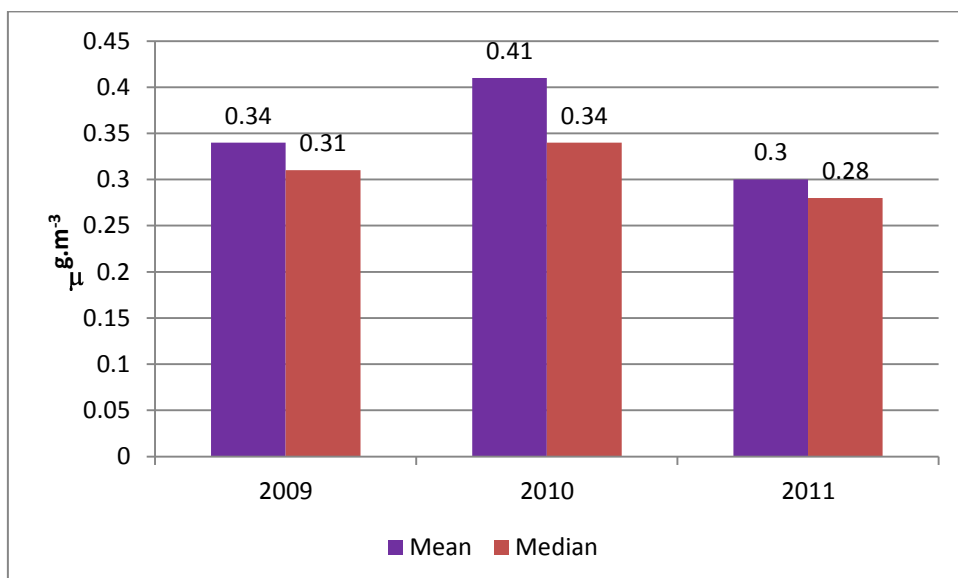
Trends in annual average Aethalometer concentrations over the period 2009 to 2011 are given along with the long-term trend in Black Carbon concentrations by converting historical Black Smoke concentrations into Black Carbon concentrations.

#### 5.5.2.1 ANNUAL AVERAGES AND MEDIANS

Figures 36 and 37 show the Network annual average and median concentrations for Black Carbon and UV component. The median concentration is shown to remove the influence of large changes in a single site skewing the overall result for the Network.



**Figure 36** Network annual average Black Carbon concentrations



**Figure 37** Network annual average UV Component concentrations

It can be seen that the annual average Black Carbon concentration has fallen over the period 2009 to 2011, while the median concentration rose very slightly from 2009 to 2010 and then fell to below 2009 levels in 2011.

Both the annual average and median UV component concentrations increased from 2009 to 2010 and then fell to below 2009 levels in 2011.

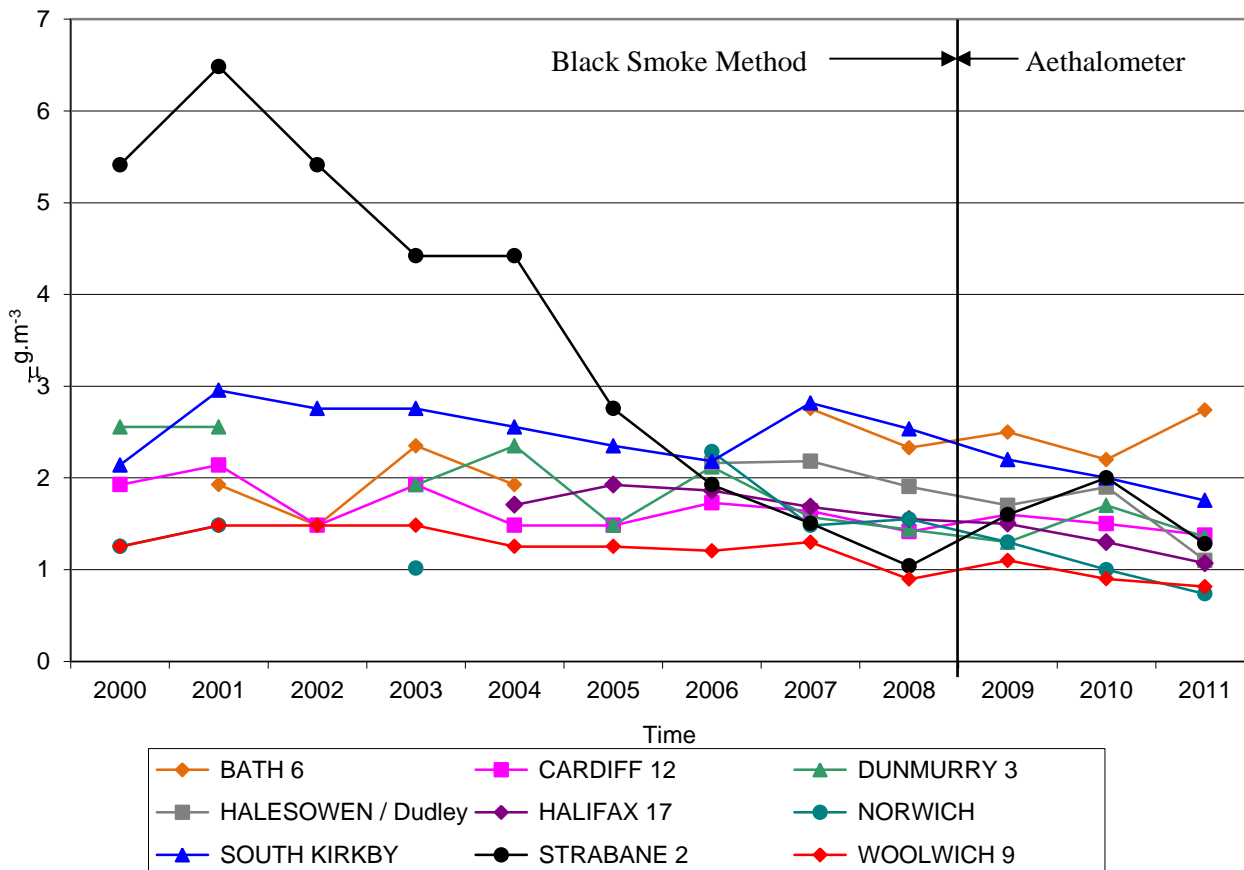
#### 5.5.2.2 LONG TERM BLACK CARBON CONCENTRATIONS

A paper by Quincey et al<sup>[7]</sup> analysing the results of the parallel running intercomparison performed in 2009 between the Aethalometer and the Black Smoke Method and tests the proposed relationship between Black Smoke Index and Black Carbon measurements. This relationship, described by Equation 1 below, was used to convert Black Smoke Index measured between 2000 and 2008 into Black Carbon concentrations. The trends in these Black Carbon concentrations are given in Figure 38.

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

where:

$C_{BC}$  =Black Carbon concentration in  $\mu\text{g.m}^{-3}$   
 $I_{BS}$  =Black Smoke Index



**Figure 38 Trends in Black Carbon Concentrations 2000 to 2011**

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

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

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

## REFERENCES

- 1 P Quincey, A relationship between Black Smoke Index and Black Carbon concentration, *Atmospheric Environment* 41 (2007) 7964–7968.
- 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.
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- 4 P Quincey, D Butterfield, D Green, M Coyle, N Cape, An evaluation of measurement methods for organic, elemental and black carbon in ambient air monitoring sites, *Atmospheric Environment* 43 (2009) 5085–5091
- 5 DC Carslaw and K Ropkins, (2012) OpenAir --- an R package for air quality data analysis, *Environmental Modelling & Software*. Volume 27-28, 52-61.
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- 7 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.
- 8 D Butterfield, R Brown, NPL REPORT AS66, Polycyclic Aromatic Hydrocarbons in Northern Ireland, February 2012.